LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS): ATOMIC EMISSION SPECTROSCOPY ONE SPARK AT A TIME

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HISTORY

In the early 1960s, very soon after the invention of the ruby laser, pulsed laser-induced sparks were produced for the purpose of performing optical emission spectroscopy [1,2]. Although the motivation for many of these early experiments was to study the physical and chemical mechanisms leading up to the ionization breakdown event [3], it was quickly realized that optical spectroscopy of the high-temperature microplasma formed during the pulsed laser ablation and subsequent breakdown could yield a spectrochemical analysis of the target material requiring very little sample preparation. In addition the sampling area and volume was inherently delimited by the size of the focused laser beam, lending the analysis an intrinsically high spatial resolution. This technique would come to be known initially as "laser-induced plasma spectroscopy" (LIPS) and eventually as "laser-induced breakdown spectroscopy" or LIBS.

The reader may now "fast-forward" five decades to August 25, 2012, the date that the Chemistry and Camera (ChemCam) instrument on NASA's Mars Science Laboratory rover Curiosity used its LIBS laser to interrogate five small patches of soil at a distance of 3.5 meters from the rover on the surface of Mars [4]. This was the first use of LIBS to investigate an extraterrestrial environment.

In the intervening 49 years, approximately 10,000 peer-reviewed papers have been published according to the abstract and citation database Scopus (Elsevier) with the phrase "laser-induced breakdown spectroscopy" or "laser-induced plasma" in the title; see Fig. 1. These papers have appeared in a wide variety of journals covering topics ranging from plasma physics, analytical chemistry, advanced optics, geology, forensics, to food safety.

SUMMARY

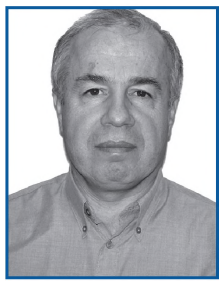
An introduction and review of the analytical technique laser-induced breakdown spectroscopy (LIBS).

The field has seen such vast and exciting growth due to the ever-increasing demand for high-accuracy quantitative elemental analysis performed in as short a time as possible. The speed of the LIBS assay combined with the relative ease with which analysis can be performed outside of a standards laboratory has led research groups all over the world to investigate a dizzying array of applications. These researchers have been attracted to the benefits of using LIBS, which include no sample preparation, no consumables, real-time elemental analysis, the ability to perform remote or standoff measurements, sensitivity to any element in the periodic table (including the low Z elements), and more. LIBS can provide part-per-million (ppm) sensitivity for elemental analysis and even offers the potential for molecular characterization.

In this paper we will give a brief overview of the light-based technique and describe some of the challenges and opportunities that it provides physicists, laser scientists, and analytical chemists in the 21st Century.

OVERVIEW

Despite the myriad experimental approaches described in the literature (see for example any of the number of excellent books or review articles that now exist in the literature [5–7]), the canonical LIBS experiment is simply described, as shown in Fig. 2. A laser pulse in the nanosecond to femtosecond pulse duration range is focussed into or onto a target, which can be in solid, liquid, or gaseous form. If the pulse energy exceeds the target material's breakdown threshold (usually given as a minimum fluence or intensity required to provide an electrical breakdown in 50% of the laser shots) a laser-induced plasma can be formed. If this occurs, the gaseous vapor atoms from the ablated target material are rapidly heated and ionized, forming a high-temperature (>50,000 K) plasma that expands at supersonic velocities away from the point of the spark initiation.



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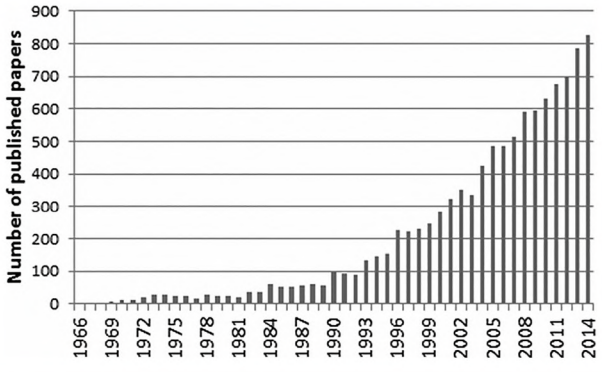

Fig. 1 The growth of laser-induced breakdown spectroscopy in the last 50 years as indicated by the number of peer-reviewed publications with either "laser-induced breakdown spectroscopy" or "laser-induced plasma" in the title.

In the immediate moments after nanosecond laser plasma initiation (extending out to approximately one microsecond afterwards) the plasma emission intensity is mostly dominated by broadband non-specific radiation from bremsstrahlung and recombination radiation. At later times, however, from approximately 1 μs to 20 μs after plasma initiation, the emission is dominated by spectroscopically narrow atomic spontaneous emission from atoms and ions from the target material and also from the gas environment in which the spark was formed. Typically, a time resolved spectroscopy achieved via the use of shuttered CCD cameras or image-intensified CCD cameras is required to obtain high signal-to-noise ratio atomic emission spectra, although the use of non-gated CCD detectors is also

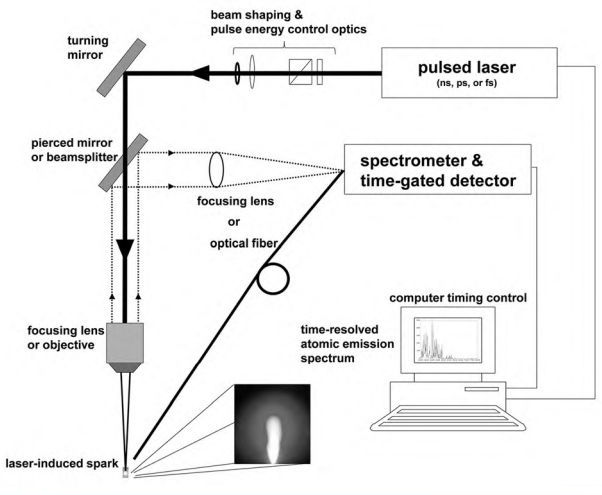

Fig. 2 A typical laser-induced breakdown spectroscopy experimental apparatus.

not uncommon [8]. It is also now known that the plasma formation process due to femtosecond laser ablation is significantly different from nanosecond ablation, depending on direct electron evaporation at time scales < 1 fs rather than thermal heating and ablation, which occurs on a picosecond timescale [9]. This allows femtosecond-LIBS plasmas to be analyzed without time-gating if desired which can simplify and reduce the cost of the spectrometer/detector apparatus at the expense of increasing laser cost and complexity.

TECHNOLOGY AS A DRIVER OF RESEARCH

Although the LIBS method has been in existence for more than 50 years, prior to 1980 interest in the technology centered mainly on the study of the physics of plasma formation. The LIBS technology was in its infancy at this time and its poorer analytical performance made it actually less attractive than conventional arc spark spectroscopy or other conventional techniques based on optical emission spectroscopy. From 1980–1990 new applications emerged, in particular the need for a real time analysis in metallurgy. This was the motivation for some laboratories in academia and industry to start engaging in LIBS research and development, but this was not widespread due to some of the difficulties inherent in LIBS. These include the transient nature of the LIBS plasma and the absence of any appropriate combination of spectrometer and detector which could provide a wide spectral range with medium to high spectral resolution and excellent time resolution.

From 1990–2000 different detection systems appeared on the market enabling the acquisition of temporally resolved spectra and allowing the electronic gating and averaging of signals. The required time resolution was achieved by moving away from the use of a boxcar averager and monochannel photomultiplier tube to the use of gated intensified charge coupled devices (ICCD) and intensified photodiode array detectors. We have seen the growth of research and development in this area go from 20 papers per year to more than 200 papers at the end of the 1990s. As the technology for analyzing LIBS plasmas improved, applications and fundamental studies developed rapidly and many groups worldwide became more involved in LIBS activities. To date, a few commercial instruments based on LIBS have been developed but have not yet found widespread use.

As the field proceeded into the 2000s, the advent of new echelle spectrometers, small compact spectrometers, as well as low-cost compact gated CCDs was the driver of more development and growth in LIBS technology in both industry and academia. As the hardware improved, efforts to make more quantitative analysis continued. The applications turned to very practical problems such as monitoring levels of environmental contamination, the control of material processing by rapidly sorting materials to put them in proper scrap or recycling bins, and slurry monitoring.

In the last decade there has been a renewed interest in the method for a wide range of applications. The technique has received greater attention due to the unveiling of significant technological developments in the components (lasers, spectrometers, and detectors) used in LIBS instruments as well as emerging needs to perform real time measurements under conditions in which conventional techniques cannot be applied. This opens the door for many applications and possibilities of developing field-deployable instruments. LIBS has even been successfully deployed on Mars, as was noted. Recently, fiber lasers have become one of the hottest topics in photonics and this new laser source has revealed itself to be a powerful tool for spectrochemistry and LIBS analysis. These compact laser sources allow LIBS to fully exploit its advantage of fast analysis. Recently the LIBS team at the National Research Council (NRC) has pioneered the use of fiber lasers for LIBS analysis in the mining sector, which has opened the way for new areas of applications for the LIBS technology, specifically in applications where rugged, easily portable instrumentation is required [10].

A thorough analysis of the state-of-the-art of the LIBS technique, both its advantage and its challenges, can be found in the recent interview conducted with experts in the field by the online journal *Spectroscopy* [11].

LIBS IN CANADA

The international LIBS community is strong and well-represented by researchers on six continents. A bi-annual international Conference, alternating between Europe, North America, and Asia has strengthened international communication. A Euro-Mediterranean LIBS conference and a North American symposium (sponsored by the North American society NASLIBS) held bi-annually in the off years further enhances the rapid dissemination of research results and the growth of the field.

Canada is well-represented in the international community. Canada has a strong tradition of plasma physics research, as demonstrated by the formation of the Plasma-Quebec research network approximately ten years ago [12]. In the specific area of LIBS, numerous Canadian researchers and physicists are involved in the effort. For example, a Past-President of the Canadian Association of Physicists (R. Fedosejevs) and colleagues at the University of Alberta have investigated the use of femtosecond laser ablation with pulse energies of only 10s of microjoules for sub-micron resolution [13] as well as the use of high-repetition frequency, low pulse energy microchip lasers coupled with laser-induced fluorescence techniques for sub-ppm elemental detection [14].

LIBS at University of Windsor

At the University of Windsor, we have instituted a program since 2011 devoted to developing biomedical applications of LIBS [15]. Specifically, we have demonstrated the ability to rapidly identify and classify bacteria based solely on their atomic composition as determined in a LIBS experiment [16]. This interdisciplinary application requires the collaboration of physicists, microbiologists, and signal processing experts to develop advanced chemometric strategies for efficient and accurate classification and discrimination of the various LIBS spectra [17]. As well as this microbiological application, we have also been investigating the detection of dietary metals in human tissues, specifically keratin nail tissue, and the detection of metals in soft tissue.

We are also interested in using the laser-induced plasma as a source of highly excited ions for fundamental physics measurements. Figure 3(a) shows three overlaid LIBS spectra obtained from a solid neodymium target ablated in a rarefied 71 torr argon environment [18]. By altering the observation delay time, spectra dominated by neutral, singly-ionized, and doubly-ionized emission peaks may be obtained. Figure 3(b) shows a corresponding Saha-Boltzmann calculation of the

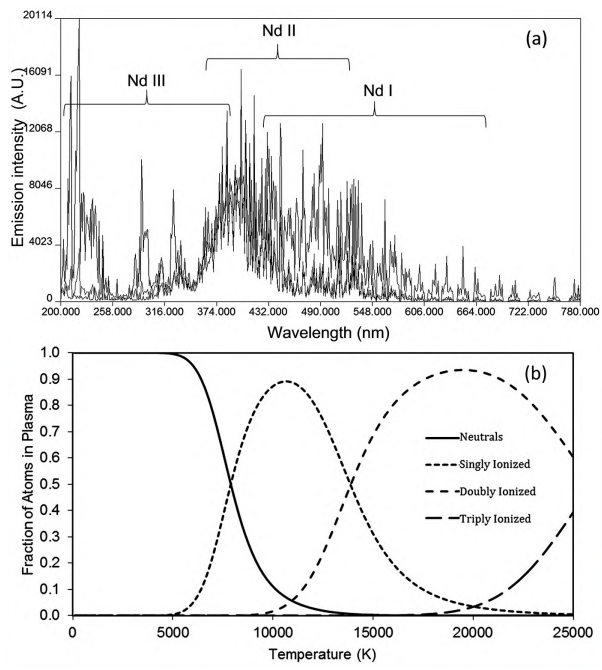

Fig. 3 (a) Three overlaid laser-induced breakdown spectra from a neodymium target (not obtained simultaneously). The spectra differ depending on the temperature of the plasma, which is varied by observing it at different times after plasma initiation. Spectra were acquired at 0.5 to 1 μs (Nd III), 1 to 3 μs (Nd II), and 3 to 13 μs (Nd I) after the laser pulse and plasma breakdown. Spectra have been overlaid and scaled for comparison. (b) A Saha-Boltzmann calculation showing the fraction of Nd atoms in the lower ionization states as a function of plasma temperature.

fraction of neodymium atoms in the first four ionization states as a function of temperature. Utilizing a broadband echelle spectrometer, the entire emission spectrum can be collected from a single laser shot, allowing relative intensity measurements of all spontaneous emission decay channels from an excited state. In this way, atomic branching ratios are obtained and used to calculate absolute emission oscillator strengths, of use in laboratory astrophysics [19,20]. To date we have measured branching ratios in four lanthanides (neodymium, praseodymium, samarium, and lanthanum) and two transition metals (copper and iron). In total we have used laser-induced plasmas to make relative intensity measurements of approximately 7800 atomic transitions from over 800 excited energy levels from those six elements.

LIBS at NRC

At the beginning of the 1990s more LIBS research surfaced in the US and elsewhere in the world. In Canada, NRC pioneered LIBS activities in 1992 where M. Sabsabi and P. Cielo jointly initiated activities in LIBS for the optical inspection of aluminum alloys responding to a request formulated by Alcan for the detection of smut (organic residue from the lubricant) on the surface of an aluminum sheet [21]. Since then, the NRC LIBS team has become one of the most active in this field with numerous publications covering theoretical modeling of the LIBS plasma, hardware advances, and applications. The NRC LIBS team holds 18 patents and has published and contributed more than 420 scientific articles in international journals, lectures, conferences and numerous scientific publications (books, conference proceedings, technical reports, scientific TV programs, etc.)

The NRC research and development LIBS interests include the optical characterization of materials, ultrafast laser spectroscopy, optical diagnostics, remote sensing, material characterization and processing, and the phenomenological study of the LIBS technology. This includes the analysis of the spatial-temporal behavior of the plasma generated by a laser pulse, influence of the pulse energy, duration, and laser wavelength, the technical reliability of material evaluation, optimal conditions for measurements, matrix effects, plasma diagnostics, and an investigation of new LIBS enhancement techniques such as the use of two ablation lasers (double pulse LIBS) or the use of lasers tuned to atomic resonances (RE-LIBS), among others.

In contrast to academic researchers, the NRC LIBS activities have a common objective of moving toward the industrial exploitation of the technique. Based on NRC LIBS inventions, there were four technology transfers to companies for industrial applications of LIBS in the mining, agricultural, metallurgical, and manufacturing industries. As well, the NRC LIBS team has pioneered applications in the pharmaceutical industry and made breakthroughs for metallurgical applications particularly in the analysis of molten metals, slurries for mineral processing, and weak acid for copper refining.

Numerous collaborations with industry and government agencies have led to the development of prototypes with practical solutions to the needs in aerospace, security, environment, mining, automotive, etc. For example, in collaboration with Centre de recherche minerale (now known as COREM, Quebec), the LIBS team developed and carried out onsite testing of an industrial LIBS prototype for the analysis of slurries of iron ore.

Studies of the fundamental aspects of LIBS were investigated in order to improve the sensitivity and the reproducibility of the technique to further this objective. While the application activities were led in collaboration with industry, the fundamental investigations were mostly performed in collaboration with universities such as the groups of Professors M. Chaker (INRS), J. Margot (Université de Montreal) and more recently with M. Laflamme (Université Laval) and S. Rehse (Université de Windsor.) In collaboration with the Institut national de la recherche scientifique (INRS) Énergie et Matériaux in Varennes and the Natural Sciences and Engineering Research Council (NSERC), an NSERC-NRC (NRCI)-INRS)/industry agreement to study femtosecond LIBS was arranged. Fundamental studies were performed on the influence of the pulse duration on the laser-induced plasma (LIP), theoretical modeling of the LIP was conducted, and also the coupling of LIBS with laser-induced fluorescence (LIF) to enhance LIBS sensitivity was investigated [22].

CONCLUSION

Canada, and specifically NRC, has been a leader in the efforts to organize and direct international LIBS research efforts. Not only were most of the LIBS activities in Canada directly or indirectly collaborative with the NRC LIBS team, in 2006 NRC organized the international LIBS 2006 conference in Montreal which was attended by more than 220 researchers from five continents. Both the authors have chaired and organized numerous sessions at conferences around the world dedicated to disseminating LIBS research and encouraging new researchers, and particularly young students, in the area.

At the present, LIBS is extremely successful, but it is still evolving. The number of LIBS papers now is similar to inductively coupled plasma-optical emission spectroscopy (ICP-OES) in the eighties and atomic absorption (AA) in the sixties. This allows us to predict that LIBS is very close to the commercialization threshold. The technology will continue to benefit from technological advancements in the development of lasers, spectrometers, and detectors. Despite these advances, LIBS still faces some important and significant challenges, particularly related to the "matrix effect" (the alteration of a trace analyte's LIBS spectrum due to the medium in which the analyte is embedded), a need for a better fundamental understanding of the laser ablation process, and the lack of reproducibility from laser shot-to-shot. Even with a field

crowded with academic and industrial players, these issues need to be addressed and there is yet more need for advanced research and development in the coming years to overcome these challenges.

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