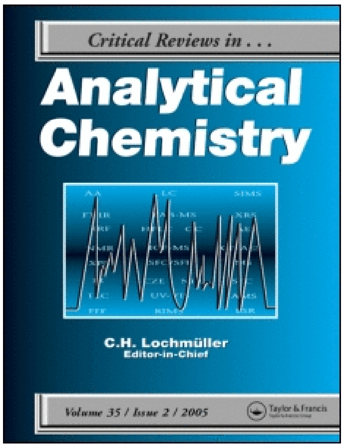

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Fundamentals and Applications of Laser-Induced Breakdown Spectroscopy

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ABSTRACT: Laser-induced breakdown spectroscopy is reviewed by dividing the literature into three categories according to target phase: solid, liquid, or gas. Within each category, the literature is further divided into a fundamental studies section and an analytical results and applications section.

KEY WORDS: laser-induced breakdown spectroscopy.

I. INTRODUCTION

There have been several publications in the last decade which have reviewed laser-induced breakdown spectroscopy (LIBS) either as a unique method of elemental analysis, or as a member of the family of atomic emission techniques. LIBS has also been addressed in reviews on laser applications, process monitoring, and materials processing. Many spectroscopic studies of laser plasmas have also appeared in the physics journals. In order to construct a meaningful review, the literature must first be reduced to a subset. In this instance, LIBS in analytical chemistry is chosen.

This review will cover fundamental studies and analytical results and applications of LIBS related to the field of analytical chemistry. The review is divided according to target phase. Solids, liquids and gases are treated in sections devoted to each. Articles from the physics literature are included when they are of interest to the analytical chemist. Spectroscopic studies of laser-induced plasmas created in pulsed-laser deposition (PLD) experiments have, for the most part, been omitted under the assumption that these papers are more pertinent to materials science than to analytical chemistry. Fundamentals and applications of laser ablation as a sampling technique are also ignored on the grounds that, in these instances, the laser plasma does not serve as the excitation source.

The time frame to be covered has not been specifically defined because the amount of literature dealing with each of the three phases of targets differs greatly. The literature on solids is easily the largest, and so the review of solids is taken almost entirely from publications within the last 5 years.

Literature on laser-induced breakdown in gases is the oldest. Many of these publications are in the physics literature and deal with mechanisms of breakdown and plasma diagnostics. There are a smaller number of papers that report upon the determination of trace metals in gas phase matrices. Most of these are intended to prove the usefulness of LIBS in hazard monitoring. In the section on gases, the analytical chemistry

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literature over the past 10 years is reviewed and appropriate additions are made from the physics literature.

The section dealing with liquids includes bulk liquids, isolated droplets, and aerosols generated from liquids. Among the chemistry journals, this literature is the smallest. The physics is of interest primarily because of medical applications of laser-induced breakdown, and publications which are judged to be of interest to the analytical chemist have been included. All publications related to the elemental analysis of liquids by LIBS during the last 14 years are included.

Previous reviews on this topic begin with a 1984 review by Adrain and Watson titled "*Laser Microspectral Analysis: A Review of Principles and Applications*."[1] This was followed by Cremers and Radziemski who published "*Laser-induced Breakdown Spectroscopy: Principles, Applications, and Instrumentation*" in 1990.[2] This paper included a brief review of theory and instrumentation for LIBS followed by a few industrial applications. In 1992, Thiem et al. reviewed LIBS theory as part of their paper titled "*Lasers in Atomic Spectroscopy: Selected Applications*."[3] The section on laser-induced plasma covered laser-material interaction, plasma production factors (wavelength, energy, and properties of target), and emission factors (temperature and electron density).

Majidi and Joseph published "*Spectroscopic Applications of Laser-Induced Plasmas*" in 1992.[4] This publication has perhaps had the most influence in terms of style and content on the review that follows. Majidi and Joseph reviewed analytical results on solids, liquids, gases, and mixed phase systems for the years 1987–1992. Emphasis was on applications of LIBS such as determination of hazardous elements in air, toxic elements in wastewater, and elements of interest in coals and iron ores. The authors stressed the fact that LIBS required only optical access to samples.

In 1993, Ibrahim and Goddard published "*An Overview of Laser-Induced Breakdown Spectroscopy*."[5] They concentrated on the topics of laser-material interaction, local thermodynamic equilibrium, and plasma diagnostics. The instrumentation was described, the use of gated detection was explained, and a few applications were presented. It was not a literature review.

In a 1993 review by Darke and Tyson titled "*Interaction of Laser Radiation with Solid Materials and its Significance to Analytical Spectrometry*," applications of LIBS were reviewed in the section on laser ablation.[6] In this paper, LIBS was referred to as laser microprobe optical emission.

The following year application of LIBS to process control was briefly reviewed by Noll et al.[7] The authors discussed fundamentals of plasma formation and laser-material interaction with respect to optical and heat penetration, laser energy, density, and absorbance. The use of fiber optics and on-line sampling was discussed, and a periodic table was presented showing elements which had been determined and their detection limits in iron ore. This idea was incorporated into the review that follows. Each section was concluded with a periodic table or tables with elements that have been determined and shaded according to detection limit.

Most recently, LIBS was briefly reviewed as a section in the comprehensive review of atomic emission by Sharp et al. published in 1995.[8]

II. SOLIDS

A. Fundamental Studies

Many papers in this area stem from the need to more fully understand the LIBS plasma in order to obtain useful quantitative results. One such paper is the 1988 publication by Chen and Yeung who used the acoustic signal generated by a laser-induced plasma as an internal standard.[9] They reported that the magnitude of the acoustic wave was proportional to the emission signal for major and minor elements within the solid target. Furthermore, they found that this proportionality was independent of laser power and focus spot size.

In the same year, Wood et al. studied the effect of laser pulse duration on soft X-ray emission from a tantalum target.[10] Using a colliding-pulse mode locked dye laser at 620 nm with pulse durations of 100 and 600 fs and a Nd:YAG laser at 1064 nm with a pulse duration of 70 ps, the plasma emission in the range from 10 to 71 nm was observed. It was found that longer pulses gave relatively more short wavelength emission and longer emission lifetimes than short pulses.

In 1989, Coche et al. used laser-enhanced ionization detection in a laser plasma to study the processes of ionization and recombination.[11] They used a N_2 laser (337.1 nm, 5 mJ, 10 ns) to ablate a solid target. A dye laser was used to selectively ionize species in the plasma at different delays relative to the ablation pulse. Optogalvanic detection was used to give an indication of the number of atoms in the probe volume at the chosen time delay. In this way, ionization and recombination rates could be inferred.

Also in 1989, Iida studied the atomic emission characteristics of a laser plasma in reduced pressure argon.[12] Using a ruby laser (1.5 J, 20 ns), a plasma about 10 mm in height, and more than 100 μs in duration was formed at pressures between 0 and 50 Torr. The plasma at 50 Torr had greatly increased line emission and background due to confinement by the Ar atmosphere. The plasma at lower pressure showed less background and less line emission.

Another investigation of plasma expansion was done by Balazs et al. in 1991.[13] These authors investigated ruby laser pulses on a copper target, and constructed a two-part model for the interaction. The first part of the model dealt with the heating and melting of the solid and included parameters such as thermal diffusivity, pulse duration, and density. The second part of the model described the plasma expansion into a vacuum.

Mason and Goldberg have characterized a laser plasma in a pulsed magnetic field.[14] The first part of the paper included spatially resolved emission studies. The authors found that when a pulsed magnetic field was oriented normal to the laser beam, it caused radial compression and axial expansion in the plasma. The emission intensities of both atoms and ions were also increased in this magnetically confined plasma.

In the second part of the paper, the authors discuss time resolved emission and absorption studies. They concluded that the increase in emission seen in the plasma was due to Joule heating caused by the induced secondary current in the plasma. This was evident by the fact that the increase in emission was seen later in time than the maximum of the applied magnetic field. Also, the intensity increase was attributed to increased atomization efficiency and longer residence times in the plasma.

The effects of buffer gas type on the plasma produced by a Nd:YAG laser (1064 nm, 100 mJ, 7 ns) on a metal target was studied by Owens and Majidi in 1991.[15] They observed an increase in the ratio of Al II/Al I intensity in helium gas relative to argon gas and air. This increase was attributed to the ability of excited helium atoms to transfer energy to a similar energy level in the aluminum ion.

More metal target studies were performed by Lee et al. in 1992.[16] These authors used an ArF laser (193 nm, 100 mJ, 10 ns) to produce plasmas on copper and lead. The lead plasma was much larger than the copper plasma (5 mm vs. 2 mm) and had a slightly lower excitation temperature as determined by Boltzmann plots. The temperature of the copper plasma was 13200 to 17200 K, the lead plasma was 11700 to 15300 K.

In 1992 Marine et al. studied plasma expansion by optical time-of-flight measurements.[17] They determined that the velocity distribution of ions produced by a UV pulse of several nanoseconds duration was broad and not well defined. In contrast, the ions produced by a picosecond IR pulse traveled with a velocity inversely proportional to the square root of their mass. Neutral atoms still had a poorly defined velocity distribution. These authors also noted the appearance of a bi-modal temporal profile for YO^+ emission and attributed this to two possible mechanisms for formation of YO^+.

Kuzuya et al. studied the effect of laser energy and atmosphere on the emission characteristics of laser-induced plasmas.[18] They used a Nd:YAG laser at 1064 nm and pulse energies from 20 to 95 mJ in atmospheres of He, Ar, and air from 1 Torr to 1 atm. The authors reported that maximum emission intensity was observed at 95 mJ in 200 Torr of Ar. However, maximum signal to background was obtained in helium at 40 Torr and 20 mJ of power. Images showed the different sizes and shape of these plasmas.

Okana et al. studied mass removal in non-metallic inorganic solids and determined relationships between laser power and atom yields.[19] Their paper described vacancy initiated laser ablation as a process by which weakly bound atoms were released from around vacancies and vacancy clusters. The atom yield was determined to be an exponential function of laser fluence.

Time resolved emission studies from a laser plasma on sodium chloride were reported by Yago et al. in 1993.[20] They used a Nd:YAG laser of 150 ns duration focused onto a NaCl pellet. The emission spectra showed self-reversal in air but not in a vacuum. The plasma was divided into two zones, a hot core behaving as an emission zone, and a low-temperature periphery behaving as a reabsorption zone. The plasma expansion rate was shown to be determined by ambient gas pressure.

In 1994, Kagawa et al. used a XeCl laser (308 nm, 15 to 70 mJ, 20 ns) to produce plasma on a Zn target in vacuum.[21] Time-resolved studies showed a number density jump that represented the blast wave expansion into the observed volume. This outermost portion of the plasma was shown to be ideal for analytical measurements because the background in this area was greatly reduced.

In 1994, Tambay and Thareja studied emission in a laser plasma of Cd metal vapor formed in a heatpipe.[22] They showed that emission from the vapor was stronger when the plasma was formed on a tungsten target than it was when the plasma was formed in the gas itself. The authors claimed that this was due to pumping of the vapor by soft X-rays formed on the tungsten target.

Transition probabilities of 28 Si ion lines were determined using a laser-induced plasma as a source by Blanco et al. in 1995.[23] Using a Nd:YAG laser (1064 nm, 280 mJ, 10 ns) to produce a plasma on pure silicon, these authors observed emission in Ar and Kr atmospheres. The plasma produced was found to have an excitation temperature of 20000 K and an electron density of 10^{17} cm^{-3}. Absolute transition probabilities for the Si ion lines were calculated.

Jensen et al. published mechanistic studies of laser-induced breakdown on model environmental samples in 1995.[24] They used a KrF laser (248 nm, 30 ns) to produce plasmas on SiO_2 containing Eu and Cr, which were added as the solids Eu_2O_3 and $K_2Cr_2O_7$ to the sand. Detection limits of 100 ppb for Eu and 2 ppb for Cr were reported. A sample was also prepared in which the source of Cr was a solution which was added to the sand and then evaporated. This method of sample preparation gave an order of magnitude less signal and a different temporal profile for the Cr emission.

In 1995, Tasaka et al. studied the emission of a laser-produced plasma on graphite.[25] They used a Nd:YAG laser in He and in air to form a plasma in which they observed a "triple plume" composed of three distinct regions. The authors claimed that these regions appeared because of three different speeds in the expanding plasma. The fastest region was composed of carbon ions from the target and N and O ions when the experiment was done in air. The second plume was composed of the compressed neutrals in the vicinity of the shock wave. The slowest plume was then the target vapor composed of larger molecules. Thareja et al. also studied graphite plasmas at low pressure and found similar temporal profiles.[26]

Intense emission from the CN radical has been observed in plasmas produced on graphite. With the use of a high-resolution spectrometer, several authors have resolved the vibrational and rotational structure in the CN emission bands. The emission from the violet band of CN around 388 nm has been used to calculate vibrational and rotational temperatures in the laser plasma.[27-30]

In 1996, Al-Wazzan et al. studied three-dimensional number densities of species in laser produced plumes.[31] They used absorption of an expanded dye laser beam to form shadow images of Ba ions in a plume produced by excimer laser ablation at 248 nm. They also used fluorescence from planar slices of the plasma to obtain sequential cross-section images that could be built into a three-dimensional image.

Al-Wazzan et al. also carried out an experiment in which they observed plasma in vacuum and in ambient oxygen.[32] In oxygen, the expanding plume showed increased temperature and electron number density at the shock front due to increased collisional excitation rates. In a vacuum, enhancement at the shock front was not observed.

Bulatov and Liang obtained full spectra at each pixel in the image of a laser-induced plasma as depicted in Figure 1.[33] They used this technique to create classification maps that gave location of any species of interest within the plasma. They studied the effects of different focal length lenses and different sampling geometries on plasma formation and location of species within the plasma.

In 1996, Mulatari et al. obtained time resolved images from a laser plasma formed on a sample at non-normal incidence.[34] They varied the angle of the incident laser beam with respect to the target from perpendicular to nearly parallel. It was found that the plume was generated in the perpendicular direction regardless of the laser angle. However, the maximum emission signal was obtained with normal incidence.

Mulatari and Cremers also published a second study that year reporting on the use of an acousto-optic tunable filter to capture spectrally resolved images.[35] They used a series of different lenses to examine the different distributions of elements within each plasma. By collecting light from the outermost edge of the plasma, they were able to use ungated detection to obtain analytically useful spectra with low background.

Nemet and Kozma studied the shape of emission lines produced on gold targets at different delays relative to the ablation laser.[36] The 406.51 and 389.79 nm lines were observed. These lines were asymmetric and shifted relative to their natural wavelength at times up to 1000 ns after the laser pulse. These lines could be described by asymmetric Lorenz-type profiles. After 1000 ns, the lines appeared to be very close to their natural wavelength and were Lorentzian and symmetric.

In 1997, Kurniawan and Kagawa used a long pulse Nd:YAG laser to produce plasma on a brass target in vacuum.[37] The authors were especially interested in the secondary plasma formed by compression in the vicinity of the shock wave. The emission in this secondary plasma was captured, and it was observed that when a wedge of aluminum was placed very close to the target, the emission signal increased in the vicinity of the wedge. The authors attributed this effect to increased compression provided by the shock

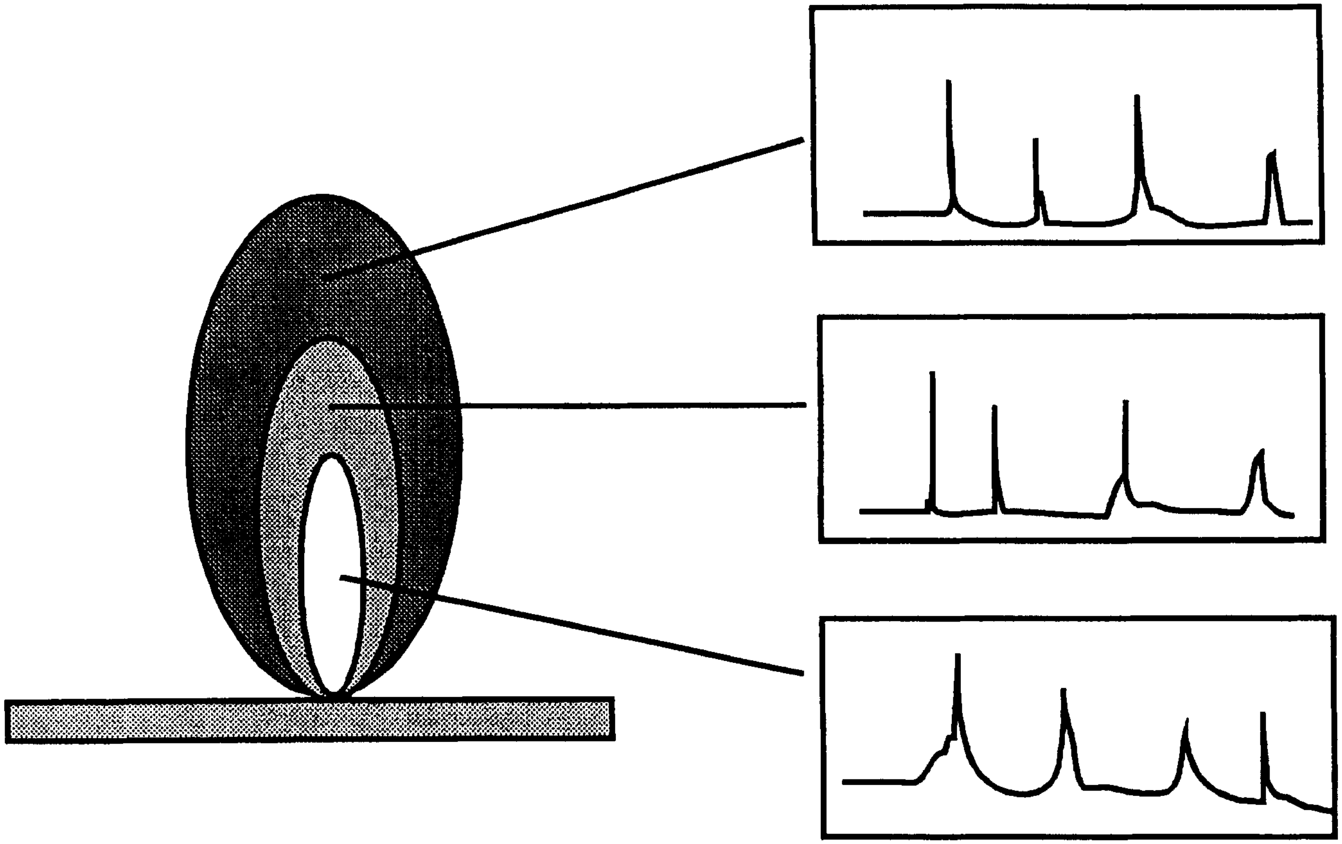


FIGURE 1. Spectroscopic imaging of a laser-induced plasma.

wave interaction with the immovable aluminum wedge.

In 1997 Martin et al. used a laser-induced plasma to establish spectral calibration of their detector.[38] A Nd:YAG laser (1064 nm, 350 mJ) was focused onto targets of ceramic, polyethylene, ZnS, and aluminum, all in vacuum. Line pairs in the deep UV were used with known transition probabilities to determine the relative efficiency of the detection at each wavelength.

Most recently, Granse et al. modeled laser-induced plasma and compared their model to experiments with different lasers and different materials.[39] The model they derived accounted for fluid dynamics of the plasma, absorption of laser energy via inverse bremsstrahlung, and the dynamics of ionization and recombination.

B. Analytical Results and Applications

The number of papers describing analytical results of LIBS studies on solids is easily larger than the number of papers dealing with either liquids or gases. For this reason, only publications after 1992 are considered in this section. Figures of merit given for specific determinations differ greatly from one author to the next. In the periodic tables which follow this section, the lowest published detection limits for the elements in the matrix of interest are used to determine the shading.

Carbon content in steel was determined by Aguilera et al. in 1992.[40] The authors observed the emission from the 193.1 nm carbon line because the 247.9 line had an interference. The experiment was done in a CO_2 free environment, and a neighboring iron line was used as an internal standard. A Nd:YAG laser at 1064 nm was used, and it was found that the slope of the calibration curves generated decreased with increasing laser power. Also, there was a slight difference in slope for stainless and non-stainless steels. At a laser power of 100 mJ, the detection limit for carbon was 65 ppm and the RSD was 1.6 %.

Also in 1992, Hader used LIBS for online quality control of rubber mixing.[41] The author called the technique "remote laser microanalysis" and used the acronym RELMA. The existing technique for quality control of rubber mixing involved a discrete sampling step in which a small portion of rubber was taken from a batch and analyzed. This led to problems when it became neccessary to distinguish between bulk composition fluctuations and inhomogenieties; with on-line sampling by LIBS in a number of randomly chosen positions in the rubber mix, the two problems could be distinguished. Analytes were elements found in the cross-linkers and plasticizers added to the raw rubber.

Lorenzen evaluated other on-line applications of LIBS in the same year.[42] This time the technique was referred to as "laser-induced emission spectral analysis" and given the acronym LIESA. The authors described applications such as the determination of minor elements in liquid steel, and depth profiling of layers on metallic substrates.

In 1993, Sabsabi et al. used a KrF laser (248 nm, 100 mJ) to analyze aluminum alloys.[43] They carefully optimized the delay time by using a PMT to look at the temporal evolution of several different emission lines. An aluminum line was used as an internal standard and magnesium was determined at a few ppm.

The following year, Thiem et al. investigated LIBS of alloy targets.[44] They determined Al, Cu, Fe, Ni, and Zn using a Nd:YAG laser at 532 nm in a vacuum chamber. Using non-resonant lines for all the elements, the authors were able to generate linear calibration curves from a few hundred ppm to a few percent for each element. For the determination of these elements at the percent level, the authors have found many potential emission lines in the spectral window from 300 to 400 nm.

Thiem and Wolf used LIBS to analyze mining ores and compared the results to those obtained by a digestion ICP-AES method.[45] Al, Ca, Cu, Fe, K, Mg, Mn, Si, and Ti were determined in aluminum and manganese ore. The comparison showed that both methods gave roughly the same accuracy, but the ICP technique had better precision. The authors also pointed out the similarity in cost for the two techniques, about $100 K for either.

Investigations of the use of resonant wavelengths in laser ablation had been made as early as 1992 by Borthwick et al. [46] Although most of the work was carried out with time-of-flight mass spectrometry, the paper is included because of its relevance to LIBS. The authors noted that when an ablation laser was scanned through specific wavelengths, an enhanced ion yield was detected. More specifically, an enhancement in Ga ions in the ablation of GaAs, and an enhancement in Al ion yields in ablation of steels were noted. The ion yields were even more pronounced when grazing angles of incidence of the ablation laser were used.

In 1995, Allen et al. employed resonant wavelengths in LIBS of thin films.[47] The authors used resonant laser ablation time-of-flight mass spectrometry to investigate copper thin films on a silicon substrate. Using a XeCl excimer laser pumped dye laser (5 mJ pulse energy at 463.51 nm) multi-photon ionization of copper was observed. By using an unfocussed laser continually and watching the decay of the copper signal, the authors were able to determine the thickness of the film between 20 and 100 Å. It was calculated that between 10^{-3} and 10^{-2} Å per shot was removed by the laser, although this was at a power below the breakdown threshold, so emission could not be collected.

Anderson et al. used LIBS for depth profiling without the resonance feature of Allen's experiment.[48] A Zn/Ni coating between 2.7 and 7.2 µm thick on a steel substrate was analyzed, and a calibration curve of signal duration with thickness was found to be linear. The depth resolution was far poorer than in the mass spectrometric experiment of Allen because the energy density at the target was much greater. Nonetheless, Sn coatings of less than 1 µm, and Cr coatings on the order of a few nm on steel could be determined by this technique.

Arnold and Cremers used LIBS to determine metal particles on air sampling filters.[49] Tl was collected on filter paper by passing contaminated air through a filter or by wiping a filter on a Tl surface. The laser beam from a Nd:YAG laser at 1064 nm was formed into a line at the focus by a pair of cylindrical lenses. The detection limit for Tl was 40 ng/cm^2 of filter paper, and the calibration curve was linear up to 40 µg/cm^2. The 535.05 nm Tl line was used for detection.

Sattmann and Sturmalso investigated the use of a multiple Q-switch Nd:YAG laser for analysis of steel samples.[50] Single, double, and multiple pulses were used to produce plasma on a low-alloy steel. Material ablation, emission intensity, electronic temperature, and electron number density were determined for each plasma type. All of these parameters were greater for the double and multiple pulses than for the single pulses presumably because of a smaller shielding effect in these cases. Calibration curves were correspondingly steeper.

Davies and Telle used a 100 m fiber optic pair to perform remote LIBS on ferrous targets.[51] A pair of 550 µm (OD) fiber optics were used to transmit laser light to the target and to return plasma emission to the spectrometer. Detection limits of 200 ppm or less were found for Cr, Cu, Mn, Mo, Ni, Si, and V. A number of potential emission lines to use for calibration were given for these elements.

Cremers et al. used a fiber optic probe to determine Ba and Cr in soil.[52] A single 1.5-mm fiber was used both to deliver laser light and collect emission. A glass plate was used to reflect the emission to the spectrometer. The Ba ion line at 493.41 nm and the Cr atom line at 425.44 were used for calibration which was linear over 4 orders of magnitude for both elements. The detection limit for Ba was 26 ppm, and the detection limit for Cr was 50 ppm.

Cremers also determined at what distance LIBS could be performed using conventional optics rather than fiber optics.[53] By using a beam expander to increase the diameter of the laser beam and a pair of lenses with adjustable distance to focus this expanded beam onto a target, he was able to produce a plasma and collect light at a distance of 24 m. Detection limits in a simulated moon rock were at the level of a few percent due mostly to the small solid angle of collection at this distance.

Bescos et al. again analyzed aluminum samples in 1995.[54] The authors simultaneously determined Mg, Mn, Fe, and Pb in aluminum using a spectral window from 380 to 410 nm. Detection limits were around 100 ppm and calibration curves were linear up to about 1%.

Gonzales et al. also analyzed steel samples.[55] Their 1995 publication dealt with sulfur determination. They reported a detection limit of 700 ppm using the 180.73 nm atom line. The analysis was done in a N_2 atmosphere, and the Fe ion line at 186.47 was used as an internal standard. Precision was 7%.

Hakkanen and Korppi-Tommola used LIBS to study elemental distributions of paper coatings.[56] An XeCl laser at 308 nm was used to generate a plasma on paper, and Ca or Si was used as an internal standard. A spatial resolution of about 250 μm could be achieved with a laser pulse power of 200 mJ. It was estimated that 2 ng of paper coating were vaporized per shot. Al, Si, Mg, Ca, and C were were monitored quantitatively in a spectral window from 220 to 290 nm.

Sabsabi and Cielo once again analyzed aluminum alloys by LIBS in 1995.[57] The authors characterized the laser plasma on aluminum targets using Stark broadening of Al ion lines to determine electron number densities and using a series of Fe atom lines to make Boltzmann plots to determine electronic temperature. Calibration curves for Mg, Mn, Cu, and Si were constructed and detection limits were as low as 10 ppm, for Mg.

Soil was analyzed by Ciucci et al. in 1996.[58] They used both a Nd:YAG laser at 1064 nm and a XeCl laser at 308 nm. The authors found that the background decay in the laser plasma was faster for the 308 nm pulse than for the 1064 nm pulse and used a correspondingly shorter delay time with the XeCl laser. Cu, Pb, and Cr in soil were determined, and an entire spectra from 350-700 nm was shown with lines identified for the geological survey soil sample GXR-2.

Ernst et al. used LIBS to determine Cu in A533b steel.[59] The first attempt was carried out with fiber optic delivery of the laser. This method would have been significant because in the hazardous environment of a nuclear reactor pressure vessel, Cu concentration in the steel is an indicator of radiation embrittlement and of expected material lifetime. Because the fiber optic could not deliver enough power to produce sensitive detection, beam delivery was done with conventional optics. The Cu line at 324.75 was used for calibration, and by using a second-order calibration curve Cu could be determined in the range between 100 ppm and 5%.

Geertsen et al. revisited LIBS for aluminum samples in 1996.[60] Using a Nd:YAG at 1064 nm and a pulse power of 230 mJ the authors formed craters ~5 μm deep in aluminum with a single shot. The detection limits for Mg and Cu were 4 and 40 ppm, respectively, with a precision of about 8%. Spatial resolution was assessed by rastering the beam over a sharp Al-Cu junction. The best spatial resolution obtained was 6 μm.

Marquardt et al. determined Pb in paint using a Nd:YAG laser at 532 nm coupled into a fiber optic probe.[61] The probe consisted of two fibers, excitation and collection, terminated in a probe head with an aspheric lens to focus the laser light to a spot and focus plasma emission into the collection fiber. The common end of this fiber is shown in Figure 2. Different combinations of excitation/collection fiber diameters were tried. The detection limit for Pb was 140 ppm, and precision was 5 to 10 % even when analysis was carried out through layers of non-lead containing paint.

Miziolek also reported on a LIBS probe in 1996.[62] This application was for determination of heavy metals in soils, and the probes were to be used in a cone penetrometer truck. In one probe, a compact laser was mounted in the probe head. In the other probe, laser light was carried through a fiber optic to the probe head. The compact laser head provided the more sensitive probe with detection limits for Pb, Hg, Cr, Cd, and Zn of 1 to 10 ppm in sand and silt. The fiber optic delivery provided less power but a higher laser repetition rate; 15 mJ vs. 28 mJ, 30 Hz vs. 1/3 Hz.

Also in 1996, Cremers et al. introduced a portable LIBS instrument and used it to determine hazardous elements in soil, in paint, and in samples on filter paper.[63] A compact laser head was used as the probe. Ba, Be, Pb, and Sr were determined in soil with detection limits of 265, 9.3, 298, and 42 ppm, respectively. In paint, the detection limit for lead was much greater because the 405.8 nm line could not be used due to spectral interference. On filter paper, Be and Pb were determined with detection limits of 21 ng/cm^2 and 5.6 μg/cm^2, respectively. In the filter paper studies, some particle size effects were evident.

Palleschi et al. used a 400 mJ Nd:YAG laser at 1064 nm for a variety of determinations, including Hg in air (5 ppm detection limit), and pollutants in powerplant smoke and soil.[64] These authors analyzed the geographical survey GXR-2 sample and determined concentrations for 18 elements.

Vadillo and Laserna analyzed geological samples of vanadinite, pyrite, garnet, and quartz.[65] These determinations were done in vacuum to increase the lifetime of the ionic species and of the ion lines observed. Fe, Mn, Mg, and Si were determined in each of the rocks, and Al was also determined in garnet. Differences in composition were as expected.

Laserna et al. used LIBS to analyze the surface of solar cells.[66] A N_2 laser at 337.1 nm was focused onto the cell and the cell was rastered under the focus providing spatial resolution of about 30 μm. The C ion line at 588.9, Ag atom line at 546.5, Si atom line at 634.7, and Ti atom line at 625.9 were used in determinations of these four elements. The concentration of each element was mapped across the surface of the solar cell.

In another application of LIBS to alloys, Kim et al. determined aluminum in a zinc alloy.[67] The authors used a Nd:YAG laser (1064 nm, 105 mJ, 3 ns) in vacuum, air, and argon. The presence of Al in the Zn alloy was important because of its detrimental effect on its welding properties. The delay and the distance from the surface of the target were optimized in each atmosphere. Because the Al atom line at 308.22 nm was used for calibration, large delay times were used to ensure no contribution from a shorter-lived Zn interference. In air, a 30 μs delay was used and in Ar a 50 μs delay was used. The Zn line at 307.59 was used as an internal standard.

In 1997, Maravelaki et al. used LIBS to monitor the laser cleaning of marble artifacts.[68] Although lasers had been used previously for the cleaning of such treasures, these authors were the first to examine the emission from the plasma. Crusts of 20 to 600 μm consisting of gypsum, iron oxides, soot, and

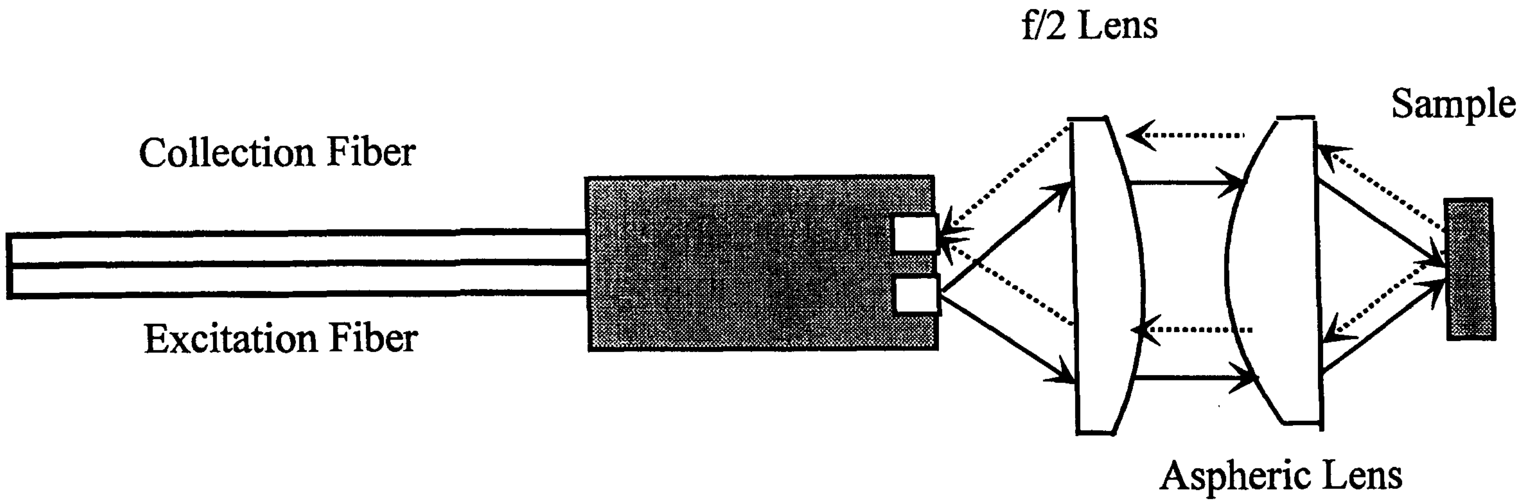


FIGURE 2. Common end of fiber optic LIBS probe used by Marquardt et al. for determination of lead in paint.

calcite were ablated from the marble by a Nd:YAG laser. The plasma formed in this ablation was analyzed spectroscopically to determine the endpoint of the cleaning.

Figures 3 and 4 show graphically the detection limits for elements that have been determined using LIBS in sand, ore, or soil and in steel or alloy.

III. LIQUIDS

A. Fundamental Studies

Besides papers in the field of analytical chemistry, there have also been a number of papers that have dealt with the physics of laser-induced breakdown in aqueous solution. Most of these deal with the processes of cavitation and the factors that can affect the breakdown threshold.

In 1984, Armstrong identified three time domains in the heating of an aerosol: the acoustic regime, the internal conductive regime, and the external conductive regime.[69] He explained the phenomenon of aerosol-enhanced air breakdown as being caused by increased electron collision frequency in the hot, dense, vapor surrounding the heated aerosol particles in the beam.

Three years later Armstrong used a CO_2 laser at 10.6 µm to explode aerosols generated by a vibrating orifice aerosol generator.[70] A UV laser was used to produce shadow images of the exploding droplet, and a phase Doppler particle analyzer system determined size and velocity of the expelled particles at a distance of 2 mm from the original drop. It was found that the CO_2 laser power affected the size of particles produced in the breakdown for original drop sizes between 30 and 50 µm. The speed of the particles produced was independent of laser power.

Chylek et al. studied the effect of size and material of liquid aerosols on breakdown thresholds in 1986.[71] The setup that they used is shown in Figure 5. A Nd:YAG laser (532 nm, 10 ns) was focused onto droplets generated by a Berglund-Liu vibrating orifice aerosol generator. Breakdown thresholds were determined on aerosols of different size generated from liquids of various refractive index, density, surface tension, and chemical structure. Thresholds were seen to decrease with droplet size. Refractive index had no apparent effect. Density, surface tension, and chemical structure had effects that could not be independently examined.

In 1987, Hsieh et al. used a Nd:YAG laser at 532 nm to examine the exact location of breakdown initiation on water droplets generated by a Berglund-Liu vibrating orifice.[72] They found that as the energy of the laser increased, the breakdown moved from outside the droplet to the inside. Theoretical calculations showed that the curved liquid gas interface of a water droplet in air focused laser energy at one point just inside the illuminated face and at another point just beyond the shadowed face.

The effect of laser wavelength and irradiance on spectra from laser-induced breakdown of single levitated aerosol droplets was examined by Biswas et al. in 1988.[73] Droplets of glycerine saturated brine solution approximately 18 µm in diameter were optically levitated and probed with a Nd:YAG laser at 1064, 532, and 355 nm. Emission lines of Na, C, and N were observed. It was shown that the energy required for breakdown, and the time of plasma emission increased with increasing wavelength. The optimum time delay for determination of these elements increased with laser wavelength and showed more variance from element to element at longer laser wavelength.

Also in 1988, Zheng et al. acquired temporally and spatially resolved spectra of laser-induced breakdown of a 40 µm 4 *M* NaCl droplet using a Nd:YAG laser at 532 nm.[74] Using fiber optic ribbons and a streak camera, these authors observed that emission began first at the shadowed face of the droplet and propagated toward the illuminated face.

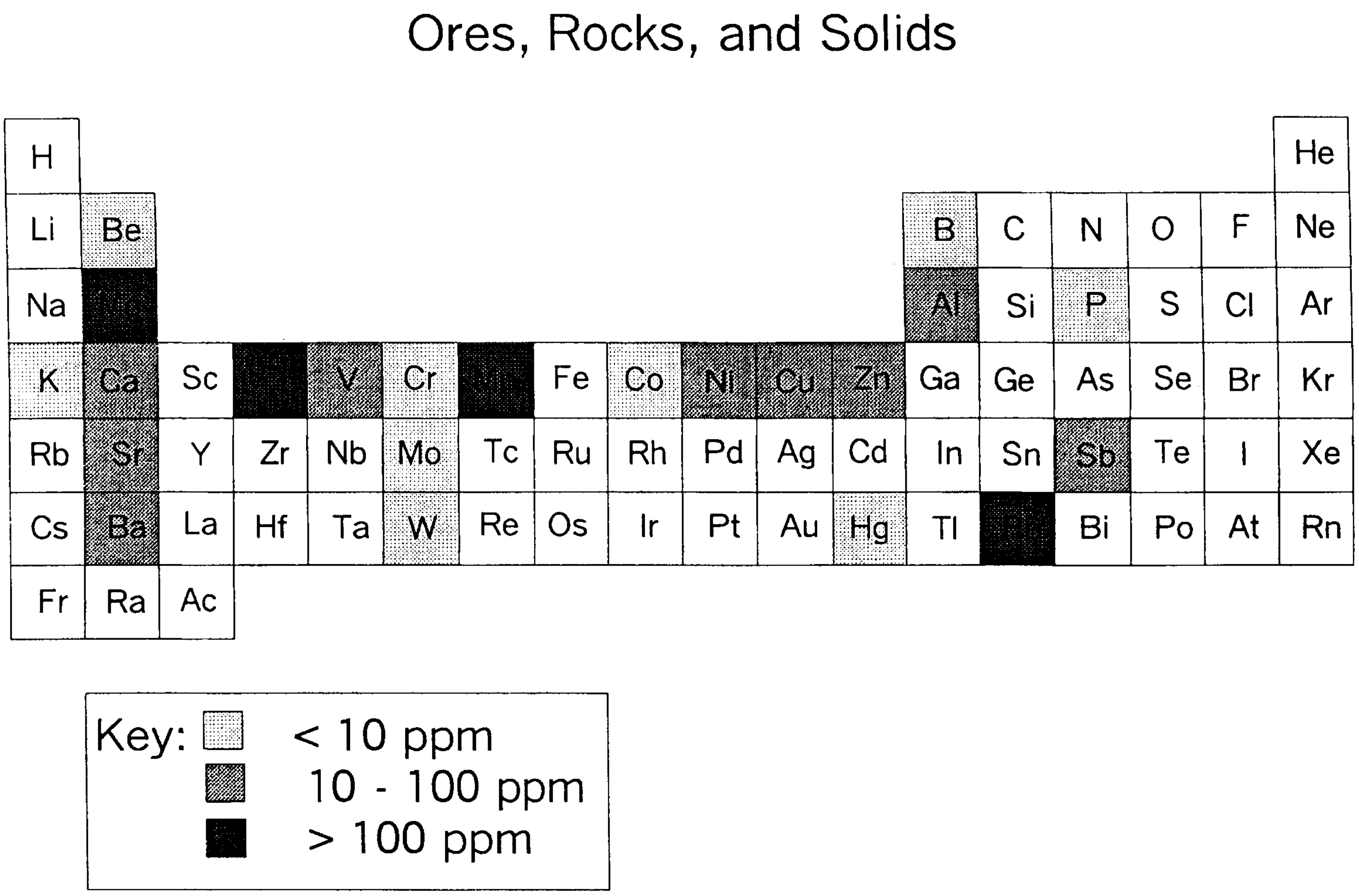


FIGURE 3. Elements determined in ores and soils shaded according to detection limit.

Metals

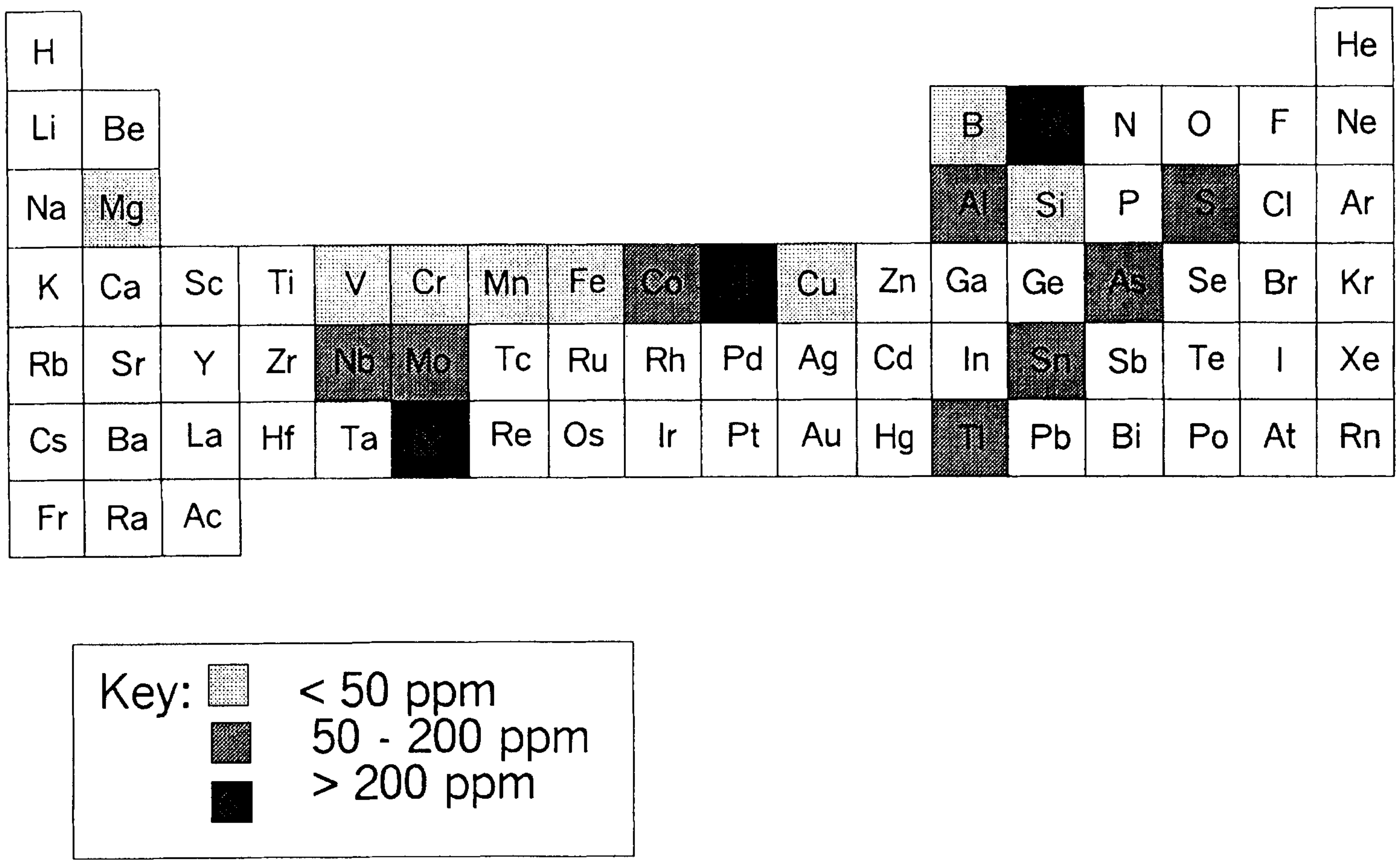


FIGURE 4. Elements determined in metals shaded according to detection limit.

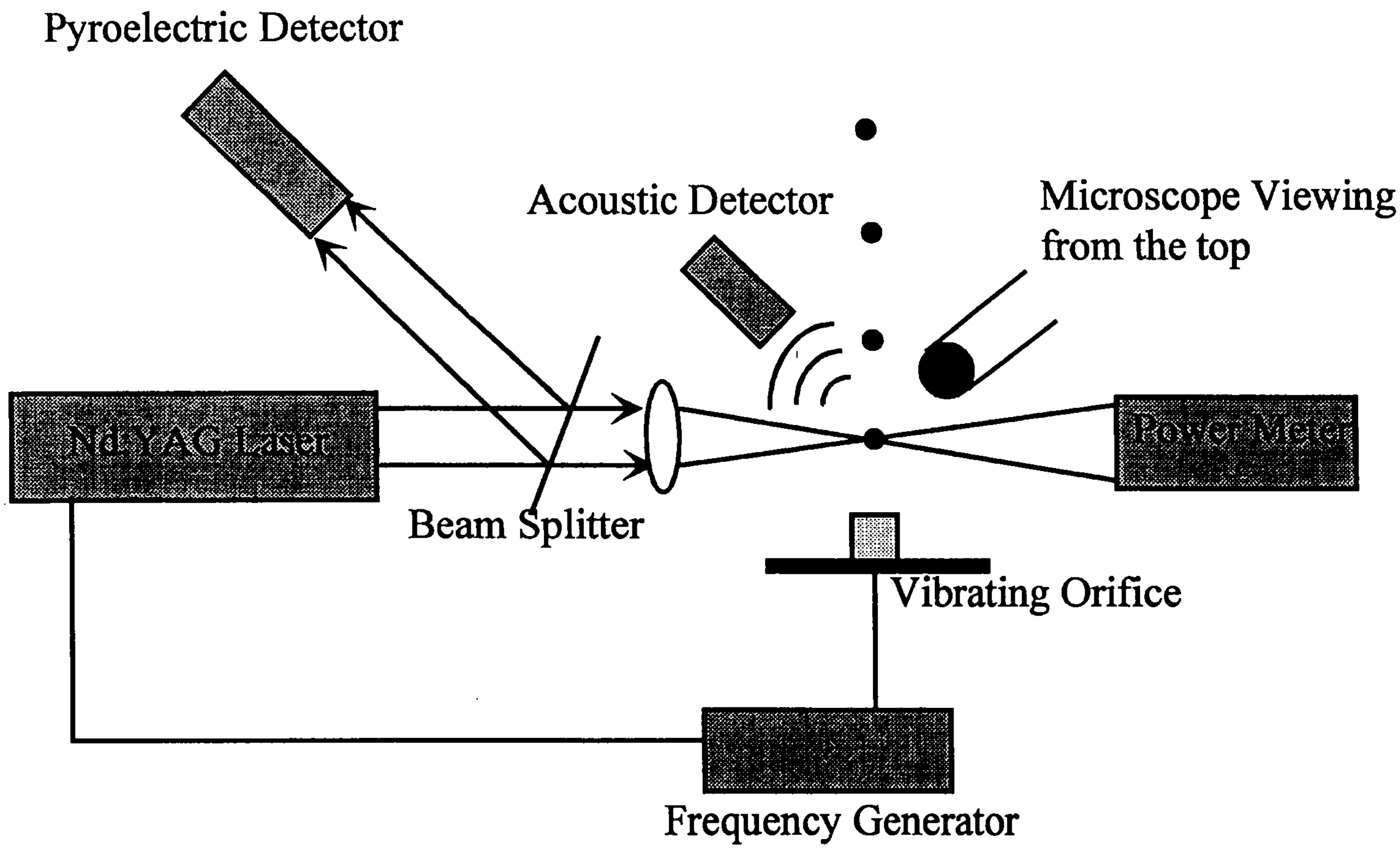


FIGURE 5. Schematic of experimental setup used by Chylek et al. to investigate LIBS of aerosols.

Hammer et al. also examined thresholds with ultrashort laser pulses.[75] Using pulses of 2.4 ps, 400 fs, and 100 fs from a pulsed dye amplifier, they determined breakdown thresholds in saline solution, high purity water, and tap water. The thresholds in these media were not significantly different. With the 2.4 ps pulse the breakdown threshold was found to be 5×10^{11} W cm^{-2}, with a 400 fs pulse it was 1.3×10^{12} W cm^{-2} and with a 100 fs pulse it was 5.65×10^{12} W cm^{-2}.

Kitamori et al. used the acoustic wave generated during particle-induced breakdown to detect polystyrene particles in aqueous solution.[76] A Nd:YAG laser (532 nm, ~1 mJ, 6 ns, 10 Hz) was focused into a solution. In pure water, the energy density produced by this beam was not sufficient to cause a breakdown. When a particle entered the probe volume, however, a breakdown occurred and subsequently an acoustic wave was generated. By detecting these acoustic waves, the probability of breakdown was determined. By analyzing solutions of known particle concentration, a calibration curve of breakdown probability vs. concentration was generated. This curve was used in the analysis of solutions of unknown particle concentration.

Vogel et al. used a Nd:YAG laser to produce and image a breakdown in water.[77] The fundamental wavelength of 1064 nm was focused into the water to produce a breakdown. A portion of the beam was frequency doubled to produce 532 nm light that was put through a beam expander and allowed to pass through the underwater breakdown, providing a shadow of the plasma and the cavitation bubble. The size of the plasma and cavitation bubble were examined for 1064 nm laser pulse durations of 30 ps and 6 ns.

Sacchi discussed the mechanisms of laser breakdown in water and described the differences in threshold for short pulse and long pulse lasers in 1991.[78] He claimed that the avalanche breakdown process or inverse bremstrahlung was responsible for breakdown when nanosecond laser pulses were used. In this case, the breakdown threshold behaved probabilistically. The probability of breakdown scaled linearly with the log of laser power for low powers, and scaled parabolically with the log of laser power at higher power. In contrast, with laser pulses of less than nanosecond duration, multi-photon ionization appeared to be the mechanism of plasma formation, and a definite threshold above which breakdown would occur could be determined.

Sacchi returned to this topic in 1996 and produced images of laser-induced breakdown on solids under water. By using a dye laser oriented parallel to the underwater target and delayed relative to the ablation laser, the authors obtained shadowgraphs of the evolving plume and shock wave. A series of images followed the growth and decay over a total time of about 700 µs. A schematic of the setup used is shown in Figure 6.

In 1992, Pinninck et al. studied the effect of resident particles on laser-induced breakdown thresholds.[79] It was found that even at wavelengths where the particles did not absorb laser light, there was a decrease in breakdown threshold in particle laden air vs. clean air. This was taken to mean that particles were focusing laser light. Location of plasma formation (inside, shadowed side, or illuminated side) was found to depend on ionization potential, gas pressure, and laser wavelength. Refractive index had no effect on breakdown threshold, in agreement with the observations reported by Chylek in 1986.[71]

In 1993, Nyga and Neu created a plasma on calcite submerged in water using two fiber optics to deliver two pulses from two XeCl lasers.[80] Both pulses were 30 ns pulses at 308 nm through 600 µm fibers that were brought in close proximety to the target with no focusing lenses. The pulses were separated in time by ~300 µs, and the second fiber was equipped with a 308 nm dielectric

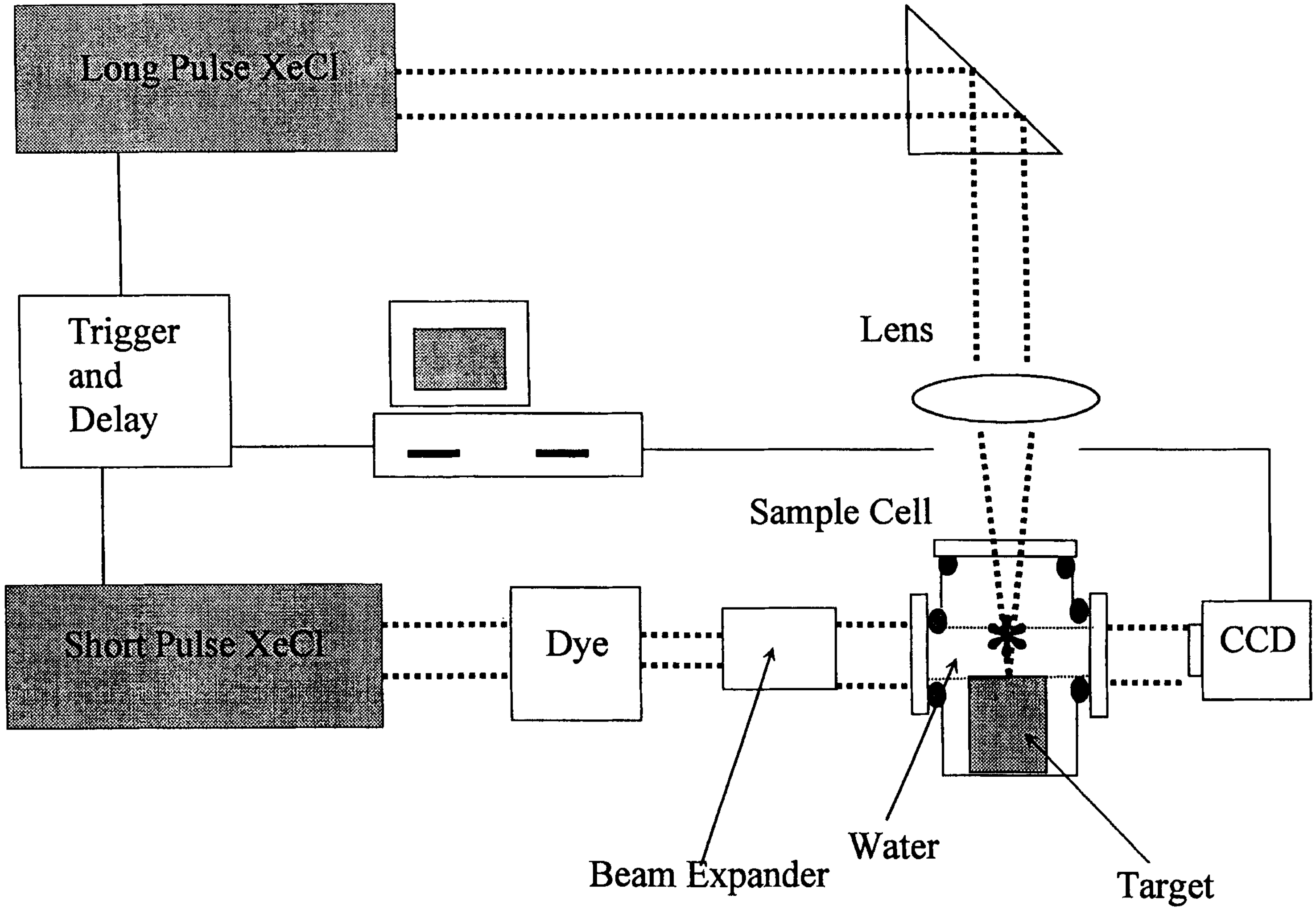


FIGURE 6. Schematic of experimental setup used to obtain shadowgraphs of a laser-induced plasma.

beam splitter and used to collect emission from the calcite. No quantitative results were reported.

Feng et al. also examined the effect of laser pulse duration on breakdown thresholds in water.[81] In their 1997 paper, they determined the mechanism of breakdown with nanosecond pulses to be due to cascade ionization, and the mechanism of breakdown with ultrashort pulses to be multi-photon ionization, similar to Sacchi's findings.[78] These authors, however, went on to model the breakdown phenomenon in water relating the breakdown threshold to laser power, spot size, and pulse duration. They derived an extended non-linear Schrödinger equation to describe the relationship.

B. Analytical Results

Quantitative results for LIBS with liquid samples are presented in two sections based on the nature of the analysis. The first section will cover determinations done in bulk liquid. This implies that a laser spark is generated either on the surface or beneath the surface of a relatively large liquid sample. The second section covers determinations done in aerosols or droplets generated from liquid samples. Analysis of dry aerosols generated from solids are included in the last section on gas phase determinations.

C. Bulk Liquid

In 1984, Cremers et al. reported the use of a repetitive single spark (RSS) and repetitive spark pair (RSP) for the determination of Li, Na, K, Rb, Cs, Be, Mg, Ca, B, and Al in aqueous and organic solutions.[82] With the single spark, detection limits for all elements except Li were >1 ppm. The detection limit for B was 1200 ppm. When a second spark which was generated from a second laser and delayed by 18 μs relative to the first was used to form the plasma, the detection limit for B was reduced to 80 ppm. This improvement was attributed to formation of the plasma within a cavitation bubble when the RSP method was used. The experimental setup is shown in Figure 7.

In 1987, Wachter and Cremers reported a detection limit of 100 ppm for uranium in solution by LIBS.[83] The plasma used was formed by a Nd:YAG laser (1064 nm, 260 mJ) on the surface of a 4 *M* nitric acid solution contained in a small glass vial. Each analysis was done by averaging 1600 laser shots. This averaging was necessary to overcome poor shot-to-shot precision due mainly to small variations in lens to sample distance.

In 1987, Cremers conducted an experiment to determine the maximum lens to sample distance (LTSD) that could be used in a LIBS experiment.[53] With a 250 mJ pulse from a Nd:YAG laser at 1064 nm, it was found that a 2 m focal length lens could produce breakdown on molten metal. The larger problem was collection of the emitted light. A fiber optic could collect enough light at 0.5 m from the plasma for modest figures of merit to be obtained. At distances farther than this, the sensitivity of the experiment decreased rapidly.

In 1993, Aragon et al. used LIBS to determine carbon content in molten steel.[84] They used a Nd:YAG laser (1064, 200 mJ, 8 ns) focused onto molten steel in a crucible under an argon atmosphere. In order to provide a homogeneous sample, a jet of argon gas was directed downward into the crucible. This served to remove the topmost layer of molten liquid which would be enhanced in the lighter elements. Carbon was determined by ratioing of the C 193.09 nm to Fe 201.07 nm intensity and a detection limit of 250 ppm was found with an RSD of 6%.

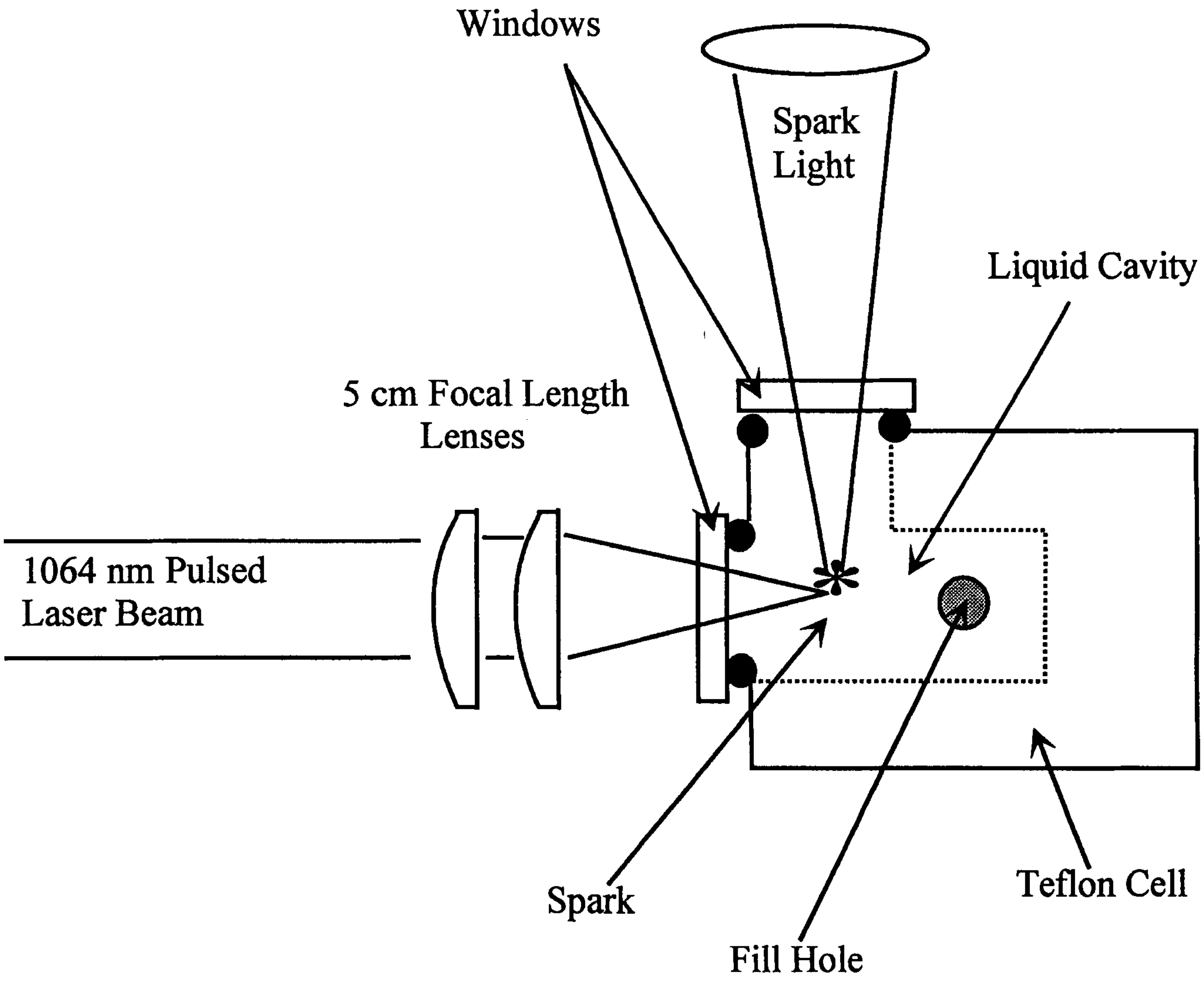


FIGURE 7. Experimental setup used by Cremers et al. to analyze aqueous solutions with LIBS.

In 1995, Stolarski et al. produced sub-surface plasmas in saline solution, triple-distilled water, and tap water with Nd:YAG laser pulses of <5 mJ and pulse durations of 5 ns and 80 ps.[85] The focussing lens used was 2.54 cm. in diameter and had a focal length of 17 mm. This lens was chosen to approximate the lens in the human eye. The authors found that an energy of 1.5 mJ was enough to produce a breakdown at either pulse duration, and found that the plasma temperatures and electron number densities depended little on pulse duration for the two studied. These authors observed sodium emission around 590 nm in a 0.9% NaCl solution, but no quantitative analysis was performed.

Also in 1995, Ito et al. used LIBS to determine colloidal iron in water.[86] They focused a Nd:YAG laser (1064 nm, 100 mJ, 10 ns) into a flowing stream of water containing FeO(OH) as submicron particles. The detection limit for iron was in the ppm range. This technique differed slightly from previous techniques in that it relied on particle-induced breakdown for the formation of the plasma. A plasma was formed only when a FeO(OH) particle was present in the probe volume. Because of the extremely small size of the particles, however, it was essentially a determination of iron in water. The following year, the same authors used a second laser delayed by 1 μs relative to the first in a technique similar to Cremer's repetitive spark pair. With this technique, they were able to improve the detection limit for iron to 16 ppb.[87]

In 1996, Knopp and Scherbaum used a dye laser at 500 nm with a pulse energy of 22 mJ to produce a sub-surface breakdown in aqueous solution.[88] They reported detection limits for Cd, Pb, Ba, Ca, Li, and Na of 500 ppm, 12.5 ppm, 6.8 ppm, 130 ppb, 13 ppb and 7.5 ppb, respectively. No signal was obtained for either Hg or Er at 0.1% in solution. When micron-sized particles of $ErBa_2Cu_3O_x$, rather than a soluble salt, were used as the source of Er, the detection limits decreased by a factor of 10^3. The improvement illustrated the increased sensitivity of particle-induced breakdown as compared to breakdown in particle-free solution. This experiment also suggested that 500 nm laser light had analytical advantages over 1064 nm light.

In 1997, Ho and Ng used both a Nd:YAG laser (532 nm, 12 ns) and an ArF laser (193 nm, 15 ns) to determine Na in aqueous solution.[89] In order to increase absorbance of the laser light, methyl violet was added to the solution to be analyzed. It was found that the 532 nm laser light produced a more visibly intense plasma; because the continuum emission was higher in the 532 nm produced plasma, the 193 nm laser light actually gave better detection limits for Na. A detection limit of 230 ppb was reported for Na in the methyl violet solution with the plasma formed by the ArF laser.

In 1996, a similar experiment was performed by Paksy et al., who used a Nd:YAG (1064 nm, 15 mJ, 4 ns) focused onto the surface of a molten alloy in an argon atmosphere.[90] Because the laser power used was significantly less than that used by most authors, the delay of the detection relative to the laser was also less. A 100 ns delay and 1000 ns gate width were used. Detection limits were 0.001% for Si in Fe, 0.006% for Cr in Fe, 0.06% for Si in Al, and 0.007% for Mn in Al.

Arca et al. determined Cr, Pb, and Cu in aqueous solution with a single laser shot on the surface of the water.[91] Detection limits were 100, 100, and 50 ppm for the three elements, respectively. Calibration curves were linear over 1 order of magnitude. The authors also analyzed aqueous solutions by placing a drop of water to be analyzed on a KBr pellet. When this technique was used, detection limits were improved by almost an order of magnitude.

D. Aerosols and Droplets

In 1983, Radziemski et al. used a nebulizer/heat chamber system to produce an aerosol from a liquid solution and analyzed the aerosol with LIBS.[92] Detection limits for Na, P, As, and Hg were reported to be 6 ppb, 1.2 ppm, 0.5 ppm, and 0.5 ppm, respectively. The authors determined that local thermodynamic equilibrium existed in the aerosol spark for time delays greater than 1 µs relative to the laser.

In 1987, Eickmans et al. spatially resolved the emission from laser-induced breakdown of an aerosol.[93] Approximately 45-µm-diameter droplets were formed by a vibrating orifice aerosol generator which was synchronized with the Nd:YAG laser beam at 532 nm. Emission of Li, Na, and H was observed in 5 *M* salt solutions of either NaCl or LiCl. Spatial resolution of the emission revealed that in the plasma plume in the vicinity of the illuminated face of the droplet, emission lines showed Stark broadening and self-reversal. Near the shadowed face of the droplet emission lines were narrower and less intense.

In 1988, Essien et al. used LIBS to determine Cd, Pb, and Zn in an aerosol.[94] A Nd:YAG laser (1064 nm, 100 mJ, 5 ns) was focused onto an aerosol generated by a nebulizer/heat chamber. Detection limits were 19 ppb, 210 ppb, and 240 ppb for Cd, Pb, and Zn, respectively.

Also in 1988, Archontaki and Crouch used an isolated droplet generator to produce equally spaced, uniformly sized droplets.[95] The experimental setup was such that a single drop of known size was always in the probe volume of the laser for a given repetition rate. A Nd:YAG laser (1064 nm, 100 mJ) was used to determine detection limits for Li, Na, Mg, Ca, Mn and Al of 0.3, 2.2, 1.9, 0.4, 7.2, and 5.2 ppm, respectively. Droplet diameter had little effect on the detection limit for sizes between 58 and 75 µm.

In 1992, Ng et al. used an ArF laser (193 nm, 150 mJ) to analyze an aerosol generated by a concentric glass nebulizer/spray chamber traditionally used for ICP-AES.[96] The authors determined the optimum delay for detection to be 6 µs relative to the laser pulse. Detection limits for Na, Li, In, Al, Ga, Ca, Mg, K, and Sr were determined to be 0.9, 0.3, 10, 3, 3, 8, 3, 2, and 20 ppm, respectively.

The following year Parigger and Lewis used a picosecond XeCl laser (308 nm, 4 mJ) to produce LIB in 66 µm water droplets.[97] Plasma diagnostics showed a temperature of ~10 000 K and an electron number density of 10^{18} cm^{-3}. The Hα line at 656 nm was used as an internal standard and the detection limit for sodium was ~1 ppm. Poulain and Alexander performed a very similar experiment in 1995 using a KrF laser (248 nm, 200 mJ). The detection limit for Na was found to be 165 ppm.[98]

Haisch and Paine reported on the characterization of colloidal particles by LIBS in 1996.[99] Field flow fractionation was used to sort particles by size and deposit them onto filter paper using partitioned pumping to retain time resolution. A cylindrical lens was used to focus the laser onto the paper to avoid ablation of the paper which could occur if the energy density became too high. Detection limits for Si were in the ppb range.

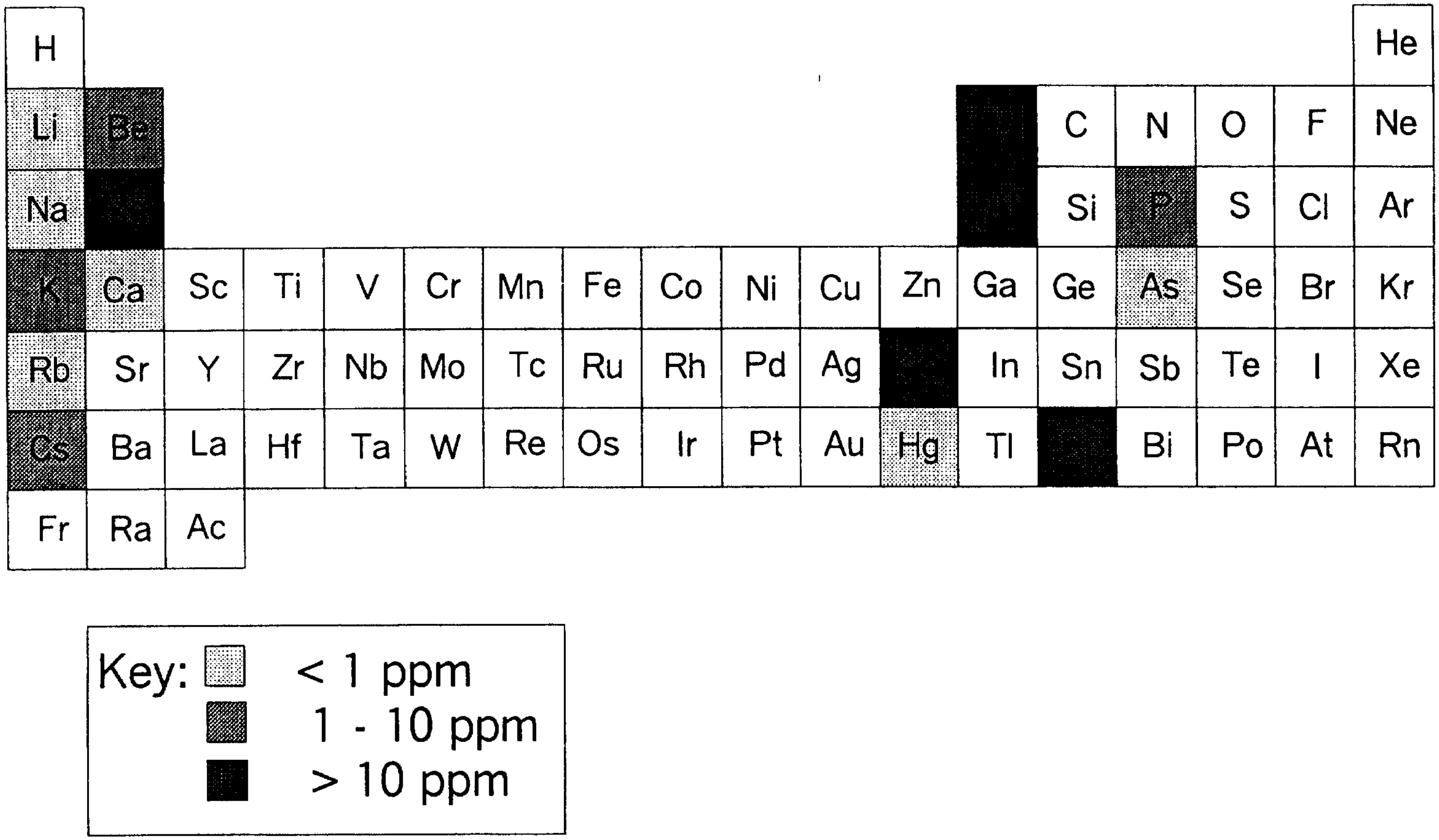
Figures 8 and 9 show graphically the detection limits for elements that have been determined using LIBS in bulk liquids and in aerosols generated from liquids.

IV. GASES

A. Fundamental Studies

In 1988, Kumar and Thareja studied laser-induced gas breakdown in the presence of an electric field.[100] They used a

Liquids



H																	He
░ Li	▒ Be											■	C	N	O	F	Ne
░ Na	■											■	Si	▒ P	S	Cl	Ar
▒ K	░ Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	░ As	Se	Br	Kr
░ Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	■	In	Sn	Sb	Te	I	Xe
▒ Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	░ Hg	Tl	■	Bi	Po	At	Rn
Fr	Ra	Ac															

Key:
░ < 1 ppm
▒ 1 - 10 ppm
■ > 10 ppm

FIGURE 8. Elements determined in bulk water shaded according to detection limit.

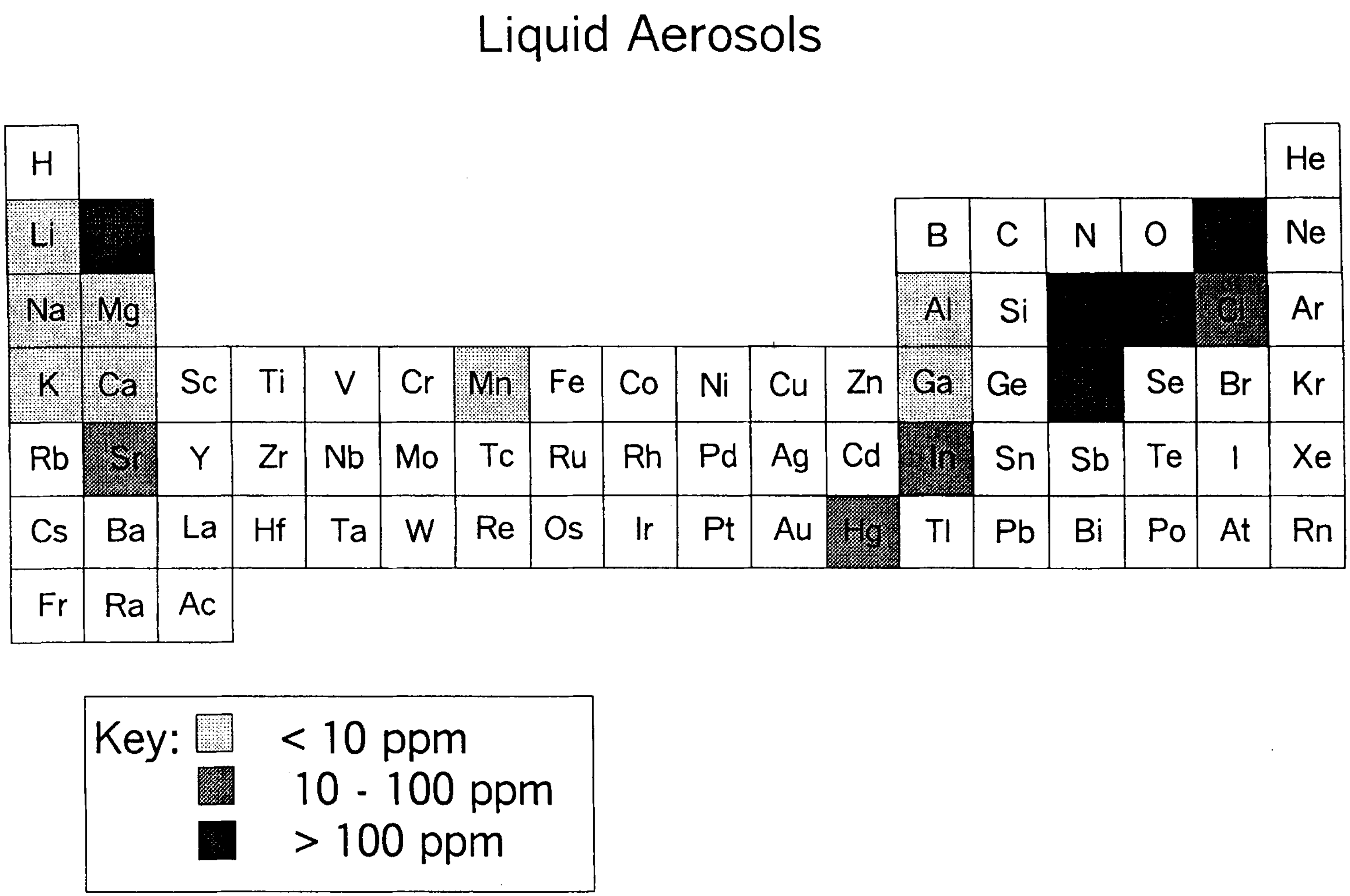


FIGURE 9. Elements determined in liquid aerosols shaded according to detection limit.

XeCl laser (308 nm, 60 mJ, 8ns) focused between two electrodes separated by 6.5 mm. A transverse static electric field was produced by applying different potentials to the electrodes. In order to study the effect of the field on breakdown thresholds, the current on the electrodes was adjusted so that no breakdown occurred using only the field or only the laser. The authors were then able to determine that pre-breakdown electron densities of 10^{10} cm^{-3} created by the field were sufficient to lower the laser energy density needed to produce breakdown.

Parigger and Lewis used a Nd:YAG laser (1064 nm, 300 mJ, 7.5 ns) to produce a plasma in CO.[101] They observed the emission of the C_2 Swan band around 565 nm to determine vibrational temperatures in the decaying plasma. The observed spectra was fit with a model in which temperature was a parameter. At a time delay of 30 μs relative to the laser pulse, a temperature of 6745°K was obtained. This temperature was confirmed by use of the CN violet band around 388 nm to calculate the vibrational temperature in a similar way.

Yagi and Huo investigated breakdown in H_2 gas at different pressures initiated by a KrF laser (248 nm, 250 mJ, 20 ns).[102] This work was related to Raman spectroscopy in that the breakdown threshold determined the maximum energy with which the Raman transitions could be pumped. The authors found that below 600 Torr breakdown thresholds were pressure independent. Thresholds decreased between 600 and 3000 Torr, and increased slightly above 3000 Torr.

Yalcin et al. investigated the sensitivity of a laser spark produced by a Nd:YAG at 532 nm to ambient conditions such as variation in background gas, presence of particles, and humidity.[103] This was done in order to assess the potential usefulness of LIBS in toxic metal monitoring. The authors found that excitation temperature and electron number density in the plasma remained essentially constant with variations in the ambient conditions.

B. Analytical Results

In this field, Cremers and Radziemski again did pioneering work. In their 1983 publication, they detected chlorine and fluorine in air.[104] Detection limits for these two gases were 8 and 38 ppm by weight, respectively. These values corresponded to absolute detection limits of 80 and 2000 ng. In a helium atmosphere, the absolute detection limits improved to 3 ng for both. Experiments were carried out in which molecular gases containing both chlorine and fluorine were introduced to the sampling chamber. The relative intensities of the chlorine and fluorine signal were found to be an indication of the number of each of these atoms in the molecular gas. All experiments were carried out using a Nd:YAG laser (1064 nm, 100 mJ, 15 ns) and detecting Cl at 837.6 nm and Fl at 685.6 nm.

These authors also detected Be in air.[105] The limit of detection in this experiment was 0.5 ppb by weight. The Be was introduced into a chamber by laser ablation and diluted by air. A second laser produced a breakdown in the chamber from which the emission was measured. It was found that the emission from the Be II doublet at 313.1 nm was stronger than any atomic emission even at delay times of 20 μs. This doublet was used for calibration that was linear over 4 orders of magnitude.

Cremers et al. used LIBS to determine sodium and potassium in a coal gassifier stream as early as 1983.[63] These elements were present as particulates in the stream and so again the question of whether the target was a gas or solid arises. Regardless, the authors were able to determine Na with a detection limit of 4 ppb by weight using the doublet at 589 nm. Figures of merit for potassium were not given. In conclusion, the authors noted that sulfur could also be monitored.

Sneddon extended this technique to the determination of P in air and lowered the absolute detection limit of Cl in air. In a 1988 paper, he detected phosphorous at 15 ppm and Cl at 60 ppm by weight in air.[106] A calculated plasma volume of 0.010 cm^3 was used to determine an absolute detection limit of 60 pg for Cl.

Ottenson et al. reported on the application of LIBS to analyze particulates in a coal combustion vent in a 1989 publication.[107] A Nd:YAG laser was triggered on the scattering from a HeNe laser to explode particles detected in the probe volume. The experiment used on-line temperature correction to account for different excitation conditions in plasmas formed on different size particles. Moreover, the size of particles to be sampled could be adjusted by adjusting the laser power. With lower laser power, only larger particles were sampled, the smaller ones were not sufficient to provide plasma formation. The on-line temperature correction automatically accounted for differences in excitation conditions with varying laser power.

In 1990, Morris et al. used laser-induced breakdown as a detector for gas chromatography.[108] The UV laser light was focussed into the effluent from a gas chromatograph at a power below the breakdown threshold of the carrier gas. When eluting carbon containing molecules were present in the effluent, the threshold for breakdown was lowered and a plasma formed. The organic analytes were indirectly detected by optically detecting plasma formation. A schematic is shown in Figure 10. No emission from the plasma was measured, and so the potential of this technique was only as a universal detector.

In 1991, Cheng et al. studied polyatomic molecular impurities in helium gas at ppm levels.[109] Using ungated detection, they determined B_2H_6, PH_3, and AsH_3 with detection limits of 1, 3, and 1 ppm, respectively. The ionic phosphorous lines at 602.4, 603.4, 604.3, and 605.5 nm were used. As lines were observed at 228.8, 235.0, 278.0, and 286.0 nm. B lines were observed at 336.0 and 434.5 nm. The plasmas were produced by a Nd:YAG laser at 532 nm.

Also in 1991, He and co-workers focused a pulsed laser onto a metal rod in an atmosphere of helium or argon seeded with a reaction gas to produce ion-molecule complexes and observe their emission.[110] Ion lenses were used to preferentially draw ions into the He or Ar gas for reaction with the seeded gas. Emission from species such as AlO, AlO-CO, Al-Ar, and Al^+H_2 was observed.

Joseph and Majidi used an electrothermal atomizer to create a gas phase sample from a liquid for analysis by LIBS.[111] A few µl sample was deposited in the furnace and was dried, ashed, and atomized. The setup is shown in Figure 11. At the onset of atomization, a Nd:YAG laser (1064 nm, 100 mJ) was focused into the furnace and fired at a repetition rate of 10 Hz. Emission from the plasma was collected through the dosing hole of the tube. Experiments with cobalt and cadmium gave absolute detection limits of 5 and 50 pg.

Casini et al. also determined several elements of interest in air using LIBS.[112] Their experiment used a Nd:YAG laser (1064 nm, 40 mJ, 7 ns) to produce plasma in an atmospheric pressure chamber as shown in Figure 12. Using the saturated concentrations of air over chosen liquids at the given temperature, and then successively diluting these concentrations in the chamber, yielded calibration curves for a number of elements. Cl was detected at 449.0 nm with a detection limit of 60 ppm, S at

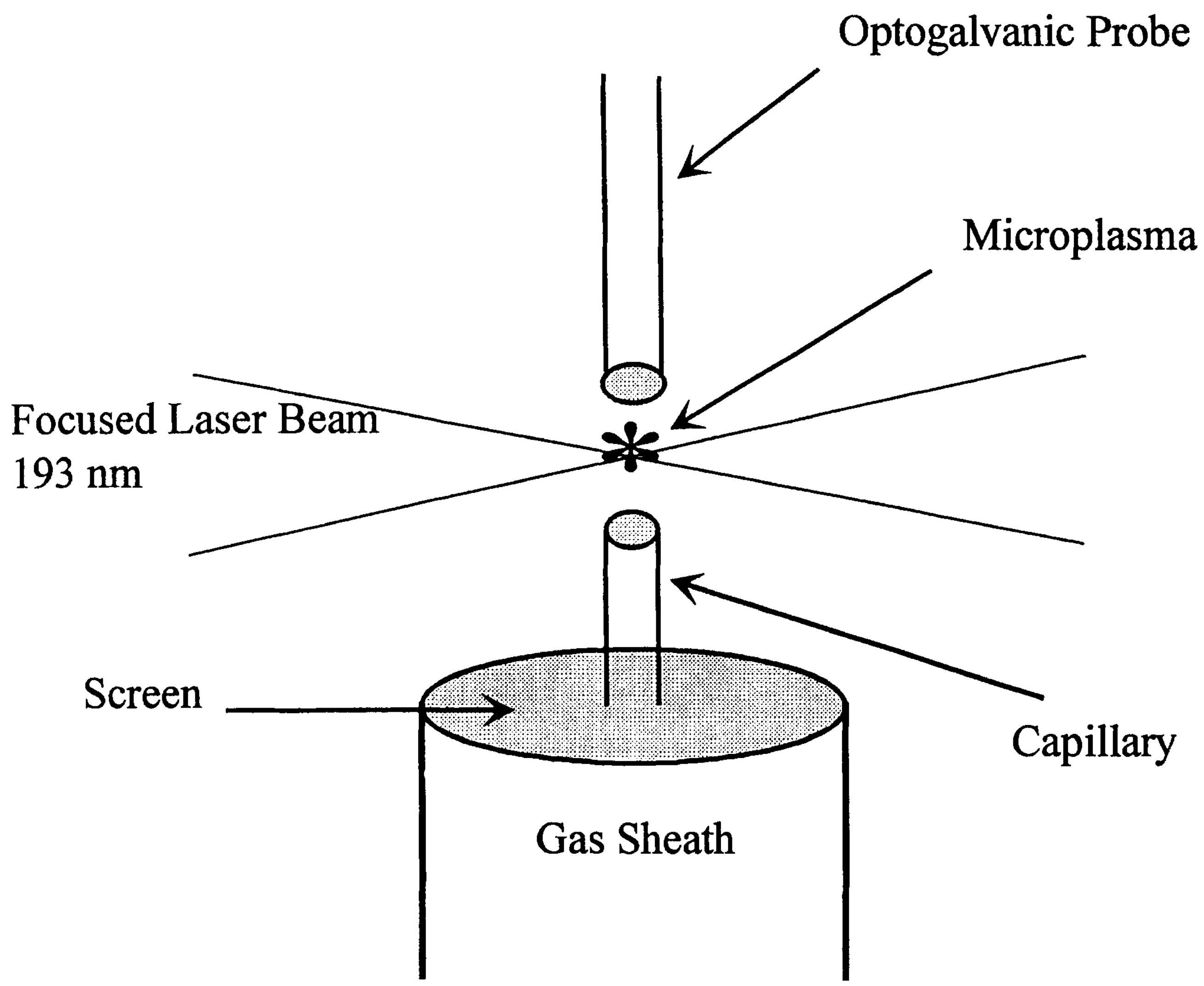


FIGURE 10. Schematic of setup used by Morris et al. for use of laser-induced breakdown as a detector in gas chromatography.

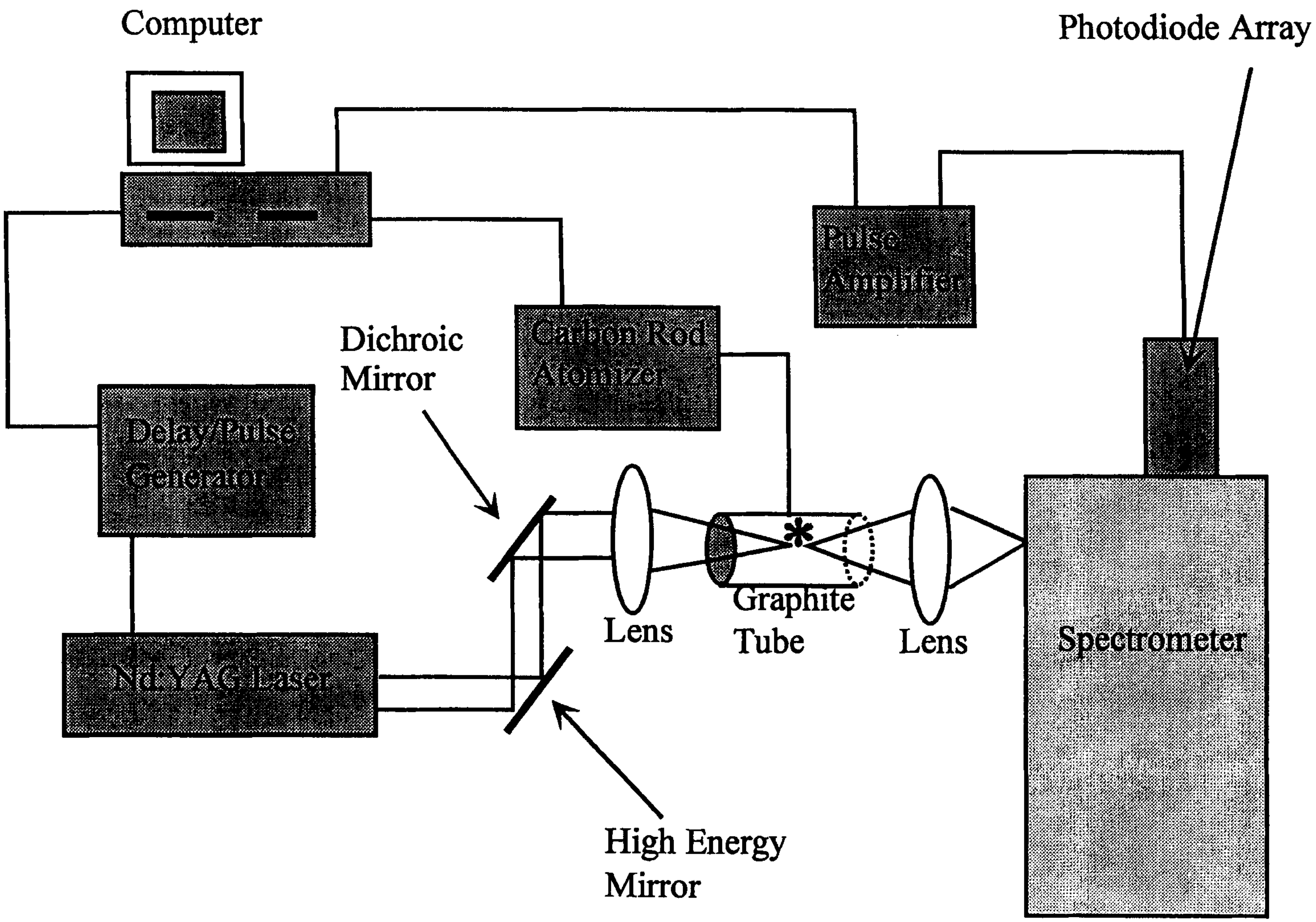


FIGURE 11. Schematic of setup used by Joseph and Majidi for LIBS in a graphite furnace.

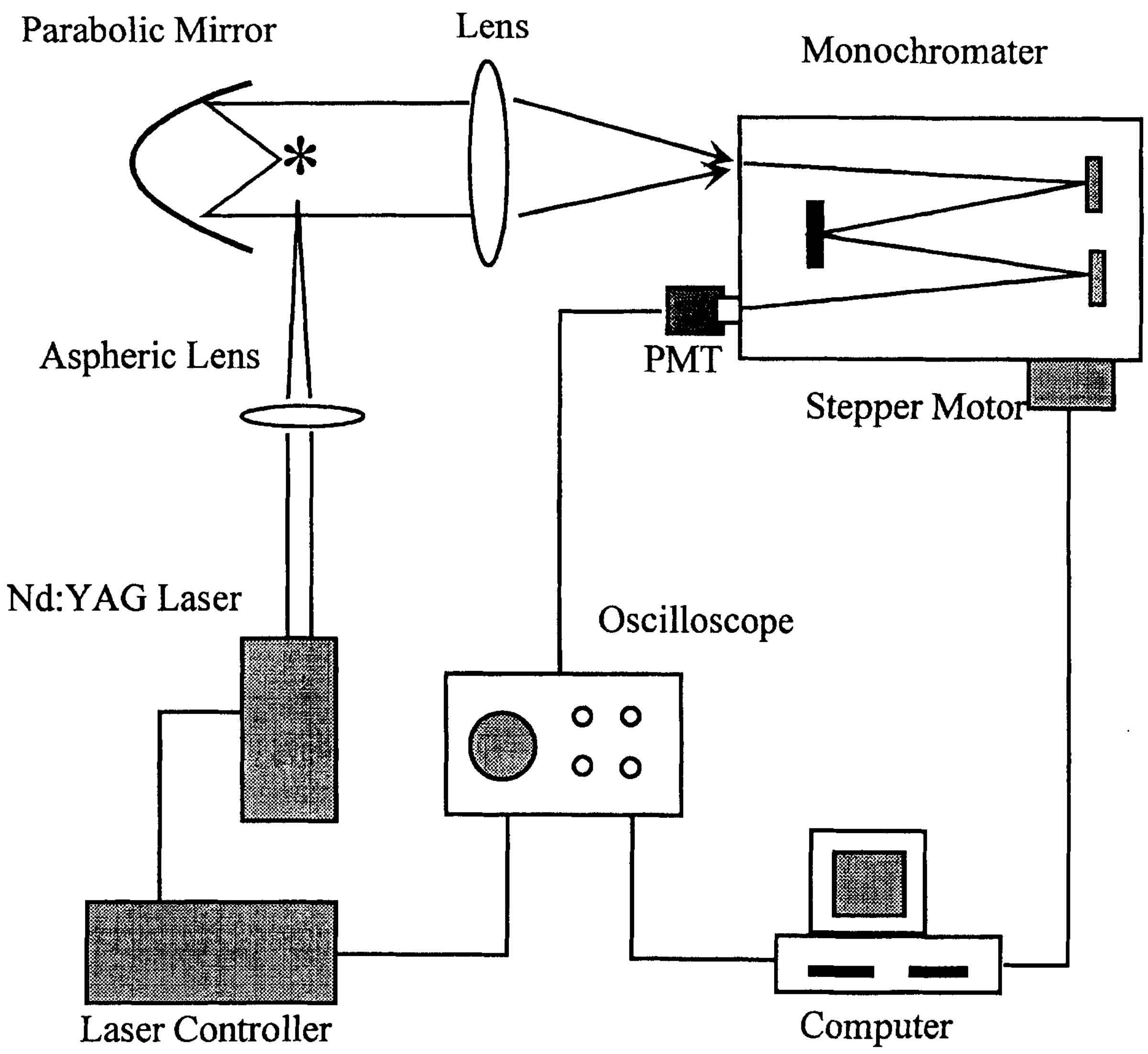


FIGURE 12. Shematic of setup used by Cassini et al. for air analysis using LIBS.

415.3 nm with a DL of 200 ppm, P at 442.1 nm with a DL of 200 ppm, Na at 371.1 nm with a DL of 110 ppm, Hg at 404.7 nm with a DL of 50 ppm, Be at 381.4 nm with a DL of 130 ppm, and As at 454.4 nm with a DL of 130 ppm.

In 1994, Flower et al. used LIBS to monitor metal aerosol emission generated by a pneumatic nebulizer.[113] A chromium salt solution was passed through the nebulizer and a heating pipe to produce a gas with known concentration of Cr. The detection limit was 200 ng Cr/standard cubic meter of air (scm). The laser used was a Nd:YAG (1064 nm, 180 mJ) and detection was at 312 nm.

In 1994, Lazzari et al. detected mercury in air using LIBS with a Nd:glass laser (400 mJ, 8 ns) to produce plasma in a chamber filled with saturated Hg vapor and successively diluted.[114] With this technique, they obtained a detection limit of 10 ppb by observation of the 253.7 line.

Zhang et al. performed LIBS in a particle loaded methane/air flame and in an oil-fueled combustor vent.[115] In their 1995 publication, they described the addition of a flange with four movable windows to a preexisting combustor vent. LIBS was performed through these windows which were kept clean by a flow of N_2 gas and could be switched out periodically for cleaning.

In 1995, Nordstrom studied the laser-induced plasma emission spectra of N_2, O_2, and ambient air from 350 to 950 nm.[116] This range was covered with approximately 0.5 nm resolution and atomic, ionic, and molecular emission from a plasma created by a CO_2 laser (10.6 μm, 320 mJ, 200 ns) was observed. Spectra were computed for N, O, and a few molecular species, and a comparison between experiment and calculation was done.

The same year, Parigger et al. again published a fundamental paper on laser-induced plasma in the gas phase.[117] This time the breakdown was produced by a Nd:YAG (1064 nm, 220 mJ, 6 ns) in hydrogen at 150 and 810 Torr. The Hα line at 656 nm was used to calculate electron number densities in the decaying plasma with temporal resolution as high as 6 ns early in the plasma and 1 μs at later times. Spatial resolution was also achieved by focusing different portions of the 1:1 plasma image onto the spectrometer entrance slit. Spatial resolution was approximately 50 μm. Surface plots for electron number densities resolved in time and space were then created. Electron number densities varied between 10^{16} and 10^{19} cm^{-3}.

In 1996, Haisch et al. again used LIBS to detect chlorine in the gas phase.[118] Two experimental setups were described. The first was a benchtop experiment using a 320 mJ Nd:YAG laser. The second setup used a miniature Nd:YAG laser built into a sensor head. This miniature laser provided 18 mJ of pulse energy. Detection of Cl in chlorinated hydrocarbons was accomplished by focusing the laser onto a copper target in the presence of the gas to be analyzed. This provided for formation of CuCl in the plasma. The luminescence of the D-system of CuCl was then detected around 440 nm. Detection limits were a few ppm.

Figure 13 shows the elements determined in a gas phase matrix and their relative detection limits.

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Gases

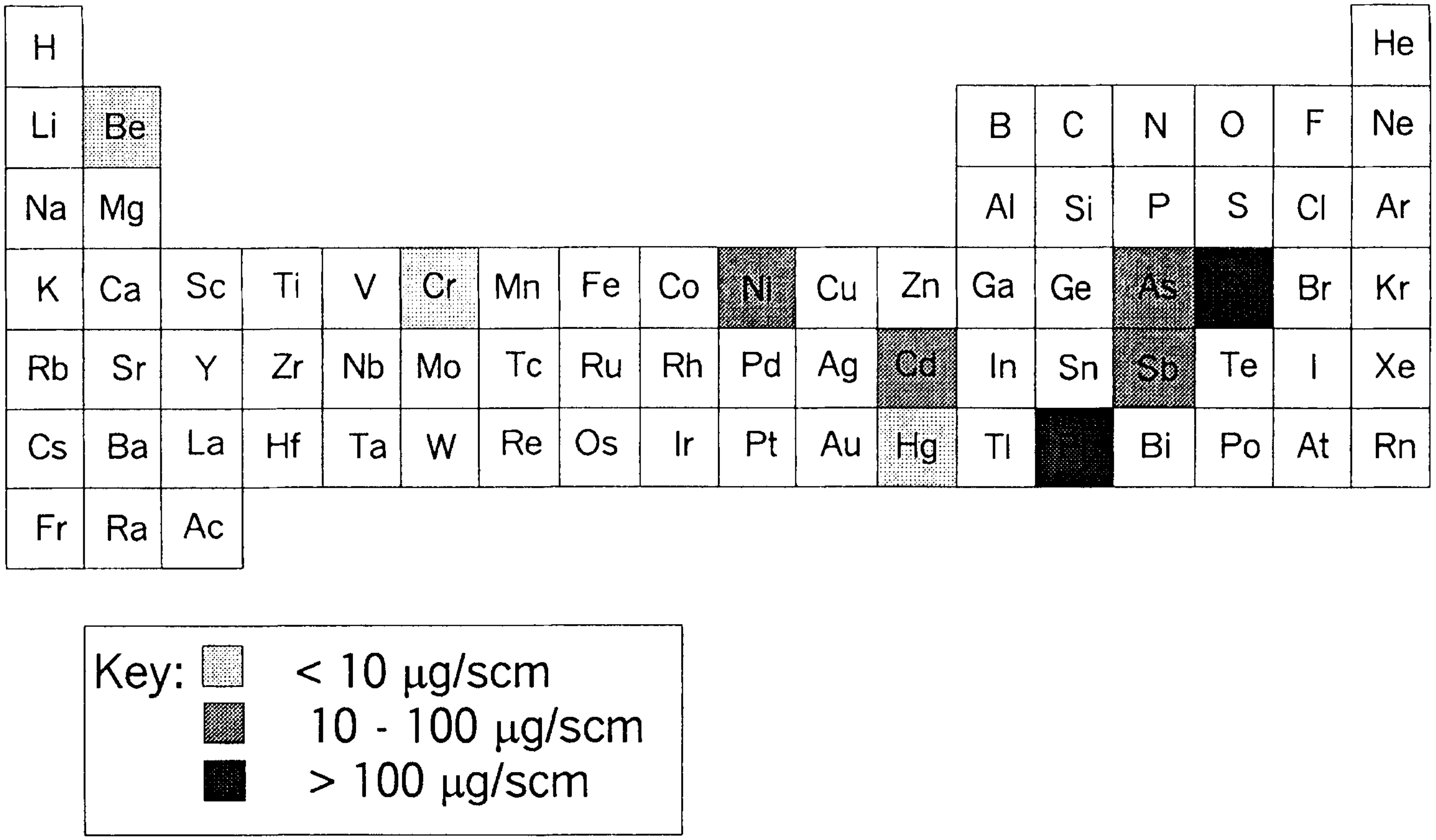

FIGURE 13. Elements determined in gas phase matrices shaded according to detection limit. The unit scm refers to a standard cubic meter of gas.

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