CHAPTER 1

INTRODUCTION
Chapter 1  Introduction

1.1 Historical background of LIBS

The development of Laser-induced breakdown spectroscopy (LIBS) and understanding of laser-induced plasma is directly related to advances in laser. The first report of laser action in ruby was appeared in 1960 [1, 2], since then, it is accepted that by bringing an intense laser light beam to a tight focus; one could excite material into a state of optical emission. The focused position would be visible as a bright spot and is termed as plasma, which is similar in appearance to a discharge spark between two electrodes. The first report about the analytical use of laser-induced plasma was published by Brech and Cross [3]. Maker, Terhune and Savage [4] reported the first observation on optically-induced breakdown in gases. In the same year, Runge, Minck and Bryan [5] used a pulsed ruby laser for direct spark excitation of metals. In 1966 Young, Hercher and Yu [6] described the characteristics of laser-induced air sparks. The effect of composition of target material on the plasma formation were discussed by workers; Cerrai and Trucco, 1968 [7], Marich et. al.1970 [8] and Scott and Stasheim, 1970 [9]. In 1972, Felske, Hagenah and Laqua [10] performed the analysis of steel by producing laser induced plasma using Q-switched ruby laser. For spectrochemists, direct ablation, excitation and observation of the spark on surfaces became a promising tool for analytical work. In 1981, fundamental studies on breakdown in gases by using laser-induced breakdown spectroscopy (LIBS) was reported by Loree and Radziemski [11].

In the early eighties a renewed interest in applications of LIBS was driven by its unique advantages for spectrochemical analysis [12-15]. From late eighties to early nineties due to the evolution of high power pulsed lasers and sensitive detectors, the interest in the area of quantitative analysis using LIBS increased many fold and many published works were appeared including the work of Millard et. al. 1986 [16], Essien et. al. 1988 [17] and Ko et. al. [18], Leis et. al. in 1989 [19] etc. Finally, the applications of LIBS turned towards many practical problems, such as monitoring environmental contaminations, control on material processing and sorting of materials. Determination of carbon content in steel was reported by Aguilera et al. [20] in 1992 with the limit of detection (LOD) for carbon equal to 65 ppm. Lorenzen [21] described the applications of LIBS in the determination of minor elements in liquid steel, and depth profiling of layers.
on metallic substrates whereas Hader [22] used LIBS for online quality control of rubber mixing. In 1993, Sabsabi et al. [23] and Thiem et al. [24] performed the analysis of alloys using LIBS technique. Thiem and Wolf [25] used LIBS to analyze mining ores and their results were in close agreement with the result obtained by ICP-AES technique. In 1995, Allen et al. [26] employed LIBS for the determination of the thickness of the thin film between 20 Å and 100 Å. Anderson et al. [27] used LIBS for depth profiling. LIBS was used to determine metal particles on air sampling filters [28]. Sattmann and Sturm [29] investigated the use of a multiple Q-switch Nd:YAG laser for analysis of steel samples. Remote LIBS by using 100 m fiber optic was demonstrated by Davies and Telle [30] and LODs of 200 ppm or less were found for Cr, Cu, Mn, Mo, Ni, Si, and V. Hakkanen and Korppi-Tommola [31] used LIBS to study elemental distributions on the surface of the paper coatings. It was estimated that 2 ng of paper coating were vaporized per shot and Al, Si, Mg, Ca, and C were monitored quantitatively. In 1995, the characterization of the laser induced plasma on the surface of the aluminum alloys was performed by Sabsabi and Cielo [32]. Ciucci et al. [33] in 1996, determined Cu, Pb, and Cr in geological survey soil sample. The first attempt to deliver laser at the target surface using fiber optic delivery of the laser for the production of laser induced plasma in the determination of Cu in steel was reported by Ernst et al. [34]. This method is very significant for the monitoring of hazardous environment such as nuclear waste management. Marquardt et al. [35] determined Pb in paint using a Nd:YAG laser at 532 nm coupled with a fiber optic probe. In 1996, Miziolek [36] fabricated a LIBS probe housed in a cone penetrometer truck for the determination of heavy metals in soils whereas in the same year, Cremers et al. [37] introduced a portable LIBS instrument to determine hazardous elements in soil, paint, and samples on filter paper. Palleschi et al. [38] used 1064 nm wavelength of a 400 mJ Nd:YAG laser for producing induced plasma in the determination of traces including Hg in air (with LOD 5 ppm), and pollutants in powerplant smoke and soil. Vadillo and Laserna [39] analyzed geological samples of vanadinite, pyrite, garnet, and quartz. Laserna et. al. [40] used LIBS to analyze the surface of solar cells. In 1997, Maravelaki et al. [41] used LIBS to monitor the laser cleaning of marble. During 1990s emphasis was given to develop LIBS for remote analysis as well as to build up rugged and mobile instrumentation [42-44]. Initially, the
optical fibers were integrated into LIBS systems, only for collecting the optical emission from the laser induced plasma. Later on the optical fibers were used both for delivery laser at the focal spot on the target surface as well as to collect the optical emission from the laser induced plasma [45].

The beginning of new millennium as witnessed a series of conferences related to LIBS: LIBS 2000 in Pisa, Italy [15], EMSLIBS I in 2002 [46], LIBS 2002 in Orlando, USA [47], EMSLIBS II in 2004 [48], LIBS 2004 [49], NASLIBS in 2006 [50] and recently LIBS2008, was organized in Berlin, Germany [51] which provided an excellent snapshot of the status of LIBS research, development and commercialization. In particular, drastic increment in the LIBS papers which deal with various categories of instrumentation development, from laboratory devices all the way to commercial systems. Clearly, the field has moved beyond the science and engineering laboratory to include the world of applications and sales as well. A search through the web site of US Patent Office showed, for example, 37 relevant patents mentioning LIBS since 1976. As 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.

1.2 Laser-induced breakdown spectroscopy

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 a past two decades. In LIBS, a high power laser pulse is focused onto a solid sample, the irradiance leads to rapid local heating, intense evaporation and ablation of material. The ablated material compresses the surrounding gas and leads to formation of a shock wave. LIBS is an appealing technique compared with other conventional analytical techniques, because setting up an apparatus to perform a LIBS measurement is quite easy. One merely focuses a laser pulse in or on a sample, which can be of any form (solid, liquid, gas) to form microplasma. The spectra emitted from the plasma are used to determine the sample’s elemental constituent. However, the basic physical and chemical processes involved are not 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 among photons, electrons and atom or molecules. In the LIBS experiment, the plasma and ejecta expand freely from the sample surface at different speeds. Excitation of specific energy levels in different atoms is likewise complex, and depends on factors such as thermodynamic equilibrium and interaction with other atoms and molecules generally lumped under the category of matrix effects. After the laser pulse has terminated (typically in 10 ns), the plasma decays over an interval of one to several microseconds, depending on the laser energy deposited. Soon after initiation, continuum and ionic spectra are seen. The continuum is the white light from the plasma that contains little spectroscopic information. As the plasma decays, the continuum is 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. A close examination of the LIBS spectrum reveals immediate qualitative information about sample composition. After calibration, quantitative information can be obtained.

Chronologically, the laser-ablation process can be divided roughly in three phases (Fig. 1.1): (i) primary laser-matter interaction (heating and evaporation), (ii) plasma generation and laser plasma interaction (laser-induced breakdown), (iii) adiabatic expansion of the plasma. Although linearly depicted in Fig. 1.1, the phenomena are temporally overlapping during laser ablation.

1.2.1 Laser-induced plasma production on solid targets

Demonstration of laser-induced plasma on solid target was shown by Ready [52]. When a high-power laser beam strikes a solid surface, it produces a plasma plume due to rapid melting, fusion, sublimation, ionization, erosion and/or vaporization of the sample surface. The plasma is produced by the ablation of the opaque target surface and subsequent absorption of laser light in this ablated material. Plasma production studies are carried out at laser irradiances of the order of \(10^9\) W/cm\(^2\) or greater which produce a denser, more absorbing blow-off material. There is a great difference in the behavior of surfaces struck by laser pulses with millisecond duration as compared to those with pulse
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Heating of material

Evaporation of material  Dissociation of molecules

Explosion called Ablation

Plasma ignition  Heating of the plasma via inverse bremsstrahlung and photoionisation

Plasma shielding of the surface  Expansion of the plasma

Plasma expansion

Shock wave generation  Plasma cooling

Figure 1.1: Laser ablation
durations of nanoseconds. As at lower power densities, the dominant mechanism is thermal vaporization: the temperature of the solid surface increases and a well defined phase transition occurs, from solid to liquid, liquid to vapor and vapor to plasma. Therefore, in this case, elements of higher vapor pressure will be enriched in the vapor relative to the target, hence unable to completely represent the true composition of sample.

The short pulses of very high power (power density > 10^9 W/cm^2 and laser pulse width ≤ ns) do not produce much vaporization; instead remove only a small amount of material from the surface. Since the laser flux density is very high, the ejected material is further heated by absorption of incoming laser radiation making it thermally ionized and opaque to the incident radiation. The absorbing plasma prevents light from reaching the target surface, which is effectively cut off from the incoming radiation for a significant duration of the laser pulse. At the end of the pulse, the blow off material becomes so hot that it begins to radiate thermally. The plasma plume, produced by ns laser pulses, white-bluish in color that can seen by naked eye. Figure 1.2 shows plasma formation in air and its lengthening in the direction opposite to the incident laser beam is demonstrated by Fig. 1.3. This interaction of the laser with a target is considerably modified by the presence of material ejected from the surface by ns pulsed high power laser irradiation [53].

The processes involved in the production of plasma by a ns laser can be understood in terms of a simple model described by Ready [54] which taking into account the pressure produced by a small amount of the blow-off material by the beginning of the laser pulse. This recoil pressure, raises the boiling point of the target above its usual vaporization temperature. If the increase in vaporization temperature is sufficiently high, the surface will be prevented from vaporizing further and the laser continuously heat the material to a high temperature (above the normal vaporization temperature) as more and more laser light from the pulse is absorbed by the target surface. Eventually, a critical point is reached, when the energy deposited into the sample is much larger than the latent heat of vaporization for all the constituents present in the target material and at that point vaporization of all the constituents can occur. In this
Figure 1.2: Optical breakdown in air

Figure 1.3: Lengthening of plasma in direction opposite to laser beam propagation
process, target thermal properties may not play significant role and it is likely that all constituents can be completely vaporized/removed to form the plasma.

Another mode which is commonly used for the explanation of laser ablation and plasma formation is given by Chan and Russo [55]. According to them, a small amount of material is ablated when high irradiance, beyond $10^9$ W/cm$^2$ with nanosecond or even shorter laser pulses are focused onto the surface of any material, an explosion occurs. Within the fraction of the leading laser pulse the vaporization temperature of the sample surface exceed the real vaporization temperature of the material due to the high pressure exerted by the laser beam on the sample surface. Before the surface layer vaporizes, the underlying material will reach its vaporization temperature. Along with the temperature, the pressure of the underlying material is raised above its critical value, causing the surface to explode. This exploded material forms the plasma.

The hot plasma already formed at the sample surface expands and interact with the surrounding gas: firstly through the production of shock waves, (which are pressure waves, produced due to the compression in surrounding gases due to the expansion of plasma) and secondly through the energy transfer to surrounding atmosphere one is energy transference in surrounding atmosphere from expanding plasma by thermal conduction, radiative transfer and heating of shock wave. Since the ablation / evaporation of material takes place by leading laser pulse, hence the rest of laser pulse energy is absorbed by the formed plasma itself (plasma shielding).

The growth of the spark in the direction opposite to the laser beam has led to the model of a radiation-supported detonation wave. A detonation wave is a shock wave which is fed by release of energy behind the shock wavefront. In this case the energy is supplied by the absorption of the incoming laser beam. As shock wave propagates from the focal region into the undistributed gas the absorption of energy from the laser beam drives the shock wave, causing it to spread. The plasma propagates in the direction opposite to the laser beam until the irradiation is terminated. The plasma front has been found to move faster before the end of the laser pulse but its expansion is slowed down after the end of the pulse.

The plasma up to the end of the laser pulse is optically thick throughout the entire UV to IR spectral range. This fuels the expansion and sustains the luminosity of the
plasma for a long time after the end of the laser pulse. A vertical cross-section of the propagating plasma is shown schematically in Fig. 1.4. More details about laser ablation can be found in several monographs [56, 62].

1.2.2 Theoretical modeling of laser-induced plasma

Laser-induced breakdown can be defined as the generation of an ionized gas (plasma) by a laser pulse [56]. Basically, laser-induced plasma is a local assembly of atoms, ions and free electrons, overall electrically neutral, in which the charged species often act collectively. Laser-induced plasmas are characterized by several parameters, the most basic being the degree of ionization. A weakly ionized plasma is one in which the ratio of electrons to other species is less than 10%. On the other hand highly ionized plasma may have atoms stripped of many electrons, resulting in very high electron to atom/ion ratios. Laser-induced plasma typically fall in the category of weak ionized plasma. In the early stage of plasma, the few nanosecond after triggering the laser beam, the ionization is high. When the plasma cools down (after few microsecond of plasma formation), electron-ion recombination takes place and neutral atoms and molecules are formed. Throughout this process, there is a background continuum that decays with time more rapidly than the spectral lines. The continuum is primarily due to bremsstrahlung (free-free) and recombination (free-bound) events. The bremsstrahlung process, also known as free-free emission transitions, correspond to loss of kinetic energy by an electron in the field of an ion. In this process, high energy electrons, emit photons upon traversing a gas or solid, through acceleration or deceleration in collisions and slow down (from German words “bremsen” to slow down / braking, and “strahlung” radiation). The other process, recombination, occurs when a free electron is captured by atom or ion and that atom/ion makes a transition to the bound energy state having energy $E_j$ and giving up its excess kinetic energy in the form of photon. These photons give the continuum background whose energies are

$$hν = \xi - E_j + \frac{1}{2} m v^2$$

where, $\frac{1}{2} m v^2$ is the kinetic energy of the free electron $\xi$ is the ionization energy of the atom. Collection of light from the plasma at different time delay relative to the trigger
Figure 1.4: Plasma expansion and formation of a shock wave after plasma ignition
time of the laser beam allows us to discriminate the region of background continuum and select the region of interest where spectral lines predominates.

It is difficult to separate emission by bremsstrahlung from that due to radiative recombination except to say that the later is dominant at higher frequencies and the former at lower frequencies.

There are two main mechanisms that lead to breakdown in material. The first mechanism involves absorption of laser radiation by electrons when they collide with neutrals. If the electron gains sufficient energy, its impact can ionize the gas or solid through the reaction

\[ e^- + M \rightarrow 2e^- + M^+ \]

This leads to the cascade breakdown, i.e. the electron concentration increases exponentially with time. This situation is very much similar to the dielectric breakdown of solids, liquids and gases. Two conditions are necessary to initiate this mechanism: (1) there should be an initial electron in the focal volume, and (2) the electrons acquire energy greater than the ionization energy of the gas (or band gap of the solid).

The second mechanism, called multiphoton ionization (MPI), involves the simultaneous absorption of large number of photons by an atom or molecule to cause the ejection of an electron. MPI is described by the reaction

\[ M + m h\nu \rightarrow M^+ + e^- \]

To proceed the above mechanism, the number of photons must exceed the number equal to \( \frac{IP}{h\nu} + 1 \), where IP is Ionization Potential. In MPI, the electron density linearly increase with time. Multiphoton ionization is important only at short wavelengths (\( \lambda < 1\mu m \)). For longer wavelengths, simultaneous absorption of \( m > 10 \) photons is necessary which is highly improbable. Both cascade and multiphoton ionization require high laser irradiances, usually in excess of \( 10^8 \) W/cm\(^2\). However, the thresholds for breakdown of solids are usually significantly lower than breakdown threshold of gases or liquids. Breakdown will occur when electrons are generated by MPI and their density grows by electron impact of neutrals in the lattice.

The initial electrons generated within the focal spot will gain energy through electron-neutral inverse-bremsstrahlung collisions (IB). Simultaneously electrons will
lose energy by elastic and inelastic collisions with neutral particles through excitation of molecules in rotational or vibrational levels and also excitation of electronic states of molecules and atoms. Some electrons lose their energy in electron-ion recombination, while some are diffused out of the focal volume. If the laser irradiance is high enough, then a few electrons, in spite of all energy losses, will gain energy larger than the ionization energy and these electrons will generate new electrons by impact ionization of the target, thereby leading to cascade growth.

In metals, absorption of nanosecond laser pulse occurs within a typical skin depth measured in nm. Unless the laser pulse is extremely short, the thermal diffusion length will be much larger than the skin depth. The generation of substantial electron density, $n_e$ (above $10^{13}$ cm$^{-3}$) above the surface due to thermionic emission before and during the vaporization has often been considered as the starting point for plasma ignition. The plasma sheath that one calculates for such a high densities is, however so thin, that electron leave the surface, reflect off the edge of the sheath, and return to the surface before they make any collision with the vapor atoms. A more likely mechanism that can explain the threshold is absorption by thermally generated electrons in the vapor [63].

Further absorption of laser radiation by the ignited plasma generally commences via electron-neutral inverse bremsstrahlung, but when sufficient electrons are generated, the dominant laser absorption mechanism makes a transition to electron-ion inverse bremsstrahlung.

### 1.2.3 Spectral emission from plasma

The LIBS technique is based on the analysis of the spectral emission collected from laser-induced plasma. The laser-induced plasma or spark dissociates the molecules in the sample and excites the atoms and ions in the sample. As the plasma cools, the ions and the excited atoms relax to their ground states and emit light of characteristic wavelengths. Analytical information about the elemental composition of the test sample is determined by the wavelength and intensity of the specific atomic emission lines observed in the LIBS spectra. After the laser pulse produces the spark, ions and neutral atoms inside the plasma excite and relax to produce high signal intensities which decay with time. These emission lines are superimposed on the background continuum.
Continuum background dominates over the discrete line spectra in the initial stage of plasma i.e. during the first few nanosecond to 3 μs time interval after the laser pulse is fired. As the plasma temperature cools down, the background continuum decreases and the emission from the excited electrons from the atoms and ions dominate the spectra between approximately after more than 1μs. When the plasma cools further, the atoms inside the plasma start to recombine and form molecules. Figure 1.5 shows the typical temporal sequence of laser-induced plasma.

The laser is triggered by the external source to eliminate the continuum background and record high signal intensities of the atomic lines. The delay time (the time between the firing of the laser pulse and the signal collection by the detector) is optimized to get good atomic emission line intensities and avoid the continuum background to a possible extent.

1.3 Advantages of LIBS and its comparison with other techniques

LIBS as a spectrochemical technique possesses many advantages which makes it especially attractive for development into an in-situ sensor for environmental research. The principal advantage of LIBS over conventional analytical techniques (such as Inductively coupled plasma-atomic emission spectroscopy (ICP-AES), Inductively coupled plasma- mass spectrometry (ICP-MS) and Graphite furnace atomic absorption spectrometry (GFAAS) is the simplicity of the LIBS system and the sampling speed. The analysis time and the sample preparation are reduced as compared to the other techniques and it avoids the use of any chemical for sample preparation. LIBS also enable in-situ measurements and the possibility of simultaneous multi-elemental analysis by means of a holographic or echelle grating. It has the capability to detect elements in the parts-per-million and more recently, in parts-per-billion range. All elements emit radiation in the wavelength range 200-900 nm and each element has its own unique spectral signature; therefore, all elements can be detected simultaneously with LIBS. In LIBS, any type of solid sample can be used to produce laser-induced plasma on its surface. Thus, there are no sample-size requirements and no typical sample preparation in this technique. Chemical analysis using LIBS requires a smaller amount of sample (< micrograms) than
Figure 1.5: Generation of laser-induced plasma and separation of atomic emission from background continuum
that required for solution nebulization (milligrams). No use of chemical reagent avoids the problem of contamination and reduces the analysis time. Depending on the analytical measurement system, picogram to femtogram sample quantities may be sufficient for analysis. Rapid analysis is possible with LIBS as it requires only one laser shot to generate plasma, therefore, a large number of measurements can be performed quickly, which allows us the analysis of elemental composition of the sample on a nearly real-time basis. In addition, a focused laser beam permits spatial characterization of heterogeneity in solid samples, with typically micron resolution both in terms of lateral and depth conditions.

LIBS has been identified as a viable technique for use in extreme hazardous / radioactive environments because direct contact with the sample is not necessary; only optical access is required [64-68]. LIBS spectrometers can also be coupled with fiber optics for remote measurements, therefore the measurements can be directly applied to the field. These benefits make LIBS useful for analysis in extreme environments suggesting that it is a viable technique for use in the environment samples. Martin et. al. performed the time resolved LIBS analysis for the total carbon and nitrogen determination in soil samples [69]. Hahn et al. have used LIBS for quantification of chromium, iron, and manganese in pyrolytic wastes and have demonstrated its use as a real time particulate emissions monitor for various processes [70]. Buckley et al. [71] and Zhang et al. [72] have implemented LIBS as a continuous monitor of toxic metals, providing real time response of concentrations of these metals in incinerator facilities. Martin et. al. [73] have used the field portable spectrometer for the detection of Chromium aerosols measurements. Neunasser et al. [74] performed in-situ detection of lead aerosols and Berman et al. [75] analyzed aqueous solutions containing nickel and chlorinated hydrocarbons.

1.4 Motivation behind the present work

Heavy metals are of environmental concern and have great impact on the local ecosystem, groundwater and human health. Heavy metal contamination results from
mining, plating, and sand blasting operations. Other contaminant sources include industrial waste treatment centers, battery dumps and shooting ranges.

Soil is contaminated in the presence of man-made chemicals or other alteration of the natural soil environment. This type of contamination typically arises from the rupture of underground storage tanks, application of pesticides, percolation of contaminated surface water to subsurface strata, leaching of wastes from landfills or direct discharge of industrial wastes to the soil [76]. The nutrient content of municipal and some industrial wastewater makes it economically, attractive for fertilizer. However, domestic sewarage, even after treatment, contains significant concentrations of potentially toxic contaminants, including heavy metals (e.g. cadmium, zinc, cobalt, nickel, lead, mercury, boron), other metal ions (e.g. sodium, potassium, magnesium, calcium), pesticide residues (e.g. atrazine and its degradation products) [77].

There are thousands of contaminant sources and pollutant types, but the following list is illustrative (pollutants indicated by parentheses):

- Petroleum hydrocarbons from rupture of underground storage tanks (benzene, ethylbenzene, toluene, xylene, alkanes, alkenes, MTBE)
- Spillage or leakage of solvents and dry cleaning agents (acetone, trichloroethylene, formaldehyde) and perchloroethylene
- Leaching of contaminants from solid waste disposal sites (lead, mercury, chromium, cadmium, bacteria, hydrocarbons)
- Water runoff which carries pollutants and may deposit them at a point of percolation
- Percolation into soils from pesticides and herbicides used (wide variety of chemicals including DDT, lindane, organochlorines, organophosphates, carbamates, cyclodienes)
- Deposition of dust from smelting operations and coal burning power plants (zinc, cadmium, lead, mercury)
- Lead deposition from lead abatement or construction demolition (lead)
- Leakage of transformers (Polychlorinated Biphenyls (PCBs))
- Radioactive materials, these include natural radioisotopes which have been moved (for instance radium bearing waste from either the production of uranium or
phosphoric acid) and man made radioisotopes such as those present within chernobyl fallout [78-79].

Among pollutants, heavy metals have been the subject of greater attention because of their long-standing toxicity when exceeding specific thresholds. Mobility of heavy metals in the ecosystems and their transfer in the food chains is the key issue in the environmental research [80-81]. Uncontrolled development in industry, agriculture and urbanization accelerates the input of heavy metals into the environment. Many scientific activities have been devoted to determine their sources, types, and degree of heavy metal pollution in soil [82]. Figure 1.6 depicts the major pollutant sources involved in the contamination of soil.

Leaching of these contaminants through the soil into water supply and groundwater is a major hurdle to the safe disposal of treated sewerage on land. The occurrence of this phenomenon is correlated with the degree of industrialization and intensity of chemical usage.

The major concern is that there are many sensitive land where people are in direct contact with soils such as residences, parks, schools and playgrounds. Other contact mechanisms include contamination of drinking water or inhalation of soil contaminants. There are large set of health consequences from the exposure to soil contamination depending on pollutant type, pathway of attack and vulnerability of the exposed population. Chromium, Cadmium and many of the pesticide and herbicide formulations are carcinogenic to all populations. Lead, Zinc etc are especially hazardous to young children’s brain and nervous system, while to all populations kidney damage is a risk. Chronic exposure to benzene at sufficient concentrations is known to be associated with higher incidence of leukemia. Mercury and cyclodienes are known to induce higher incidences of kidney damage, liver toxicity, and sometimes leads to neuromuscular blockage. Many chlorinated solvents induce liver damage, kidney damage and depression of the central nervous system. There is a further range of health effects such as headache, nausea, fatigue, eye irritation and skin rash. At a sufficient high dosage a large number of soil contaminants cause death.

The concern over soil contamination stems primarily from health risks, both of direct contact and from secondary contamination of water supplies. Mapping of
Figure 1.6: Contaminant sources and various pollutants types which are the origin of soil pollution
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Contaminated soil sites are necessary so that cleanup technology can be applied. Currently there is no in-situ method commercially available for rapid on site characterization of heavy metal contamination. The most common way to determine the extent of subsurface contamination is to collect samples from soil borings or monitoring wells and send them to a laboratory for analysis. Frequently, additional efforts are required to complete the characterization of the site. Consequently, the spatial resolution of the contaminant distribution is often very coarse. The approaches such as atomic absorption/emission spectroscopy, X-ray fluorescence, polarographic techniques, molecular methods, Chemical analysis, ICP- AES, ICP-MS and GFAAS has proven to be time-consuming, lengthy sample-preparation and expensive.

Consequently, improved methods of monitoring contaminants in the subsurface are important for both the characterization as well as the remediation of a site. Laser-induced breakdown spectroscopy (LIBS) technique is suitable to delineate heavy metal contamination in soils in-situ and in real-time [83-84]. Therefore, we have developed the LIBS technique in the laboratory for detection and quantification of heavy metals in the soil of near by industries.

1.5 Organization of the thesis

The present thesis is divided into nine chapters, which cover trace metal detection in environmental sample such as soil as well as biological sample like coral skeleton. A data processing scheme for dealing with Calibration-free Laser-induced breakdown spectroscopy (CF-LIBS), its application in soil and biological sample is also the part of the thesis.

The first chapter deals with the general introduction whereas the second chapter outlines the experimental design of fabricating and developing the Laser-induced breakdown spectroscopy technique.

The presence of heavy metals in agricultural soil, due to excess enhancement in industrial activity, may cause alarm to human either by direct impact or through food chain. The rate of migration into deep interior of the soil is different for heavy metals and
not much work has been done in this direction. Thus, Chapter three describes the monitoring of vertical migration of heavy metals in agricultural soil.

EPA has decided the lower safe limit for each heavy metal concentration above which it shows toxic effect. Therefore, it is necessary to quantify the toxic elements in soil/ environment. Quantification of some of the heavy metals present in the soil near brick-kiln area using LIBS technique is presented in Chapter four.

For the quantitative determination of elements, any technique requires a calibration curve for which standard reference material is essential. But in the case of environmental and biological sample, it is difficult to get standard reference material and quantification of their constituents is a difficult task. Therefore, Chapter five deals with the model named as calibration-free LIBS, based on the basic equation derived from LTE assumptions and avoid the need for reference materials.

Chapters six and seven focus on the application of above developed model to study the traces as well as major constituents present in the soil samples (Chapter six) and biological sample i.e. coral skeleton (Chapter seven). In environmental and biological samples, it is difficult to obtain reference materials to draw calibration curve, therefore, \textit{in-situ} quantitative analysis of samples is obtained using CF-LIBS.

Sensitivity of the LIBS technique depends upon the composition (major and minor constituents) i.e. matrix of the target material. Therefore, a model, which eliminate matrix effect, while using calibration curve for quantitative estimation, is prepared. Chapter eight describes the development of this new working calibration curve which minimizes the matrix effect. Chapter nine presents the summary of the thesis and future prospects of LIBS in various fields.
Bibliography

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