1 History

1.1 ATOMIC OPTICAL EMISSION SPECTROCHEMISTRY (OES)

1.1.1 CONVENTIONAL OES

Since the early 1800s, scientists realized that elements emitted specific colors of light. As atomic theory developed, spectroscopists learned that those colors, wavelengths or frequencies were a unique signature for each atom and ion. Hence spectra became fingerprints of the emitting atomic species. This is the basis for spectrochemical analysis using atoms.

Early sources of spectra were the sun, flames and gas discharges, such as the old Geissler tube. These were plasma sources, with varying degrees of ionization depending on the source conditions. Against the 5000 K photosphere of the sun, we see the Fraunhofer absorption lines due to neutral and once ionized species. In the solar corona highly ionized spectra are observed because of temperatures that reach into the hundreds of thousands of degrees.

Many sources have been developed for spectrochemistry, but two workhorses have been the conventional electrode spark and, more recently, the inductively coupled plasma (ICP). These are illustrated in Figure 1.1 (Plate 1), which also contains a photograph of the laser spark. The electrode spark has excitation temperatures up to 50 000 K, while the argon ICP temperature is more typically about 10 000 K. Typically they are used for laboratory analyses but occasionally are pressed into service for situations requiring more rapid data acquisition. For example, the conventional spark has been used for decades to monitor the steel making process by withdrawing a molten sample which is then solidified and transported to a laboratory located in the plant for rapid analysis. Decisions on additives are made based on these spectroscopic data.

1.1.2 LASER OES

As soon as the laser was developed in the early 1960s, spectrochemists began investigating its potential uses (Radziemski, 2002). An early observation was that a pulsed laser could produce a small plasma in air. The emission from that plasma

Handbook of Laser-Induced Breakdown Spectroscopy D. Cremers and L. Radziemski

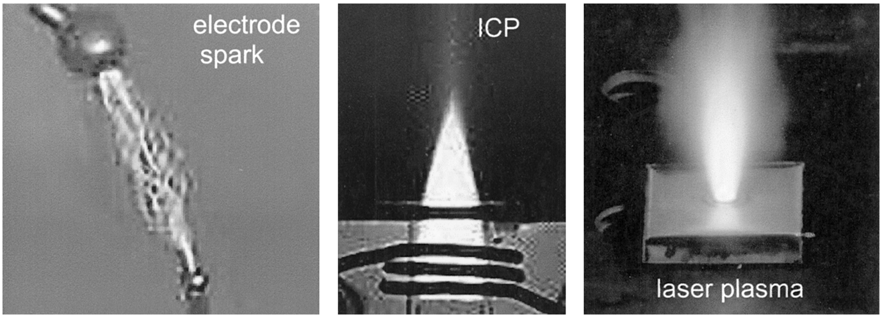

Figure 1.1 Photographs of a conventional electrode spark, an inductively coupled plasma, and a laser-induced spark. The size scales are different (see Plate 1)

showed the potential for spectrochemical analysis. However, from 1960 to 1980 the analytical capability was so inferior to that of the conventional spark and laser technology was in its infancy, so that the technique was less favored than a related one – laser ablation into a conventional plasma source. Here the laser was used to vaporize a small amount of sample for analysis by, for example, the conventional electrode spark (Moenke and Moenke-Blankenburg, 1973). However, that was not the only way the laser could be used in spectrochemistry.

The development of tunable dye lasers meant that one could illuminate a prepared source of atoms with radiation resonant with a transition in one of the atomic species. Then either the absorption of the laser beam or the laser-induced fluorescence could be used as an analytical signal. These techniques discriminated against background and increased the signal to noise considerably by recycling the same atoms many times. Sometimes the atoms were placed in the laser cavity itself. The intra-cavity absorption technique was a very sensitive spectrochemical method, if difficult to employ generally.

Both absorption and fluorescence are used in many applications. However, because the laser needs to be tuned to a specific transition in a specific species, it is not as broadly useful as a hot plasma in which a variety of species can be excited and monitored simultaneously.

1.2 LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

Laser-induced breakdown spectroscopy (LIBS), also sometimes called laser-induced plasma spectroscopy (LIPS) or laser spark spectroscopy (LSS) has developed rapidly as an analytical technique over the past two decades. As most commonly used and shown schematically in Figure 1.2, the technique employs a low-energy pulsed laser (typically tens to hundreds of mJ per pulse) and a focusing lens to generate a plasma that vaporizes a small amount of a sample. A portion of the plasma light is collected and a spectrometer disperses the light emitted by excited atomic and ionic species

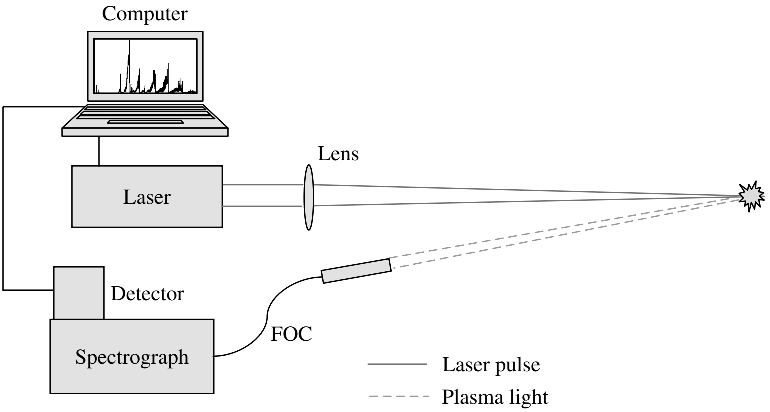

Figure 1.2 A schematic of a simple apparatus for laser-induced breakdown spectroscopy illustrating the principal components

in the plasma, a detector records the emission signals, and electronics take over to digitize and display the results. The **book cover** shows a LIBS spectrum with certain strong spectral features standing out from the continuous background plasma light.

LIBS is an appealing technique compared with many other types of elemental analysis, because setting up an apparatus to perform a LIBS measurement is very simple. One merely focuses a laser pulse in or on a sample, which can be a gas, liquid, aerosol or solid, to form a microplasma, examples of which are shown in Figure 1.3. The spectra emitted are used to determine the sample's elemental constituents. However, the basic physical and chemical processes involved are not so simple. The initiation, formation and decay of the plasma are complex processes. Absorption of the incident laser radiation occurs through the mechanism of inverse bremsstrahlung, involving three-body collisions between photons, electrons, and atoms or molecules. In gases and liquids the plasma creates a shock wave in the surrounding medium transferring energy by means of conduction, radiation and the shock wave. When the experiment deals with a sample surface in a vacuum, the plasma and ejecta expand freely away from the surface at different speeds. Excitation of specific energy levels in different atoms is likewise complex, and depends on factors such as thermodynamic equilibrium and interactions with other atoms and molecules generally lumped under the category of matrix effects. After the laser pulse has terminated (typically within 10 ns), the plasma decays over an interval of one to several microseconds, depending on the laser energy deposited. In vacuum that temporal process is shortened. Most LIBS experiments involve repetitive plasmas with frequencies of 10 Hz or greater.

The spectra observed change as the plasma evolves temporally as shown in Figure 1.4. Soon after initiation, continuum and ionic spectra are seen. The continuum

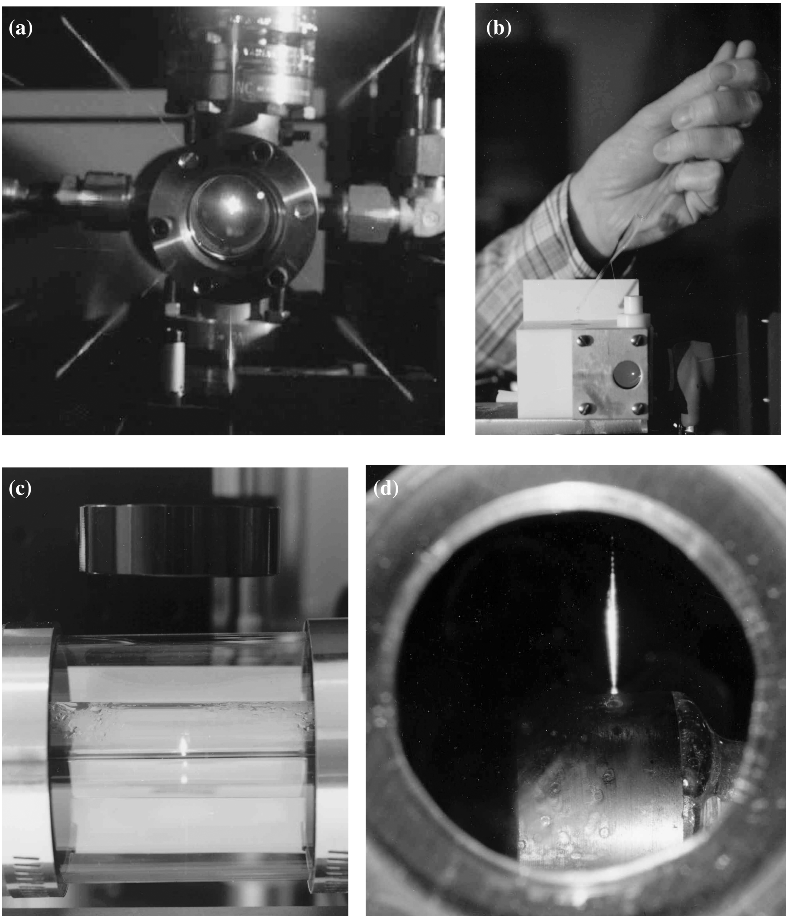

Figure 1.3 The laser spark (a) in a gas, (b) in a liquid, (c) on the surface of a liquid, and (d) on a beryllium (see Plate 2)

is the ‘white light’ from the plasma that contains little spectroscopic information and the ions result from electrons ejected by neutral atoms. As the plasma decays, these are followed by spectra from neutral atoms and eventually simple molecules formed from the recombination of atoms. Throughout the temporal history, one observes a diminishing continuum spectral background due to recombination of free electrons with ions. Inspection of the LIBS spectrum reveals immediate qualitative information about sample composition. After calibration, quantitative information can be obtained. These issues will be treated in greater depth in subsequent chapters.

During the past 10 years, the LIBS technique has made significant progress towards becoming a viable commercial technology. Over the years many useful reviews have been published (Adrain and Watson, 1984; Cremers and Radziemski, 1987; Radziemski and Cremers, 1989; Radziemski, 1994; Lee *et al.*, 1997;

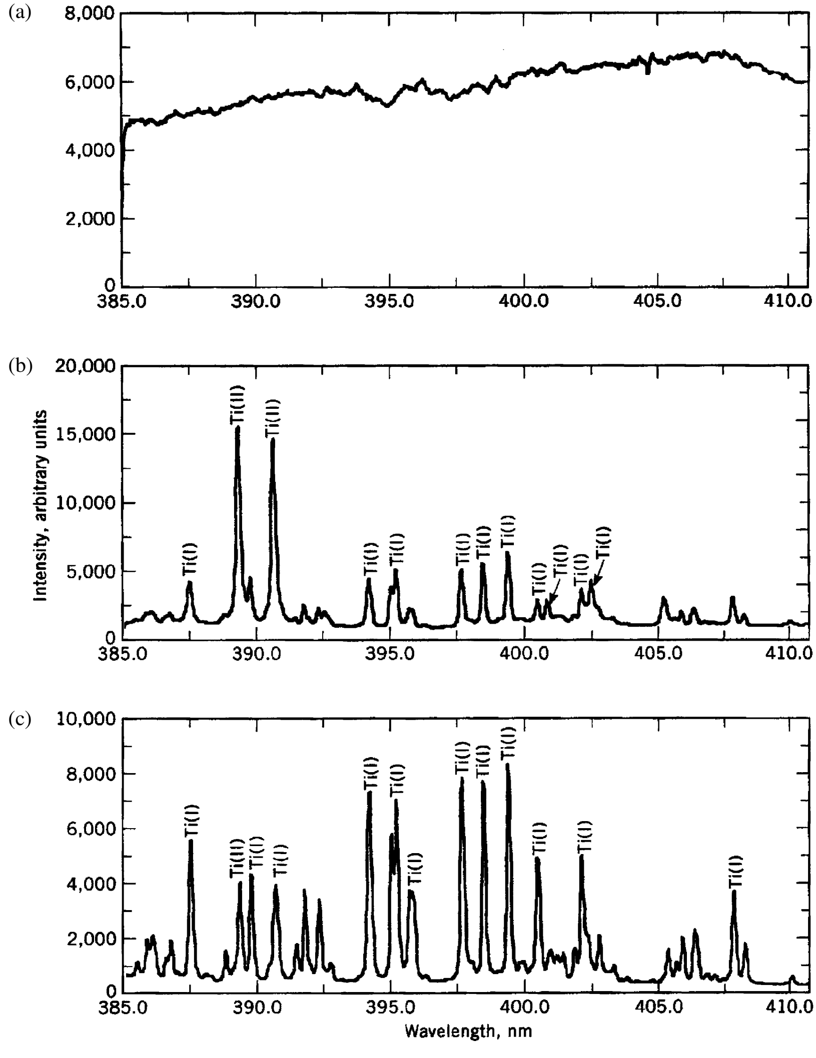

Figure 1.4 Gated titanium spectra of a LIBS plasma illustrating the development of the spectra as a function of the time after plasma initiation. The time intervals are: (a) 0–0.5 μs; (b) 0.5–5 μs; and (c) 10–110 μs

Rusak *et al.*, 1997; Tognoni *et al.*, 2002; Lee *et al.*, 2004). In this chapter we consider the history of the technique and some applications that have spurred its development. We focus on the first time an innovation or application appeared on the scene, rather than tracing every innovation through to the present day. Note however, that contemporary improvements in apparatus, techniques and fundamental understanding are driving reexaminations of old applications. Conversely, the emergence of new applications drives improvements in a recurring spiral of progress.

Table 1.1 Significant milestones in the development of LIBS as an analytical technique applicable to a variety of samples and circumstances

1960	Ted Maiman develops the first pulsed laser
1963	First analytical use of a laser-plasma on surfaces, hence the birth of laser-induced breakdown spectroscopy
1963	First report of a laser plasma in a gas
1963	Laser micro-spectral analysis demonstrated, primarily with cross-excitation
1963	Laser plasmas in liquids were initially investigated
1964	Time-resolved laser plasma spectroscopy introduced
1966	Characteristics of laser-induced air sparks studied
1966	Molten metal directly analyzed with the laser spark
1970	Continuous optical discharge reported
1970	Q-switched laser use reported, results compared with normal laser pulses
1971	Biological materials investigated with LIBS
1972	Steel analysis carried out with a Q-switched laser
1978	Laser spectrochemical analysis of aerosols reported
1980	LIBS used for corrosion diagnostics in nuclear reactors
1982	Initial use of the acoustic properties of the laser-induced spark
1984	Analysis of liquid samples and hazardous aerosols demonstrated
1988	Attempts made to enhance intensities through electric and magnetic fields
1989	Metals detected in soils using laser plasma method
1992	Portable LIBS unit for monitoring surface contaminants developed
1992	Stand-off LIBS for space applications demonstrated
1993	Underwater solid analysis via dual-pulse LIBS demonstrated
1995	Demonstration of fiber optic delivery of laser pulses
1995	Multiple-pulse LIBS reported for use on steel samples
1997	LIBS use in applications in painted works of art and illuminated manuscripts
1998	Subsurface soil analysis by LIBS-based cone penetrometers shown
1998	Reports on the use of echelle spectrometers coupled with CCD detectors
1999	Trace metal accumulation in teeth observed with LIBS
1999	Pulses from different lasers used to enhance LIBS performance
1999	Calibration-free LIBS introduced
2000	Report on commercial instrument for coal analysis
2000	Demonstration of LIBS on a NASA Mars rover
2000	First International conference on LIBS – Pisa, Italy
2002	Second International Conference on LIBS – Orlando, FL
2004	Third International Conference on LIBS – Malaga, Spain
2004	LIBS approved for 2009 Mars mission

Table 1.1 illustrates some significant milestones in LIBS development. These will be addressed individually in the following sections.

1.3 LIBS HISTORY 1960–1980

Shortly after the pulsed ruby laser was invented in 1960 the laser-induced plasma was observed. The first published report mentioning the plasma was a meeting abstract by Brech and Cross in 1962 (Brech and Cross, 1962). Early on, the laser was used primarily as an ablation source with cross-excitation to provide the spectrum. In 1963, Debras-Guédon and Liodec published the first analytical use for spectrochemical analysis of surfaces (Debras-Guédon and Liodec, 1963). Maker *et al.* in 1964 reported the first observation of optically induced breakdown in a gas (Maker *et al.*, 1964). Runge *et al.* in the same year discussed the use of a pulsed Q-switched ruby laser for direct spark excitation on metals (Runge *et al.*, 1964). Linear calibration curves were obtained for nickel and chromium in iron, with precisions of 5.3 % and 3.8 %, respectively. They also analyzed molten metal. In 1966, Evtushenko looked at the effect of sparks from two lasers (Evtushenko *et al.*, 1966). About the same time, Young *et al.* described the characteristics of laser-induced air sparks (Young *et al.*, 1966).

In the period from 1964 to 1967 the first instruments based primarily on laser-ablation with cross-excitation were developed by Zeiss (Germany), Jarrell-Ash (USA) and JEOL Ltd (Japan). Although they could be operated with the laser plasma generating the spectral emissions, most often the laser was used only for ablation followed by cross-excitation with a conventional spark. Because the auxiliary spark could contaminate and complicate the analysis through the introduction of electrode material, auxiliary excitation by electrodeless methods was also developed. The instruments could not typically compete in accuracy and precision with conventional spark spectroscopy, although they could handle nonconducting samples. Some instruments continued in use through the 1990s. An excellent discussion of those devices and the associated techniques is contained in the book entitled *Laser Micro Analysis* (Moenke-Blankenburg, 1989).

Time resolution of the decaying plasma helps to monitor the plasma evolution, to discriminate against the continuum light, and to sort out spectral features. It is especially valuable in reducing interferences between spectral features that appear at the same or adjacent wavelengths but in different temporal windows as illustrated in Figure 1.4. Different detection systems to obtain temporally resolved spectra were used in the 1960s, including a streak camera and rotating mirrors. A method more suited to modern detectors, electronically gating and averaging the signals from many plasmas, was developed by Schroeder *et al.* (Schroeder *et al.*, 1971). As detectors have developed, the preferred methods of time resolution have moved from boxcar averagers, for example, to gated, intensified charge coupled detectors. Fast photodetectors are used to record the temporal profile of plasma emissions from single pulses. An early review of the field was published by Scott and Strasheim in 1970 (Scott and Strasheim, 1970).

During this period, much of the research on the laser plasma and its uses appeared in the Russian literature. For example, Afanas'ev and Krokhin published on the vaporization of matter exposed to laser emission (Afanas'ev and Krokhin, 1967). In 1966, Raizer reported on breakdown and heating of gases under the influence of a laser beam, which was a summary of original work and a review of the state of the art (Raizer, 1966). Biberman and Norman did a thorough analysis of the origins of the continuous spectrum from the laser plasma which underlies the discrete spectral lines (Biberman and Norman, 1967). In 1974, Buravlev *et al.* commented on using a laser in spectral analysis of metals and alloys (Buravlev *et al.*, 1974). Much of the physics covered in the Russian literature was summarized in the classic book by

Raizer, *Laser-induced Discharge Phenomena*, published in English in 1977 (Raizer, 1977). Underlying that is the classic book on the physics of shock waves and high-temperature hydrodynamic phenomena, a text originally published in Russian in 1964, translated into English in 1966, and recently reprinted (Zel'dovich and Raizer, 2002).

Early on it was recognized that physical and chemical matrix effects would have to be dealt with if LIBS was to develop as a quantitative method. Cerrai and Trucco discussed matrix effects in laser-sampled spectrochemical analysis (Cerrai and Trucco, 1968). They focused on the dependence of spectral line intensities on physical conditions such as grain sizes and boundaries. This was followed by a paper by Marich *et al.* concluding that physical effects were more important than chemical ones (Marich *et al.*, 1970). However others, like Scott and Strasheim, found signal suppression due to various effects linked to the components of the matrix (Scott and Strasheim, 1970). It is now accepted that a variety of physical and chemical effects play important roles in signal strength, and repeatability.

Biological media with metallic contamination were investigated by the laser plasma as reported in papers by Marich *et al.* and Treytl *et al.* (Marich *et al.*, 1970; Treytl *et al.*, 1972). The former deals with the effect of the matrix on the spectral emission from a variety of samples, including human serum and liver. The latter provides detection limits for the analysis of metals in biological materials. Metals in the form of reagent grade salts were incorporated into gelatin or albumin matrices. Limits of detection ranged from 2×10^{-15} gm for magnesium and copper to 3×10^{-13} gm for mercury and iron.

A novel variation of the pulsed plasma is the continuous optical discharge (COD). In this case a continuous wave (CW) laser beam is focused to sustain a plasma as long as the laser remains on. The laser is usually of the continuous CO_2 variety. Initiation requires another pulsed laser or a conventional spark. Early papers on this subject were published by Generalov, and Keefer (Generalov *et al.*, 1970; Keefer, 1974). Spectrochemical analysis by the COD was investigated by Cremers *et al.* (Cremers *et al.*, 1985).

Materials processes such as welding were obvious applications of high powered lasers. The plasma literature in that field overlapped with that of spectrochemical applications. In the first of a series of books, Ready (Ready, 1971) provided an overview of the variety of phenomena induced by high power laser pulses. Some of the subjects discussed were: optical damage of materials; the interaction between laser radiation and surfaces resulting in ablation, melting, and crater formation; the effect of laser light on biological systems; and optically induced gas breakdown. The most recent version edited by Ready is a compendium of 30 years of research, the *LIA Handbook of Laser Materials Processing* (Ready, 2001).

Generating a plasma in water was considered first by Buzukov *et al.* (Buzukov *et al.*, 1969). Lauterborn (Lauterborn, 1972) conducted high-speed photography of plasmas in liquids. This was followed by measurements of shock waves and cavities caused by laser-induced breakdown in water, glycerin, and benzene by Teslenko (Teslenko, 1977). These mechanistic studies focusing on the shock wave formation and propagation continued throughout the 1970s.

In the mid to late 1970s aerosols became a subject of research. The effects of dust and particles in the beam as they influenced breakdown were studied by Lencioni (Lencioni, 1973). He found that when long focal-length lenses were used, dust in the beam initiated strings of mini-plasmas. Belyaev *et al.* discussed laser spectrochemical analysis of aerosols in a 1978 publication (Belyaev *et al.*, 1978). In 1979 Edwards and Fleck Jr published on the two-dimensional modeling of aerosol breakdown in air (Edwards and Fleck Jr, 1979). This was followed by a study in 1982 by Ivanov and Kopytin on selective interaction of a train of laser pulses with an aerosol medium (Ivanov and Kopytin, 1982).

A spin-off method of LIBS called TABLASER was described by Measures and Kwong starting in 1979 (Measures and Kwong, 1979). That technique uses an ablation laser pulse followed by a laser pulse through the plume. The second pulse from a dye laser is tuned to a transition in the element of interest and results in laser-induced fluorescence. Interest in this type of arrangement surfaced again in the 1990s.

1.4 LIBS HISTORY 1980–1990

As lasers and other LIBS components became smaller and the *in situ* advantages of the laser plasma became more obvious, additional applications appeared. Interest at Los Alamos National Laboratory was kindled by two 1981 papers on the time-integrated (Loree and Radziemski, 1981) and time-resolved (Radziemski and Loree, 1981) forms of the technique in gases. The term LIBS was originally used in the former 1981 paper, and TRELIBS, identified with the time-resolved version, in the latter. Currently LIBS is the term used for either method.

Los Alamos then funded an internal study of the use of this technique for detection of toxic beryllium dust, resulting in papers on detecting beryllium in air (Radziemski *et al.*, 1983a) and on filters (Cremers and Radziemski, 1985). Figure 1.5 shows a long spark created by using a cylindrical lens, on a rotating stage on which a blackened piece of filter paper has been set for contrast. During that period, Los Alamos scientists studied the detection of hazardous gases (Cremers and Radziemski, 1983), aerosols (Radziemski *et al.*, 1983b), and liquids (Cremers *et al.*, 1984; Wachter and Cremers, 1987). Sensing of steels and other metals in molten or solid forms were also investigated (Cremers, 1987).

Some research focused on diagnostics and enhancements. The plasma generates shock waves that can be heard and recorded as acoustic signals, whose strengths are related to the energy deposited in the medium. The acoustic properties of the spark were first studied by Belyaev *et al.* (Belyaev *et al.*, 1982). Kitamori (Kitamori *et al.*, 1988) started an interesting line of research in particle counting in liquids by using the acoustic effect produced by the plasma. He also made observations of the optical emission. Beginning with the early 1990s, more quantitative uses of acoustic signals were reported, for example by Diaci and Mozina (Diaci and Mozina, 1992), who studied the blast waveforms detected simultaneously by a microphone and a

Figure 1.5 A long spark created by using a cylindrical lens, on a filter set on a rotating stage

laser probe. Starting in 1988, there were several reports of attempts to enhance the plasma by the use of auxiliary magnetic or electric fields. None have reported dramatic success.

Much interest was shown in the initiation of the spark on single microspheres or droplets. Results included a paper by Chylek *et al.* (1986), on the effect of size and material of liquid spherical particles on laser-induced breakdown. This line of research was continued in a paper by Biswas *et al.* (1988) detailing the irradiance and laser wavelength dependence of plasma spectra from single levitated aerosol droplets. Chang *et al.* (1988) discussed laser-induced breakdown in large transparent water droplets.

In the late 1980s interest increased in making LIBS more quantitative by addressing the factors such as differential excitation. These included many works from the Niemax group in Dortmund (Ko *et al.*, 1989; Leis *et al.*, 1989). In the study by Ko *et al.* the stability of internal standardization was investigated. They found that the chromium to iron intensities in binary mixtures were not a function of time after plasma initiation, hence temperature, or completeness of vaporization. This was in contrast to zinc to copper ratios in brass. The conclusion was that internal standardization was not a given in all cases, but the conditions for its use needed to be established for each situation. In the study by Leis *et al.*, the atomization and propagation properties of the plasma plume were investigated.

Studies of toxic and superconducting materials were made. These included analysis of beryllium in beryllium-copper alloys (Millard *et al.*, 1986) and detection of cadmium, lead and zinc (Essien *et al.*, 1988). The superconducting materials community published many papers on laser ablation for deposition of superconducting thin films, and sometimes addressed the optical emission as a diagnostic technique for process monitoring. A method of monitoring corrosion in the core regions of nuclear reactors was detailed by Adrain (Adrain, 1982) and a working system was described.

At the close of the decade, a book edited by Radziemski and Cremers, *Laser-induced Plasmas and Applications*, summarized the relevant physics, chemistry and applications at that time (Radziemski and Cremers, 1989). It contained detailed chapters updating the physics of breakdown and post-breakdown phenomena, and an updated review of the technique.

1.5 LIBS HISTORY 1990–2000

As the field proceeded into the 1990s, applications and fundamental studies developed rapidly. There were several useful reviews during this decade (Radziemski, 1994; Song *et al.*, 1997; Rusak *et al.*, 1998). Hou and Jones (Hou and Jones, 2000) reviewed several techniques with field capability and presented the advantages and disadvantages of each.

More research groups surfaced in the US and in other countries. In Australia, Grant *et al.* provided detection limits for minor components in iron ore (Grant *et al.*, 1991). This was done with a view to developing a field-based technique. Later Chadwick's group in Australia analyzed lignite and produced a commercial instrument for coal analysis (Wallis *et al.*, 2000). Sabsabi and Cielo (Canada) started publishing their work on aluminum alloy targets with papers in 1992 and 1995 (Sabsabi and Cielo, 1992, 1995). Palleschi's group in Pisa, Italy began addressing applications with respect to pollutant detection such as the paper by Lazzari *et al.* on the detection of mercury in air (Lazzari *et al.*, 1994).

The application of LIBS to remote analysis, begun in the 1980s, developed rapidly in the 1990s. It was an important area of investigation by Cremers' group at Los Alamos. Cremers *et al.* (Cremers *et al.*, 1995) discussed remote elemental analysis by laser-induced breakdown spectroscopy using a fiber optic cable. Angel's group also published on the use of a fiber optic probe to determine lead in paint (Marquardt *et al.*, 1996). LIBS for the analysis of lunar surfaces was first mentioned in papers by Blacic *et al.* and Kane *et al.* (Blacic *et al.*, 1992; Kane *et al.*, 1992). This was followed by a seminal paper by Knight *et al.* (Knight *et al.*, 2000) on characterization of LIBS for planetary exploration, and a report on the use of LIBS on a prototype Martian rover (Wiens *et al.*, 2002). Figure 1.6 shows a K9 rover with the LIBS sensor unit on the mast.

Efforts to make LIBS more quantitative continued. Davies *et al.* (Davies *et al.*, 1996) reported on relevant factors for *in situ* analytical spectroscopy in the nuclear industry. Russo's group at Lawrence Berkeley Laboratory undertook detailed studies of the ablation process as reported by Mao *et al.* (Mao *et al.*, 1995). Winefordner's group at the University of Florida initiated studies of the variables influencing the precision of LIBS measurements. Their first publication in this area was by Castle *et al.* (Castle *et al.*, 1998) where a variety of factors were considered and inter- and

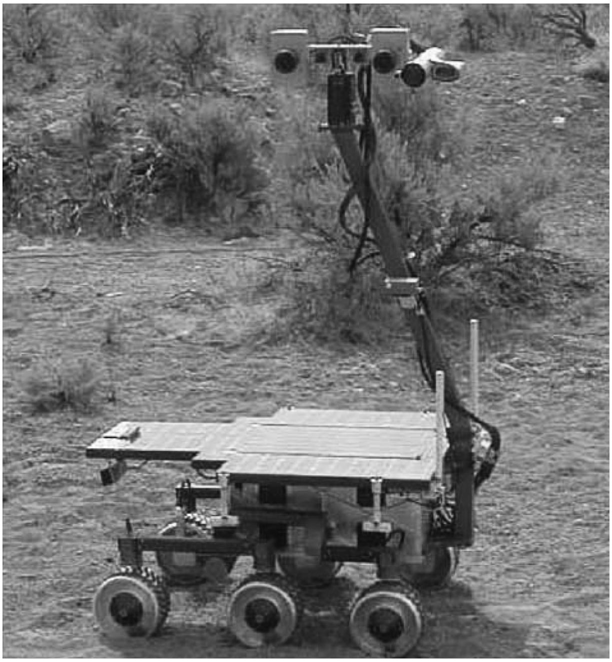

Figure 1.6 The K9 rover in the field with the LIBS sensor mounted on the right side of the mast head instrument suite. (Photo courtesy of NASA Ames Research Center)

intra-shot measurement precisions were calculated. The best precision obtained was 0.03 %. Gornushkin *et al.* reported on a curve of growth methodology applied to laser-induced plasma emission spectroscopy (Gornushkin *et al.*, 1999). A procedure called ‘calibration-free LIBS’ (CF-LIBS) was developed in Palleschi’s group, as explained in a paper by Ciucci *et al.* (Ciucci *et al.*, 1999). In effect, one assumes thermodynamic equilibrium, and uses spectral lines representing the bulk of the vaporized material, to deduce the concentration of the element of interest. Matrix effects continued to be studied. For example, the effects of water content and grain size were reported by Wisbrun *et al.* (Wisbrun *et al.*, 1994). These works and others have sharpened the focus on factors that can enhance or hinder the ability to obtain quantitative results.

Throughout the decade unique applications continued to emerge. Harith *et al.* studied the hydrodynamic evolution of laser driven diverging shock waves (Harith *et al.*, 1990). Quantitative simultaneous elemental determinations in alloys, using LIBS in an ultra-high-vacuum, was reported by Theim *et al.* (Theim *et al.*, 1994). The US Army Aberdeen Proving Ground laboratory under Miziolek began its investigations of LIBS with two publications by Simeonsson and Miziolek (Simeonsson and Miziolek, 1993, 1994). They studied LIBS in carbon monoxide, carbon dioxide, methanol and chloroform, and used a variety of laser wavelengths from 193 to 1064 nm. The group of Aragón, Aguilera and Campos (Aragón *et al.*, 1993) applied LIBS to determining carbon content in molten steel. Poulain and Alexander (Poulain and Alexander, 1995) used LIBS to measure the salt concentration in seawater aerosol droplets. Singh's group published on quantification of metal hydrides (Singh *et al.*, 1996) and LIBS spectra from a coal-fired MHD facility (Zhang *et al.*, 1995).

Art analysis has received much attention, for example as described by Anglos *et al.* (Anglos *et al.*, 1997), who worked on diagnostics of painted artworks using LIBS for pigment identification, and Georgiou *et al.* (Georgiou *et al.*, 1998), who described excimer laser restoration of painted artworks. Vadillo and Laserna published work on depth-resolved analysis of multilayered samples, a technique that is used in forensic archeometry (Vadillo and Laserna, 1997). Applications to biological materials were developed. Samek *et al.* studied trace metal accumulation in teeth (Samek *et al.*, 1999). Pallikaris *et al.* (Pallikaris *et al.*, 1998) reported on the use of LIBS for monitoring corneal hydration, while Sattmann *et al.* started work on polymer identification that resulted in an apparatus to sort plastics (Sattmann *et al.*, 1998).

Determination of the composition of soils and contaminants received considerable attention. Eppler *et al.* (Eppler *et al.*, 1996) reported on matrix effects in the detection of Pb and Ba in soil. Detection limits of 57 and 42 ppm (w/w) for Pb and Ba, respectively, were achieved. A cylindrical focusing lens yielded higher experimental precision than a spherical lens. Miles and Cortes performed subsurface heavy-metal detection with the use of a cone penetrometer system (Miles and Cortes, 1998). A real-time fiber-optic LIBS probe for the *in situ* detection of metals in soils was used by Theriault *et al.* (Theriault *et al.*, 1998).

Much work was directed to improvement in instrumentation and techniques. Undoubtedly the greatest impact was achieved by the introduction of the compact echelle spectrometer mated with the ever-more capable CCD detectors, intensified or not. A good introduction to these subjects can be found in Vadillo *et al.* (Vadillo *et al.*, 1996), who reported on space and time-resolved LIBS using CCD detection. Also Barnard *et al.* (Barnard *et al.*, 1993) commented on the design and evaluation of echelle grating optic systems for ICP-OES, and Harnley and Fields (Harnley and Fields, 1997) wrote on solid-state array detectors for analytical spectrometry. Bauer *et al.* described an echelle spectrometer and intensified CCD combination (Bauer *et al.*, 1998).

Diode lasers may be sources of the future because of their small size and simplicity of operation. An introduction to the subject for laser spectrochemistry was given by Lawrenz and Niemax (Lawrenz and Niemax, 1989). A passively Q-switched Nd:YAG microchip laser was described by Zayhowski (Zayhowski, 2000). The laser was 1 to 2 mm on a side and was diode pumped. Peak powers approaching 0.5 MW were reported.

As lasers with new parameters became available they were put to use on LIBS applications. The result of 60 ps Nd:YAG 532 nm pulses was reported by Davis *et al.* (Davis *et al.*, 1993). Kagawa *et al.* (Kagawa *et al.*, 1994) wrote on XeCl excimer laser-induced shock wave plasmas and applications to emission spectrochemical analysis. Sattman *et al.* (Sattman *et al.*, 1995) discussed analysis of steel samples using multiple Q-switched Nd:YAG laser pulses. Lasers with pulses of different lengths were used and their results compared. Femtosecond, picosecond, and nanosecond laser ablation of solids was discussed by Chikov *et al.* (Chikov *et al.*, 1996). Fedosejevs' femtosecond LIBS group has focused on laser pulses of hundreds of microjoules, dubbed 'microlibs,' as reported by Rieger *et al.* (Rieger *et al.*, 2000). Microline imaging was discussed by Mateo *et al.* in Laserna's group (Mateo *et al.*, 2000). Angel *et al.* reported on using dual pulses and pulses of 1.3 ps and 140 fs (Angel *et al.*, 2001). Both show very low background signals, so time resolution is not necessary; however the low signal levels dictate a higher repetition rate and adequate summing of spectra.

Later in the 1990s the applications turned to very practical problems, such as monitoring environmental contamination, control of materials processing, sorting of materials to put them in proper scrap bins, and slurry monitoring. Barrette and Turmel (Barrette and Turmel, 2000) used LIBS for on-line iron-ore slurry monitoring for real-time process control. Buckley *et al.* (Buckley *et al.*, 2000) implemented LIBS as a continuous emissions monitor for toxic metals. Palanco and Laserna (Palanco and Laserna 2000) studied the full automation of a laser-induced breakdown spectrometer for quality assessment in the steel industry with sample handling, surface preparation, and quantitative analysis capabilities. St-Onge and Sabsabi (St-Onge and Sabsabi, 2000) published on quantitative depth-profile analysis using LIPS on galvannealed coatings on steel. Laser ablation continues as an active area, and is well summarized in a review by Russo *et al.* (Russo *et al.*, 2002).

An emphasis on developing rugged, moveable instrumentation emerged at this time. Optical fibers were built into LIBS systems, primarily for carrying the spark light to the spectrometer, but also for the delivery of the laser pulse as well. More compact echelle spectrographs have been developed. An instrument the size of a small suitcase, used for analysis of contaminants in soils and lead in paint, was made

Figure 1.7 A portable LIBS surface analyzer, circa 1998

in Cremers' Los Alamos laboratory as reported by Yamamoto *et al.* (Yamamoto *et al.*, 1996). A later version of this unit is shown in Figure 1.7. Capability and compactness have improved since that time. The maturity of LIBS was demonstrated by its recent adoption for use in planetary geology on a 2009 mission to Mars.

1.6 ACTIVE AREAS OF INVESTIGATION, 2000–2002

As we entered the new millennium, international meetings in Pisa, Italy (Corsi *et al.*, 2001), Cairo, Egypt (Harith *et al.*, 2002), Orlando, FL, USA (Hahn *et al.*, 2003), Crete (Anglos and Harith, 2004) and Spain (Laserna, 2005) provided excellent summaries of the current status of LIBS applications. New areas of study include increasing exploration of the vacuum ultraviolet region of the spectrum. Biological applications on human teeth, bones and tissue are becoming more common. Pollen, spores and bacteria are being studied to see if unique signatures can be determined. Homeland security applications are proliferating. Surface mapping and imaging modes using line sparks are proving useful to determine surface compositional variations. Sophisticated statistical techniques are being applied to extract signals and reliability factors. New papers are appearing in relevant journals every month. The growth of publications involving LIBS through 2002 is illustrated in Figure 1.8. LIBS instruments are being marketed, especially for materials analysis and toxic materials identification. Because LIBS is the most versatile analytical method yet developed, many applications studied in the earlier LIBS periods have resurfaced because of increased needs or improved instrumental capabilities. Likewise patents

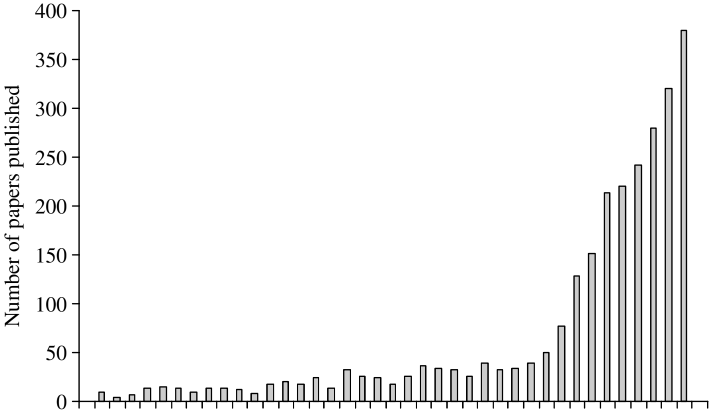

Figure 1.8 LIBS papers per year, 1966–2005. In the last 5 years, about 1140 papers have been published relating to LIBS. (Courtesy of M. Sabsabi)

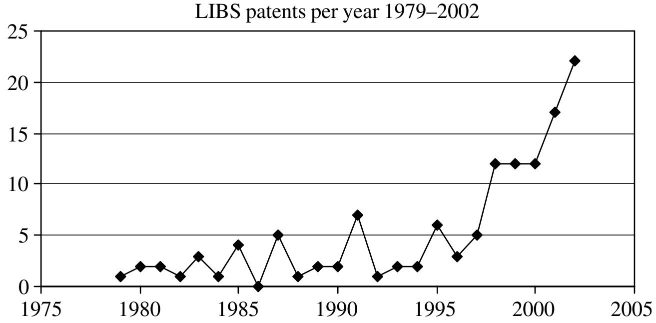

Figure 1.9 LIBS patents per year, 1979–2002. (Courtesy of M. Sabsabi)

involving LIBS are proliferating rapidly, as illustrated in Figure 1.9. All this points to the fact that interest in LIBS as an analytical technique is increasing, a trend which we believe will continue in the coming years.

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