DEVELOPMENT OF A RAPID METHOD FOR DETERMINATION OF CHROMIUM AND CADMIUM IN TANNERY WASTEWATER USING LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

By

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DEDICATION

Dedicated to my beloved family; their help and support was a major factor in enabling me to complete this work well in time.

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ABSTRACT

As a result of the fairly obnoxious waste generated by the leather processing, this industry is a major contributor to water and soil contamination. The elemental composition of wastewater coming from tanneries is generally determined by chemical digestion of samples followed by analysis using conventional analytical techniques such as Flame Atomic Absorption Spectroscopy (FAAS), Optical Emission Spectroscopy in Inductively Coupled Plasma (ICP-OES), or coupling of an ICP with Mass Spectrometer (ICP-MS). All these techniques require multi-step and time-consuming sample preparation that in turn increases the cost of analysis. Laser Induced Breakdown Spectroscopy (LIBS) is an emerging multi-element detection technique for a wide range of samples, requires very little sample preparation, and has the capability to simultaneously detect elements in a sample. This research study aims at a systematic development of a convenient analytical method for the determination of chromium and cadmium in tannery wastewater using LIBS. This was achieved by converting aqueous phase metal samples into solid phase using absorbent paper for petri. Optimization of LIBS parameters was carried out and demonstrated strong spectrum lines for each metal keeping the background noise at minimum level. The calibration curves exhibited linearity over many orders of magnitude with fairly high correlation coefficients, R^2 in the range of 0.992 to 0.998. The analysis of real tannery wastewater samples by the newly developed LIBS technique and a comparative study with FAAS showed similar results.

Chapter 1

INTRODUCTION

1.1. BACKGROUND

It is now an established fact that industrialization is the major cause of generation and release of toxic wastes which pollute our environment including water resources especially with heavy metals (Gondal and Hussain, 2007). Heavy metals can neither be degraded nor destroyed over longer periods of time and can enter human bodies via food, drinking water, and air. At higher concentrations they cause to poisoning and life-threatening diseases (Manahan, 1999). Development of new, convenient and rapid analytical methodologies for the quantification of such pollutants is therefore essential for their proper mitigation.

The number of tanneries has grown immensely in Pakistan, reflecting an increased economic growth and likewise the demand for leather. Leather industry, including leather products is one of the major industrial sectors in Pakistan that contributes substantially towards national economy in terms of foreign exchange (Din and Ghani, 2005).

Leather tanneries in Pakistan produce all three categories of waste: wastewater, solid waste and air emissions but toxic wastewater and solid waste pose significant environmental challenges (Iqbal, 1998; Nazir and Bareen, 2008). The wastewater generally contains high concentrations of organic matter, solids, sulfates, sulfides, chromium and cadmium, thus exhibit very high levels of chemical oxygen demand and biochemical oxygen demand (Haydar and Aziz, 2009). The contamination levels of chromium and cadmium in tannery wastewater are observed to be several hundred times higher as compared to the values recommended in the National Environmental

Quality Standards (NEQS) set by the Government of Pakistan (NEQS, 1997; CCP, 1999). In a study, the analysis of heavy metals using Atomic Absorption Spectrometer (AAS) has revealed that the metals like chromium, iron, manganese, copper, lead and cadmium exceeded the standard limits in effluents of textile and tannery industries (Alves *et al*., 1993). The measurement of exact concentrations of metals present in the tannery wastewater is extremely important to justify the kind of treatment method being applied for minimization of the pollution load (Alves *et al*., 1993).

Analysis of industrial wastewater for heavy metals is generally performed using conventional analytical techniques like Atomic Absorption Spectroscopy (AAS) and UV-Visible Spectrophotometry. Both these methods require time consuming sample preparation protocols (Tahir and Naseem, 2007; Rafique *et al*., 2010). The other conventional analytical techniques like Optical Emission Spectroscopy in Inductively Coupled Plasma (ICP-OES) and Inductively Coupled Plasma with Mass Spectrometry (ICP-MS) require chemical digestion of the wastewater samples prior to the analysis (Ludke *et al.,* 1994; Paudyn and Smith 1990). All these techniques require multi-step and time-consuming sample preparation that in turn increases the cost of analysis. The present study aims to establish an alternate instrumental methodology that uses the direct introduction and analysis of tannery wastewater (after solidification) without undergoing time consuming sample preparation steps. Laser Induced Breakdown Spectroscopy (LIBS) could be one such technique as it has been applied successfully in a number of studies for the determination of elemental concentrations of a wide range of samples (Michel, 2010).

The proposed research aims at developing rapid and robust analytical methodologies for the detection and quantification of elemental contaminants in environmental samples (water/wastewater and air) using LIBS system ‘Ocean Optics LIBS2500plus’

1.2. LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

1.2.1. An Introduction to LIBS

LIBS is an emerging multi-element analysis technique for a wide range of samples. It is a type of an atomic emission spectroscopy in which an intense pulse laser beam is focused onto the sample, resulting in the dissociation and partial ionization of the sample in a fast growing plasma cloud with temperatures up to 10,000–25,000K (Yalcin *et al.*, 1999; Blankenburg, 1989; Steven *et al.*, 2000; Russell *et al.*, 2005). At such high temperatures the sample dissociates into ionic and atomic plasma which emits characteristic atomic emission lines. The resulting emission can be collected and resolved both, spectrally and temporally, to yield spectra containing the atomic emission lines corresponding to the atoms present in the sample (Cremers and Radziemski, 2006). The instrument consists of three main parts – an ablation laser, focusing and collection optics and a detector. LIBS spectra also provide information about the concentration of the elements present in a sample (Tognoni, 2002).

1.2.2. Application to Liquid Samples

LIBS has been effectively applied in a number of studies to find out elemental concentrations of a wide range of samples (Radziemski, 2002). Rapid measurement of metal contents in liquid waste water samples is a challenging problem; and since LIBS is a sensitive technique, its application to these samples can be fruitful. It has been applied to the analysis of heavy metals in liquid samples; a new approach was developed in which liquid solutions were converted into solid pellets of calcium hydroxide by mixing with CaO replacing liquid sample analysis with solid matrix analysis (Diaz *et al*., 2006). The present study seeks to establish an alternate methodology for the solidification of wastewater samples for direct LIBS analysis without undergoing time consuming and expensive chemical digestion steps.

1.2.3. Advantages of LIBS

LIBS has many distinct advantages over other conventional analytical techniques (Miziolek, 2006) such as:

- simultaneous multi-element detection capability
- rapid or real time analysis
- ability to detect both metals and non-metals
- simplicity - little or no sample preparation
- good sensitivity for some elements like chlorine and fluorine that are difficult to monitor by conventional atomic emission spectroscopic methods
- robust plasma formation that is not possible for conventional plasma forming methods

Another important feature of LIBS is its suitability for remote and in-situ applications (Lee and Sneddon, 2002). A few field portable instruments have also been developed over the years in various research laboratories. LIBS technique is also being used for the radioactive elements samples efficiently better than other technique (Yueh *et al.,* 2000; Miziolek, 2006).

1.2.4. Quantitative Analysis

Like other analytical techniques, LIBS may also be used for the quantification of elements (particularly metals) in both solid and liquid samples. In this regard, several analytical methods have been reported to obtain quantitative information from LIBS measurements (Song *et al*., 2002). The most common and practical approach is to measure the LIBS intensities in relation to known calibration standards (Cremers and Radziemski, 2006; Tognoni, 2002).

1.3. OBJECTIVE

Currently, the analysis of environmentally significant heavy metals in wastewater samples is done by conventional analytical techniques. Such techniques require time-consuming, multi-step digestion of the samples (Neuhauser *et al.*, 1999).

The objective of the present study is to develop an analytical method for the rapid analysis of environmentally significant heavy metals present in tannery wastewater using Laser-Induced Breakdown Spectroscopy (LIBS) system.

The LIBS2500plus system present in IESE has the capability of analyzing solid samples only. This study seeks to establish a technique for the solidification of wastewater samples for direct LIBS analysis without undergoing time consuming and expensive sample preparation steps. Therefore, liquid phase samples and standards were converted into solid phase for subsequent analysis on LIBS.

The execution of the research is divided into six stages:

- Optimization of operating parameters of the LIBS system for the selected heavy metals
- Preparation of solid phase metal standards (of varying concentrations) on absorbent paper for quantitative analysis of the solidified samples
- Development of LIBS method for analysis of solidified metal standard
- Preparation of calibration curves
- Field sampling of tannery waste water samples followed by LIBS analysis using the developed method
- Comparison of the quantitative results obtained by the developed method with the quantitative results obtained by a conventional analytical technique, Flame Atomic Absorption Spectrophotometry (FAAS)

Chapter 2

LITERATURE REVIEW

2.1. WATER POLLUTION

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by human activities (Daniel, 2006).

Very few factories have end-point treatment facilities, most of which are not functional. As a consequent the effluent discharged from such factories is directly thrown into the water bodies causing a change in water pH, an increase in temperature, turbidity, and toxicity due to presence of heavy metals (Santiniketan *et al*., 1994).

The number of tanneries in Pakistan is causing severe environmental degradation as the untreated effluent used in the tanning process is released into nearby water reservoirs and the sea.

2.2. TANNERY WASTEWATER

Tanning industries in Pakistan are resulting in grave consequences for the environment due to the disposal of untreated effluent over land and in water bodies. In recent years, developing countries have seen an increase in leather production because of the shift over from the developed world as a result of more stringent environmental pollution control requirements and high labour costs. Leather export from Pakistan increased from US$ 672 million in 2002 to 1.13 billion in 2007, which indicates an increase of 68% in a short span of 5 years (EPB, 2007). The total estimated 725 tanneries in Karachi, Lahore, Multan, Kasur, Faisalabad, Peshawar, Gujranwala, and Sialkot; registered and non-registered, favor chrome tanning because of the rapid processing, low cost and better quality of the finished leather products (Hafeez *et al*., 2002).

Statistics provided by the Ministry of Industries and Production, suggest the production of 7.4 million hides and 36.2 million skins with an average annual growth of 2.9% and 1.47%, respectively in approximately 650 registered leather tanneries in the country including small, medium and large units. Various steps require huge amounts of water and chemicals for processing the skins, with 50-60 litres of water per kilogram of hide used commonly (Iqbal, 1998).

The primary pollutants that leather tanning in Pakistan creates include heavy metals (chromium, cadmium, etc.), various organic chemicals, and acids (Naqvi, 1995; Deepali *et al*., 2010). Tannery wastewater is also highly polluted in terms of COD and BOD, suspended solids, settleable solids, total nitrogen, conductivity, sulphate, sulphide and chromium (Iqbal, 1998).

The release of hazardous substances such as preservatives, azo dyes and Cr (VI), present in leather and leather products, is making the authorities and consumers concerned about regulation of the processing operations. Although only chromium compounds in the form of Cr (III) are used in the tanning process, presence of more hazardous Cr (VI) in finished leather product and effluent discharge necessitates that close monitoring be done. (Hauber, 1999).

2.2.1. Chromium and Cadmium in Tannery Wastewater

Most of tannery units discharge untreated effluent directly into recipient water bodies or onto open land. High amount of chromium is observed in the effluents discharged from chrome tanning process (Tahir and Naseem, 2007). Cadmium and chromium are amongst the heavy metals considered as the primary pollutants that leather tanning in Pakistan creates apart from various organic chemicals, and acids. The analysis of leather tannery effluents revealed that the discharges are contaminated with toxic metals and contained 0.30 mg/L of copper, 0.15 mg/L of cadmium, 7.0 mg/L of zinc, 1.14 mg/L of nickel, and 1.8 mg/L of lead (Sandhu, 1993).

The chrome tanning method using salts of chromium is extensively used compared to vegetable tanning methods using a combination of chrome and vegetable tanning (Tahir and Naseem, 2007). Traditionally 60 – 70% chrome applied in the form of Basic Chromium Sulphate (BCS) is absorbed by the hides and skins during processing, while the remaining is discharged as waste (Awan *et al*., 2003). In about 80% of the tanneries, the effluent is discharged directly into water bodies or over open land; the remaining 20% goes to municipal sewers that also drain into natural water bodies. The economical loss due to the drainage of unused chromium salts in the effluent, which is almost 25–30% of total chromium applied in the tanning process, is also very evident (Alves *et al*., 1993). Chromium is displaced from leathers during re-tanning and dyeing processes in the re-tanning system. This chrome initially soluble, changes into precipitates when mixed with waste from other processes especially in the presence of proteins; leading to sludge formation. Such highly resistant sludge alters the biological process in both surface waters and causes disruption in water treatment plants. If broken down, chromium hydroxide precipitates can persists in the ecosystem for an extended period of time causing damage to the food chain (Hauber, 1999).

Tannery wastewater is highly polluted with respect to chromium and its concentration is several times higher than the limit set by National Environmental Quality Standards (NEQS, 1997). The NEQS allow only 1.0 mg/L of chromium in tannery wastewater; whereas in actual the quantity is much higher in the real effluents. A study conducted by United Nations Industrial Development Organization under the Regional

Programme for pollution control in the tanning industry in South-East Asia, (1999) indicated Cr (VI), Cr (III) and cadmium as toxic chemicals in the tanning and dying process, harmful to the existing biota. Due to its carcinogenicity and mutagenicity, the United States Environment Protection Agency (USEPA) has designated chromium as a “Priority Pollutant” or “Class A” pollutant (Srinath *et al*., 2002; Lee and Jones, 1998). Two forms of chrome are associated with the tanning industry, Cr (III), less soluble or less toxic and Cr (VI), more soluble and highly toxic (Hauber, 1999; James, 2002). The uncontrolled discharge of untreated tannery wastewater causes many problems to tannery workers and the local communities. Various studies have shown tanneries to release Cr (VI) ranging from 40 – 25,000 mg/L of wastewater (Lee and Jones, 1998; Palmer and Puis, 1994; Benazir *et al*., 2010).

Metal compounds are non-biodegradable in nature; that can have long term environmental impacts. Due to their accumulative properties, and playing a vital role in the process of biomagnification, metals are a subject of close attention (Bosnic *et al*., 2000). Heavy metals such as chromium and cadmium are toxic even at low concentrations; a gradual buildup of these toxins in the human body may cause long term health damages (Islam *et al*., 2007). Analysis for metals, using Atomic Absorption Spectrometer (AAS), in Haridwar, India, showed that metals like chromium, iron, manganese, copper, lead and cadmium exceeded the standard limits in effluents of textile and tannery industries and associated soil samples. Here chromium contamination in groundwater samples was observed only in those taken in close proximity of the tannery. The findings also indicate that the chromium contamination was higher than the other metals (Deepali and Gangwar, 2010).

In order to determine the level of chromium in tannery wastewater, atomic absorption spectrophotometry is usually applied after boiling the known volume of sample with concentrated nitric acid for suitable dilution. For the analysis of high levels of chromium, iodine/thiosulphate titrations are sometimes used, however the technique becomes inappropriate at low chromium concentrations (Hauber, 1999).

2.3. ENVIRONMENTAL AND HEALTH IMPACTS OF CHROMIUM AND CADMIUM IN TANNERY WASTEWATER

Some metals in trace amounts are important for proper functioning of biological systems and their deficiency or excess could lead to a number of disorders (Ward, 1995). Through industrial effluents, however, heavy metals are released, untreated, on land as well as dumped into the surface water which have toxic properties even in small amounts, this eventually results in leaching and accumulation of toxic metallic components into ground water that leads to its contamination resulting in a series of well documented problems in living beings (Malarkodi *et. al*., 2007).

Heavy metals can be transported from one place to another and released in the water bodies' trough effluent discharge (AMAP, 1997). Accumulation of heavy metals in the body by inhalation or ingestion can be responsible for a wide range of health effects such as cancer, neurotoxicity, immunotoxicity and cardiotoxicity leading to increased morbidity or even mortality (Dockery *et al.,* 2001; Pope *et al.,* 1995; Silbergeld *et al.,* 1995; Silbergeld *et al.,* 1996). Metals like chromium can also damage cell membranes, alter enzyme specificity, disrupt cellular functions and damage the structure of DNA (Bruins *et al*., 2000). Incidents have been documented for the effects of chromium in the form of chrome ulcers, corrosive reaction on the nasal septum, acute irritative dermatitis and allergic eczematous dermatitis (Alves *et al*., 1993).

According to a report released by the Bangladesh Society for Environment and Human Development (SEHD), a large numbers of the people, working at, or residing near, tanneries suffer from gastrointestinal, dermatological and other diseases (hypertension and jaundice, etc.) that could be related to the chemical pollution released by the industry. Over 90% of these people die before the age of 50 compared to less than 60% for the country as a whole. Chromium is one of the most harmful chemicals found in the tannery waste because of its carcinogenic potential. Acidic effluents and gaseous emissions also add to severe respiratory problems (John, 2001).

Discharges in high volume even with low chromium concentrations can not only disrupt the food chain, but also inhibit photosynthesis by having toxic effect upon daphnia. Mainly coming from the chrome tanning process, chromium is harmful to the biota (Deepali, 2010). Dichromates that may form, can be absorbed through the gills and accumulate there, thus being toxic to aquatic life since these swiftly penetrate cell walls (Bosnic and Daniels, 2000).

Cadmium is considered highly toxic. It is accumulative and has a chronic effect on a wide range of organisms. It not only affects the biota (Srinath *et al.*, 2002; Lee and Jones, 1998) but if present in drinking water, it can induce brittleness of bones in humans (Hauber, 1999). Cadmium poisoning, on the other hand, can lead to problems in kidneys function to remove acids from the blood in proximal renal tubular dysfunction (Deepali, 2010). The average daily intake of cadmium should be less than 30μg/day; else 1% of the entire population may suffer from cadmium-induced tubular damage. Women with low iron stores are more susceptible as the percentage can be higher, up to 5%. Both human and animal studies reveal that osteoporosis (skeletal dysfunction) may be a critical effect of cadmium exposure (Järup *et al.*, 1998).

Apart from kidneys, cadmium accumulation has also been seen in eyes, and other tissues and organs of environmentally exposed individuals along with its association to diabetes, diabetic nephropathy, hypertension, peripheral artery disease (PAD), myocardial infarction, diminished lung function, periodontal disease, and age-related macular degeneration (AMD) with life prognosis (all-cause mortality) and excess cancer mortality for the lung, pancreas, breast, endometrium, prostate, and urinary bladder (Soisungwan *et al.*, 2010).

2.4. ANALYTICAL TECHNIQUE FOR WASTEWATER ANALYSIS

Analysis of industrial wastewater for heavy metals is generally performed using conventional analytical techniques like Atomic Absorption Spectroscopy (AAS) and UV-Visible Spectrophotometry. Both these methods require time consuming sample preparation protocols (Tahir and Naseem, 2007; Rafique *et al.*, 2010). The other conventional analytical techniques like Optical Emission Spectroscopy in Inductively Coupled Plasma (ICP-OES) and Inductively Coupled Plasma with Mass Spectrometry (ICP-MS) require chemical digestion of the wastewater samples prior to the analysis (Ludke *et al.,* 1994; Paudyn and Smith, 1990). The motivation for the present study was to adopt an alternative instrumental method that uses the direct introduction and analysis of samples without undergoing extensive sample preparation steps. LIBS was, therefore, looked as an option.

2.4.1. Laser Induced Breakdown Spectroscopy (LIBS)

LIBS is an emerging multi-element detection technique for a wide range of samples and is based on emission spectroscopy where atoms and ions are primarily formed in their excited states as a result of interaction between a highly focused laser beam and the sample (Sun *et al*., 2000). One of the important features of this technique is that it does not require elaborate sample preparation, unlike conventional spectroscopic analytical techniques. LIBS has, thus, rapidly developed into an important analytical technique with the capabilities of detecting most elements in the sample particularly for real-time analysis (Cremers and Radziemski, 2006).

LIBS operates by focusing the laser beam on to a very small area at the surface of the sample or analyte, which can be gas, liquid, aerosol or solid. When the laser is discharged it ablates a very small amount of material which instantaneously superheats generating a plasma plume. At such a high temperature the ablated material dissociates (breaks down) into excited ionic and atomic species. During this time the plasma emits radiations which do not contain any useful information about the species present, but in very less time, the plasma expands at supersonic velocities and cools, at this point the atomic emission lines of the elements can be observed (Miziolek *et al.*, 2006).

The laser ablation process begins with target evaporation just at the impact of the leading edge of the laser pulse on to the surface of the sample. The energy to produce a luminous plume depends on the target material, its morphology as well as the laser pulse wavelength, distance from the laser source and duration. The temporization of the spectroscopic system (t_d) is extremely important because of the rapid expansion of the plume (Capitelli *et al*., 2004).

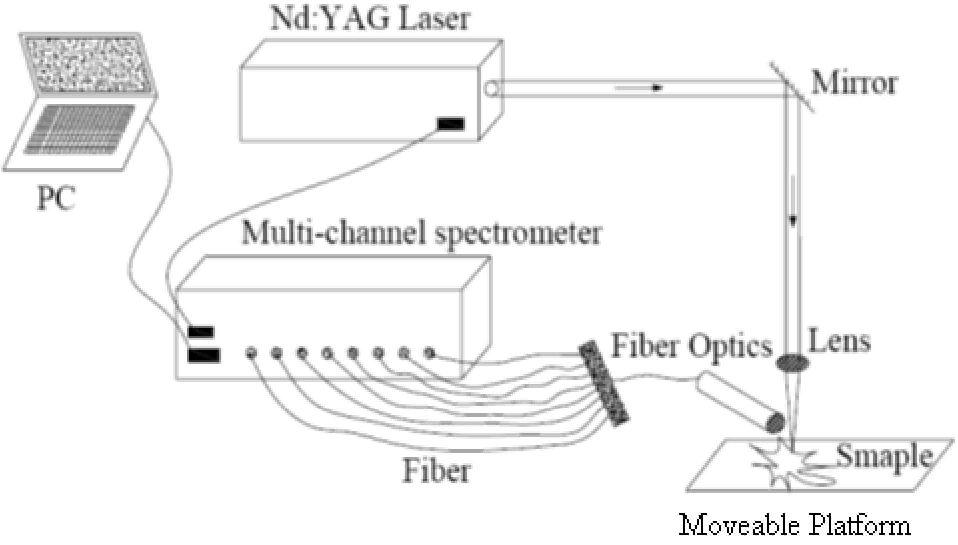


Figure 2.1: Schematic diagram of a LIBS system

The LIBS plasma exhibits a very intense continuum background that subsides rapidly with time to allow detection of elemental emission. Most LIBS methods utilize a timing system to delay emission integration until the continuum has decayed to a reasonable level. Plasma shielding and subsequently the intense continuum emission are greatly reduced by using lasers with femtoseconds or picoseconds pulse widths (Miziolek *et al*., 2006; Lazic *et al*., 2001; Yueh *et al*., 2000). Time resolution of the plasma light in LIBS allows for discrimination in favor of the region where the signals of interest predominate (Lee *et al*., 2000; Cremers and Radziemski, 2006: Capitelli *et al*., 2004).

The radiation of plasma is collected by lenses or fiber optics. The signal is sent to a spectrograph with a gated detector such as an intensified optical multichannel analyzer (OMA) or an intensified charge-coupled device (ICCD), a digital delay generator (delay time, t_d) is used to gate the detector. The detector remains off for a certain amount of time after receiving a trigger pulse from the laser, until a signal from the delay generator is received (t_d) (Cremers and Radziemski, 2006).

In practice, the wavelength of the emitted radiation is recorded and used as an identifying marker for each element. The relationship between wavelength (λ) and energy of a transition (*E*) is given in equation 2.1

$$E=hc/\lambda \tag{2.1}$$

where c is the speed of light and *h* is Plank's constant.

2.4.2 Qualitative and Quantitative Analysis Using LIBS

Analytical spectra are presented as intensity versus wavelength, refer Figure 2.2. Atomic and ionic transitions are unique to each element and identification is readily determined based on location of the emission peak in the spectrum. In addition, intensity of each emission line is also related to the concentration of the respective element in the sample and can be used for quantitative analysis (Tognoni *et al.*, 2002).

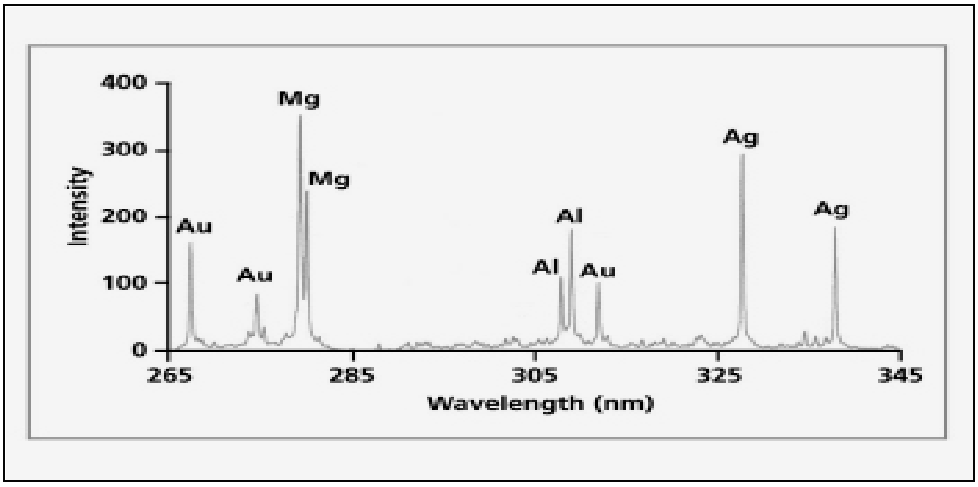


Figure 2.2: LIBS spectrum showing presence of Au, Mg, Al, and Ag in a sample

Like any analytical technique the goal of LIBS is to provide an accurate quantitative analysis, that is, to determine, with high degree of precision and accuracy, the concentration of a species in a sample. One of the possible approaches is to determine the concentration of each element independently, by working with elemental emission lines of accurately known transition probabilities and making absolute measurements of the integrated intensities. A second approach is to measure the integrated intensities of the elemental emission lines, relative to the line intensity of the specimen's most abundant element. In this case, only the ratios of the transition probabilities of the emission lines need to be known. Both of these methods rely upon a calibrated spectroscopic measurement system. Moreover, the quantitative data obtained reflects the composition of the laser-induced plasma, and not necessarily of the actual sample (Cremers and Radziemski, 2006).

The most common approach is to measure the LIBS intensities in relation to known calibration standards. (Gondal, *et al*., 2008). This approach is generally the most practical for extracting quantitative information on sample composition. As the laser material interaction is highly matrix dependent, therefore variations in the matrix between the unknown sample and the standard must be minimal (Cremers and Radziemski, 2006; Tognoni *et al* ., 2002).

Calibration has been an important issue since Cremers *et al*., (1984) first demonstrated the ability of LIBS for detection of atomic species from aerosol samples. For quantitative analysis, a calibration curve of instrument response (signal) versus absolute mass (gram, nanogram, etc.) or concentration (%, part per-million or ppm) of the element to be detected is usually prepared.

Ideally, there will be a linear relationship between the element response and the mass or concentration over the entire range investigated and a linear fit to the data. For more accurate results, each data point on the curve should be an average of various individual measurements (Tawfik and Saafan, 2006). This approximation can be considered satisfactory only if all parameters affecting the plasma characteristics (including the sample morphology and composition) are constant during calibration and measurement. Nonlinear behavior is sometimes observed at the lower and higher concentrations (Cremers and Radziemski, 2006; Capitelli *et al*., 2004).

The slope of the calibration curve at a certain concentration is termed as the sensitivity, and it is the change in signal for a given incremental change in the concentration (or mass). Figure 2.3 shows a typical calibration curve with a loss of sensitivity at high and low concentrations, on either side of the central linear region. The loss of sensitivity of the curve, at low concentrations may be due to (Cremers and Radziemski, 2006; Miziolek *et al*., 2006):

- Spectral interference of the analytical line with the concentration of the interfering species remaining constant as the analyte concentration decreases.
- Constant background concentration of the analyte being determined that is not included in the stated concentration of the analyte.
- Incorrect determination of the analyte signal so that a portion of the background signal is included in what is assumed to be only the analyte signal.

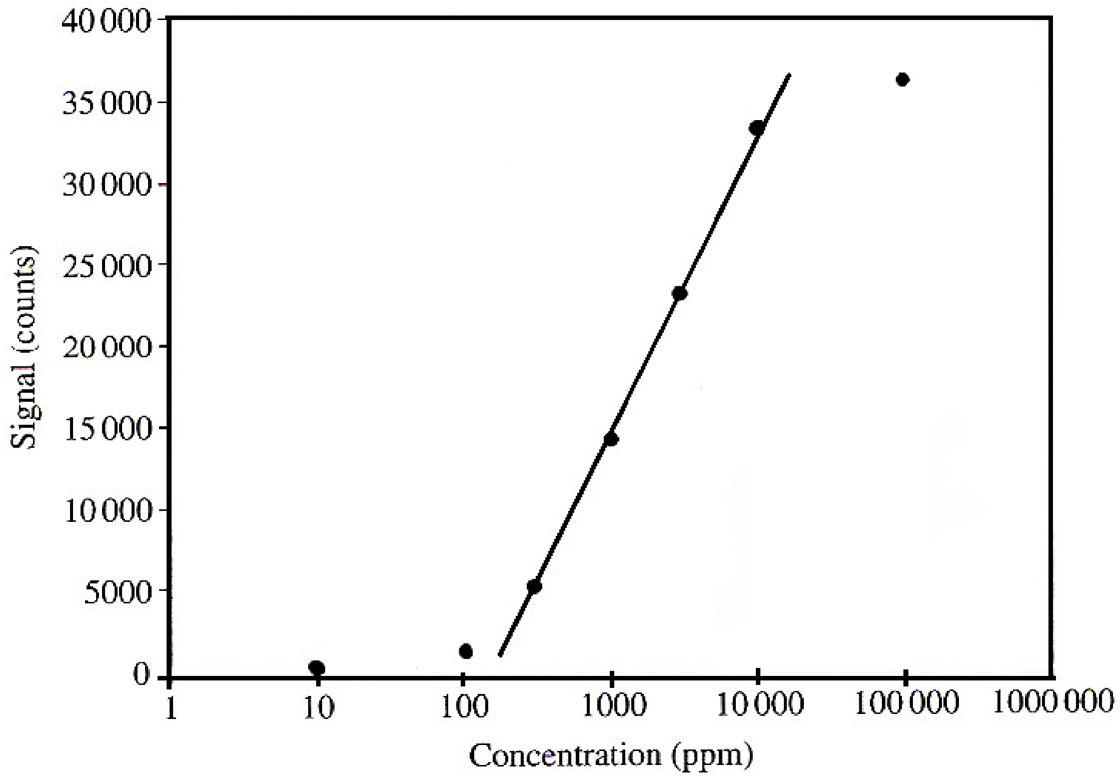


Figure 2.3: A typical calibration curve with a loss of sensitivity at high and low concentrations (Cremers and Radziemski, 2006)

The loss of sensitivity at high concentrations is most often due to 'self-absorption', typically observed for emission lines in which the lower level of the transition is the ground state or close to the ground state. Because transitions are element specific and quantized or of a specific wavelength, a given species has the highest probability of reabsorbing a photon emitted by a member of the same species.

Because of the high density of atoms in the microplasma and its high temperature and electron density gradients, the outer layer of the plasma will be populated by “cool” atoms, residing mostly in the ground state and the central core of the plasma will contain a higher density of excited atoms. As these atoms decay to the ground state, the emitted photons, corresponding to the resonance transitions will have a high probability of being absorbed by the cooler atoms in the outer layers, thereby reducing the observed intensity of the emission line. As the concentration of the atoms in the target sample increases, the number of “cooler” atoms in the outer layer increases and self-absorption becomes evident (Cremers and Radziemski, 2006). In order to evaluate and correct self-absorption, several methods are found in the literature (Moon *et al*., 2009; Amamou *et al*., 2002; Bulajic *et al*., 2002) and proper selection of the emission lines is the key to accurate results for LIBS analysis (De Giacomo, 2007; Gaudiuso *et al*., 2010).

2.4.3. Application of LIBS Technique

Metal analysis using LIBS significantly reduces the time and cost associated with the sample preparation and is therefore a useful technique for environmental monitoring and other related applications (Lee and Sneddon, 2002; Hussain *et al*., 2008). It is commonly used for the rapid elemental analysis of solid sample, however LIBS has also been reported as an important analytical tool for the detection of metals in water samples (Gondal *et al*., 2007; Nasr *et al*., 2011; Sergey *et al*., 1999). Still a lot of research work is required to make this technique conveniently applicable to a variety of samples.

LIBS is overcoming the well-known difficulties and drawbacks of the analysis of liquid samples. In a study, water analysis was carried by converting liquid phase samples to solid matrix prior to analysis that detected chromium, lead, cadmium and zinc (Diaz *et al*., 2006).

Lin *et al*., 2009 studied wastewater containing heavy metals such as arsenic from industrial smelting process. The established setup used Nd : YAG laser beam to produce plasma on the focused sample, detected by an intensified charge-coupled device (ICCD) to achieve spectral lines of the element; calibration curves were then used for the quantitative analysis of arsenic with an unknown concentration in the industrial wastewater.

Bakry (2007), determined elements present in steel waste samples using LIBS. The study carried out in steel manufacturing plant identified the presence of iron, aluminum, magnesium, calcium, sodium, manganese, phosphorus, sulfur, and titanium accurately. Standard deviation of 2-3 % was obtained by rigorous intensity calibration procedure.

Gondal and Hussain (2006) developed a method using LIBS to determine toxic metals in wastewater collected from a paint manufacturing plant. The analysis depicted quantification of lead, copper, chromium, calcium, sulphur, magnesium, zinc, titanium, strontium, nickel, silicone, iron, aluminum, barium, sodium, potassium and zirconium in paint wastewater. Parametric dependence study of the LIBS system was done to assess the optimal experimental conditions for improving the sensitivity. Comparative analysis with of the relative accuracy of the LIBS system for various elements was done with ICP technique.

Gondal *et al.,* 2008 studied in detail the dependence of the parameters on LIBS for the detection of trace metals. LIBS parameters like distance between the plasma and optical fiber, sample rotation speed, laser pulse energy, gate delay, and position of the focal spot on the pellets were optimized. The limits of detection under optimized LIBS parameters were calculated for calcium, iron, magnesium, copper, zinc, sodium, nickel, and molybdenum at the ppm level.

Nasr *et al*., 2011 detected highly toxic contaminants like chromium, arsenic and lead in chrome-tanning process of animal skin to produce leather by applying locally developed LIBS and found the maximum concentrations of chromium, lead, arsenic, sulfur and magnesium. The limit of detection (LOD) for chromium, lead, arsenic, sulfur, and magnesium was also calculated.

MATERIALS AND METHODS

This chapter describes the systematic development of a new method for the analysis of two environmental of significant heavy metals (chromium and cadmium) in tannery wastewater samples using LIBS.

3.1. MATERIALS

3.1.1. Chemicals

In the LIBS optimization study the metal standards were prepared using the selected metal salts, chromium chloride and cadmium nitrate (99%); nitric acid for the preservation of wastewater samples was also used. All chemicals were from Merck (Germany).

ALBET (Germany) absorbent papers for petri (size 47mm) were used for solidification of liquid standards and tannery wastewater samples. 500 mL polyethylene bottles were used for sample collection and transportation of tannery wastewater.

3.1.2. Equipment

For characterization of metals in tannery wastewater

Laser Induced Breakdown Spectrometer; Ocean Optics LIBS2500plus, USA

Atomic Absorption Spectrometer; Varian AA 240, USA

3.2. EXPERIMENTAL SETUP: LASER INDUCED BREAKDOWN SPECTROMETER

The main components of the LIBS system used for the elemental analysis of metal standards and samples depicted in Figure 3.1 are as follows:

- Ocean Optics LIBS 2500plus spectrometer with seven spectrometer channels and USB-compatible Windows PC
- A sample chamber (ablation chamber)
- A Q-switched Nd:YAG laser (Big Sky Laser CFR 200)
- OOILIBS software

Figure 3.1. LIBS system used in this study

The Ocean Optics LIBS2500 plus Laser-induced Breakdown Spectrometer is a detection system that permits real-time, qualitative measurements of trace elements. This high-resolution instrument allows for spectral analysis from 200-980 nm, with a resolution of up to ~0.1 nm (FWHM). Q-switched Nd:YAG laser operates at 1064 nm wavelength and delivers maximum pulse energy of 200 mJ with a pulse width of 10 ns and runs at a 10 Hz pulse repetition rate. A high-intensity, 10 nanosecond long laser pulse beam is focused on the sample area. When the laser is fired, the high temperature of the laser ablates the surface of the sample and creates a plasma. As the plasma decays or cools the excited atoms in the plasma emit light of the characteristic wavelengths of the elements present. Fused-silica optical fiber is used to collect the emission light from the plasma plume at 45º angle to the incident laser radiation and feeds it to an optical detection system. The LIBS 2500plus has seven spectrometer modules to provide high resolution (FWHM 0.1 nm) with a gated charge-coupled detector (CCD) having 14,336 pixels for simultaneous recording of the spectrum in the 200-980 nm wavelength region. All detectors acquire data simultaneously. OOILIBS software has spectral-saving and data-logging capabilities; it displays and identifies the emission spectrum. Figures 3.3-3.5 exhibit the power supply to LIBS, Laser head along with sample chamber and LIBS 2500pluse spectrometer respectively.

Figure 3.2. Power supply for the LIBS laser

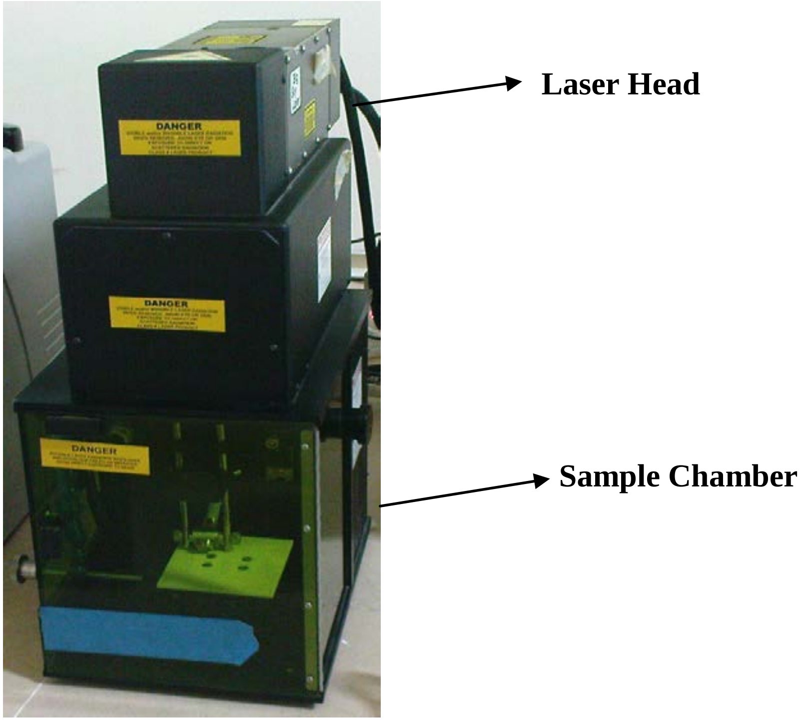


Figure 3.3. Laser head and the sample chamber

Figure 3.4. Ocean Optics LIBS 2500plus spectrometer

Specification of the LIBS 2500plus spectrometer used in the study are presented in Table 3.1:

Specification	Value
Spectrometer	200-980 nm
Resolution	0.1 nm full-width at half-maximum (FWHM)
Detection	CCD with a combined 14,336 pixels
Frame rate	Up to 100 Hz capability, computer-controlled
Integration time	2.1 ms; variable in the free-run mode
Trigger delay	-121 µs to +135 µs in 500 ns steps, computer-controlled
Computer	USB 1.1 (in all computers)
Software	OOILIBS software
Power	5 volts at < 1 amp, power supply included
Input optical	2-meter, multimode sampling probe with connector and collimating

Table 3.1: Specification of LIBS 2500plus Spectrometer

3.3. METHOD DEVELOPMENT

Four studies (1-4) were undertaken to develop and optimize the analytical technique for the determination of selected heavy metals.

3.3.1. Preliminary Characterization of Metals using LIBS (Study-1)

Metal spectra for the entire study were obtained by setting the instrumental parameters as energy at 89.5 mJ, lens distance from the sample at 75 mm and delay time of 5µs.

Since the study aimed at using the above mentioned instrument for liquid samples, the first step was to solidify the liquid samples to be run on LIBS. Metal standards of varying concentrations were prepared in methanol which was found to be most suitable as it is volatile in nature, dries quickly and dissolves the metal salts rapidly.

3.3.1.a. Solidification of the Liquid Samples for Tannery Wastewater

Solidification of liquid chromium and cadmium standards was achieved by introducing a small amount of liquid standard on absorption paper followed by ambient drying. The absorption papers are made of pure cellulose and have an open pore structure for a high degree of liquid absorption in homogenous fashion (uniform spread). In the present study, the absorption papers were used to uniformly distribute or spread the liquid standards and samples to obtain solidified surface for LIBS analysis.

Chromium and cadmium standards were prepared by dissolving 1g of respective metal salts in 1 mL of pure methanol in a clean test tube. 500 µL (0.5 mL) of the solution was poured on a piece (one quarter) of the absorption paper. The paper was dried at ambient temperature for subsequent analysis on LIBS (Figure 3.6). For the formation of calibration curves, chromium and cadmium standards were prepared using the above mentioned procedure.

Figure 3.5. One quarter of the absorbent paper with chromium standard

Given below is the solidification protocol on absorbent paper:

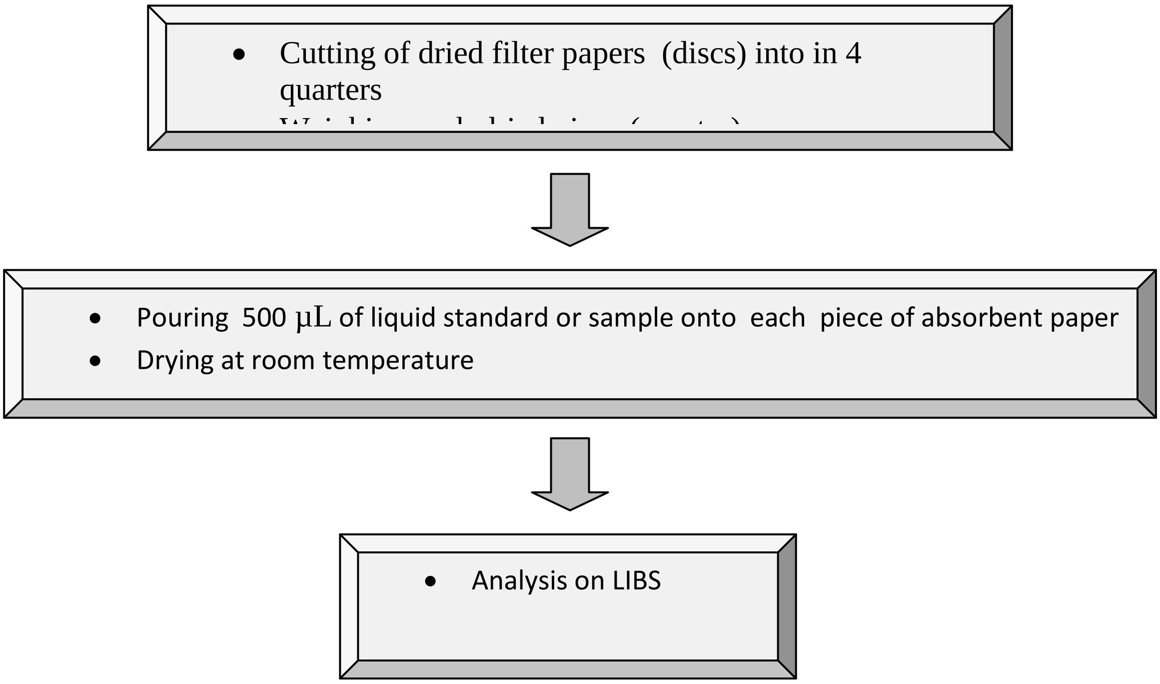


Figure 3.6. Solidification protocol on absorbent papers

The developed solidification method is much simpler (single step/direct) as compared to the reported technique involving calcium oxide for liquid-to-solid matrix conversion (Pace, *et al.*, 2006).

3.3.2. Optimization of LIBS Parameters (Study-2)

The LIBS system was optimized for four parameters: CCD delay time; laser pulse energy; distance of light collection system (fiber optic) to sample surface and lens to surface distance in order to obtain strong spectrum lines for each metal, keeping the background noise at a minimum level. The optimization was carried out using the solidified metal standards. Chromium and cadmium calibration standards were analyzed (in replicate) by LIBS, under optimized instrumental parameters.

The corresponding instrumental settings (parameters) used during optimization studies are summarized in Table 3.2.

Optimization Parameters	Ranges
Studied Wavelength	200 to 900nm
Lens to Sample distance	55 - 90 mm
Laser Pulse Energy	10 to 230 mJ
Delay time	0 to 10µs
Light Collection System to Surface distance	4-8 mm

Table 3.2. LIBS settings (parameters with their respective ranges)

3.3.3. Preparation of Calibration Curves (Study-3)

Since the concentrations of chromium and cadmium are generally very high in tannery wastewater, the calibration curves were constructed in high concentration ranges (Table 3.3). Standards were prepared using calculated amount of the metal salt stock solutions and then diluted to the desired concentration levels. The dilutions were made in clean test tubes and 500 µL of each standard was spread on to one quarter of the absorbent paper using a micropipette. All standards were analyzed (20 replicates each) by LIBS under optimized parameters.

Metals	Concentration (mg/L)						
Chromium	250	490	730	980	1450	1950	2400
Cadmium	50	90	180	270	450	900	-

Table 3.3 Concentrations of standards for calibration curves for wastewater

3.3.4. Field Sampling (Study-4)

Five waste water samples were collected from tanneries from different locations in Lahore and Sambrial regions. The samples were collected in 500 mL polyethylene bottles, first cleaned with metal free nonionic detergent and washed with tap water, acidified using HNO_3 and then rinsed thrice with de-ionized water (Rosin, 1967). Two samples were collected directly from tanning drums and the remaining three from the main drains in polyethylene bottles and acidified with HNO_3 till the pH dropped below 2.

SAMPLE ID	**LOCATION**
Sample-1	Dilawar Hussain Tannery, Wazirabad Road, Sambrial
Sample-2	**Humayun Tanneries, Mundair Khurd, Sambrial**
Sample-3	**Naz Tannery, Wazirabad Road, Sambrial**
Sample-4	Bashir Tanneries, G. T. Road, Lahore
Sample-5	Haji Tanneries, Sheikhupura Road, Lahore

Table 3.4. Sampling sites for tannery wastewater samples

The samples were brought to the laboratory in ice box. 100 ml of each sample was filtered using Whatman filter papers. 500µL from each was poured onto one-quarter of the absorbent papers, dried at ambient temperature and analyzed for the metal contents by LIBS under optimized parameters.

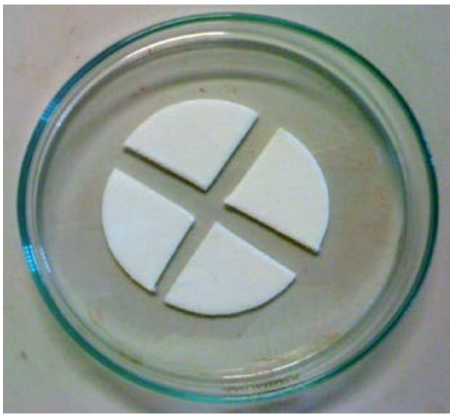


Figure 3.7. Absorbent Paper cut in quarters to be used for LIBS analysis

3.4. SAMPLE ANALYSIS BY FLAME ATOMIC ABSORPTION SPECTROSCOPY (FAAS)

Flame Atomic Absorption Spectroscopy (FAAS) is a standard analytical technique that is effectively used for quantitative analysis of metals present in environmental samples. The metal (chromium and cadmium) contents of the selected samples were determined by FAAS in order to compare the results with those obtained by LIBS.

FAAS calibration curves were prepared using five chromium and cadmium standards of different concentrations. Calibration curves for chromium and cadmium were constructed over the concentration ranges 10-80 mg/L and 1-8 mg/L respectively using the standards. The samples were then run on FAAS to determine the chromium and cadmium concentrations. As the field samples contained very high concentrations of the selected metals, dilutions were thus made to achieve a detectable range for FAAS to analyze the samples. The respective 100 mL dilutions in deionized water were stored in polyethylene bottles and were analyzed on FAAS and the concentration of both the metals were determined using the calibration curves.

Chapter 4

RESULTS AND DISCUSSION

4.1. ANALYSIS OF METAL STANDARDS BY LIBS (STUDY-1)

LIBS measurement is based on the analysis of the plasma spectrum which contains information about the elements in the sample. This information is in the form of emission lines, located at specific wavelengths. In Study – 1, the laboratory prepared standards (on filter discs) were analyzed in order to select spectral lines of maximum emissivity for each heavy metal. LIBS analysis gives information about the elements present in the sample in the form of emission lines located at specific wavelengths (Cremers and Radziemski, 2006). The spectral lines that exhibited significant "signal-to-background ratio" (SBR) were selected for identification of metals.

The solidified metal standards (on absorbent paper) were used to select spectral lines of maximum emissivity for chromium and cadmium. Figure 4.1 shows LIBS spectra with prominent emission lines at the wavelength of 427.481nm for chromium and 226.502nm cadmium respectively. The spectra were obtained by setting LIBS parameters at laser energy: 146.7 mJ for chromium and 89.5 mJ for cadmium; lens distance (from the sample surface): 75 mm; delay time: 4.5µs and light collection system (fiber optic) to sample surface distance: 7mm. The emission line for each metal was confirmed using National Institute of Standards and Technology (NIST) electronic database (NIST, 2010). The spectral data was recorded in terms of 'signal-to-background ratio (SBR)' in order to reduce the effect of background noise due to matrix effect, as illustrated in Table.4.1. The analysis of the solidified metal standard at different locations exhibited precise SBR values (RSD< 2%) which confirmed the uniform distribution of the metal on the absorbent paper (Figure 4.2).

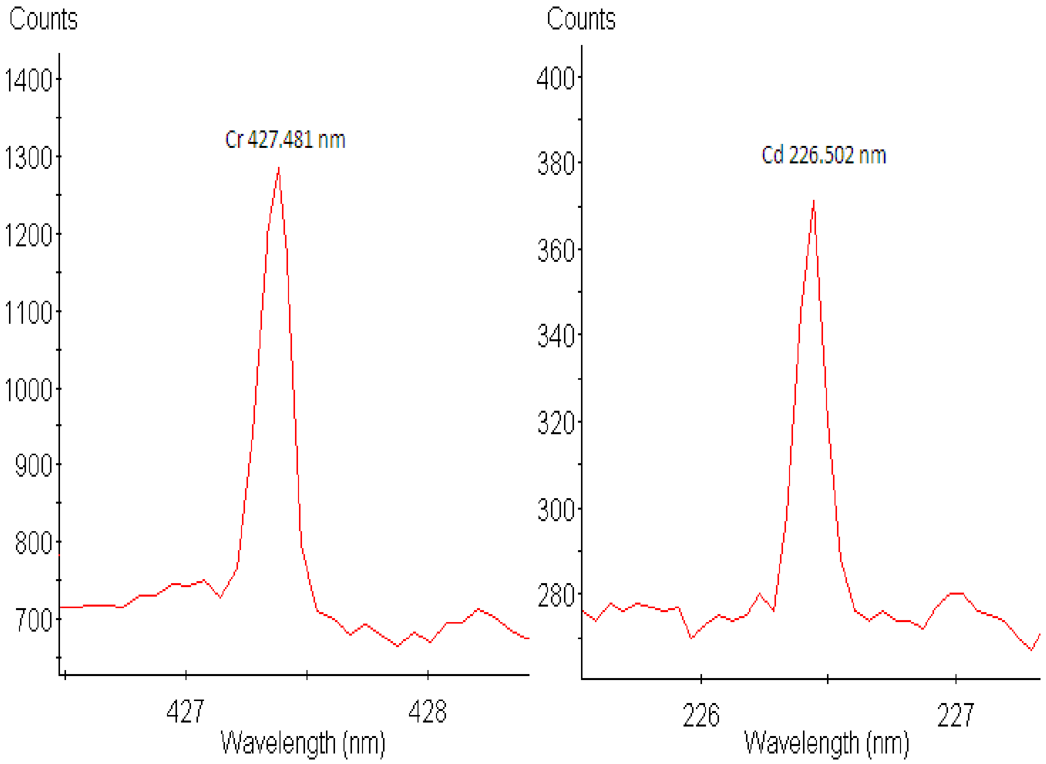


Figure 4.1. LIBS spectra of Chromium and Cadmium standards showing emission lines at 427.481 nm and 226.502 nm respectively

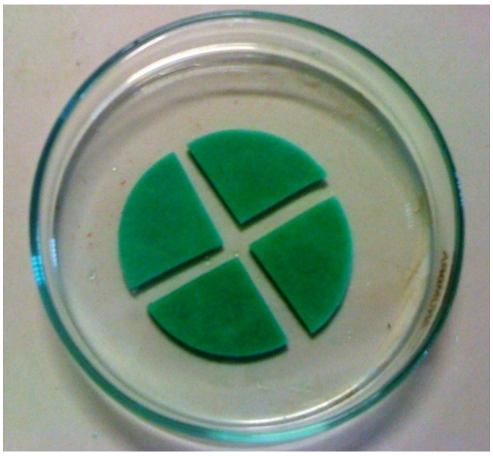


Figure 4.2. Pieces of absorbent paper showing homogenous spread of chromium standard

4.2. OPTIMIZATION OF EXPERIMENTAL PARAMETERS (STUDY-2)

LIBS like other analytical atomic emission techniques, requires proper calibration for the generation of uniform and authentic quantitative results. This requires proper optimization of the important parameters which can influence the sensitivity of LIBS system and they include (Bakry, 2007):

- Charge-coupled detector (CCD) delay time
- Laser pulse energy
- Lens to surface distance and
- Light collection system (fiber optic) to sample surface distance

All these parameters were optimized to achieve the best limit of detection using our system prior to its applications for the analysis of tannery waste water samples.

4.2.1. Charge Coupled Detector (CCD) Delay Time

Delay time is the time between the firing of the laser pulse and the opening of the camera shutter. Detection limits for individual elements is dependent on the delay time. Measurements were, therefore, carried out to find the optimum delay time; the time between the firing of the laser pulse and the opening of the camera shutter to collect the emissions from the sample surface (Cremers, and Radziemski, 2006); controlled by a Q-switch trigger pulse to the laser and the trigger pulse to the gate of the CCD.

A series of measurements, on chromium and cadmium standards were carried out to determine the optimum delay time for maximum LIBS signal intensities (in terms of SBR). Figure-4.3 shows signal intensity versus delay time trend for chromium and cadmium standards at 427.481 nm and 226.502 nm respectively. The intensity of the emission line increased with time and attained a value at 4.5 μs (Figure 4.2) which agreed with the reported value (Gondal *et al*., 2006). Beyond 4.5 μs, the intensity of emission line decreased probably due to cooling down of the plasma. Hence, a delay time of 4.5 μs was selected for the subsequent analysis.

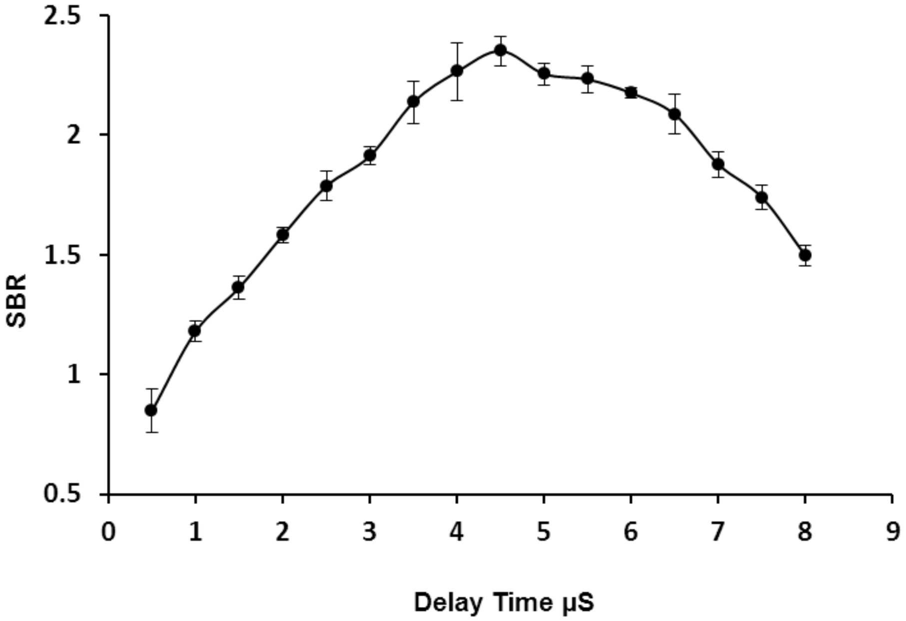


Figure 4.3. Signal intensity (SBR) versus delay time for Cr standard at 427.481nm

4.2.2. Laser Pulse Energy

The laser source of a LIBS system vaporizes, atomizes and excites the sample material and the light emitted from plasma is spectrally resolved and analyzed for the identification and concentration of the trace elements present in the sample (Song *et al.*, 2002). In the present study, signal intensities were examined as a function of laser pulse energies in the range of 10 to 230 mJ in order to determine the optimum pulse energy at CCD delay time of 4.5 μs and lens to surface distance of 75 mm.

Figure 4.4 shows the signal intensity in terms of SBR versus laser pulse energy for both the metal standards. LIBS signals increased proportionally to the laser pulse energy till the plasma density became too high where the phenomenon of self absorption starts by the metals (Gondal *et al*., 2008). The dense plasma formed by leading laser pulse starts absorbing energy from the later part of the laser pulse which leads to higher continuum emission and lowers the analyte signal (Alsulmi, 2008). A reasonable line intensity and precision was obtained at 146.7 mJ for chromium and 89.5 mJ for cadmium. Hence, these values of laser pulse energies were selected for subsequent analysis.

The LIBS signal exhibited linear dependence on the laser energy with least square fit having R^2 = 0.99. At higher laser energies (>150 mJ), the rate of increase becomes slower and saturation sets in.

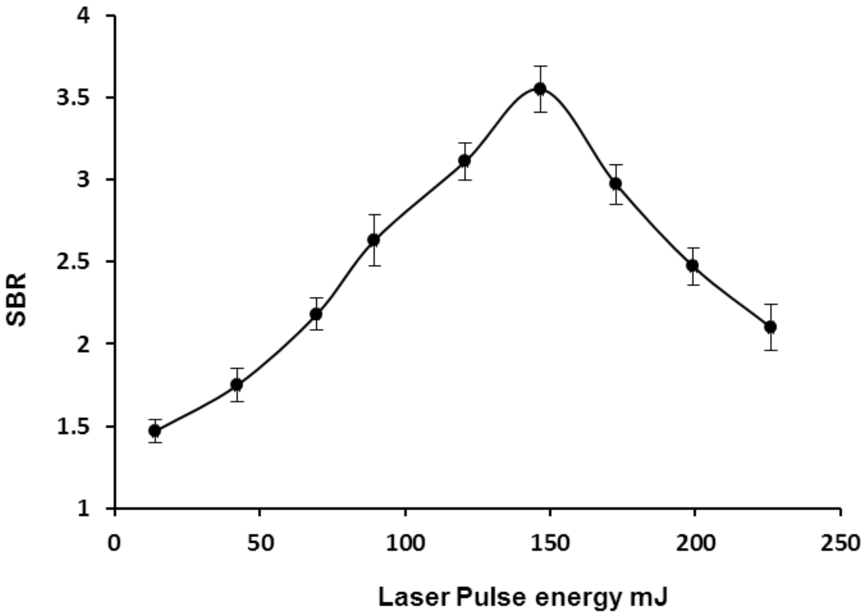


Figure 4.4. Signal intensity of Cr (427.481 nm) vs. laser energy (mJ)

4.2.3. Lens to Surface Distance (LTSD)

Analytical measurements by a LIBS system may vary greatly by changing distance between the focusing lens and the sample surface (Multari *et al.*, 1996). The intensity of the analyte emission line/s, can vary even with a slight change in the LTSD. Therefore, it is important to find out optimized value of LTSD where analyte signal intestines are maximum. Keeping the value fixed is an important factor governing precision and accuracy.

Figure 4.5. shows LIBS signal intensity (SBR) versus LTSD trend for Chromium and Cadmium standards at 427.481 nm and 226.502 nm respectively. The highest maximum signal intensity (SBR) was obtained at 75 mm of LTSD and was thus selected for subsequent analysis.

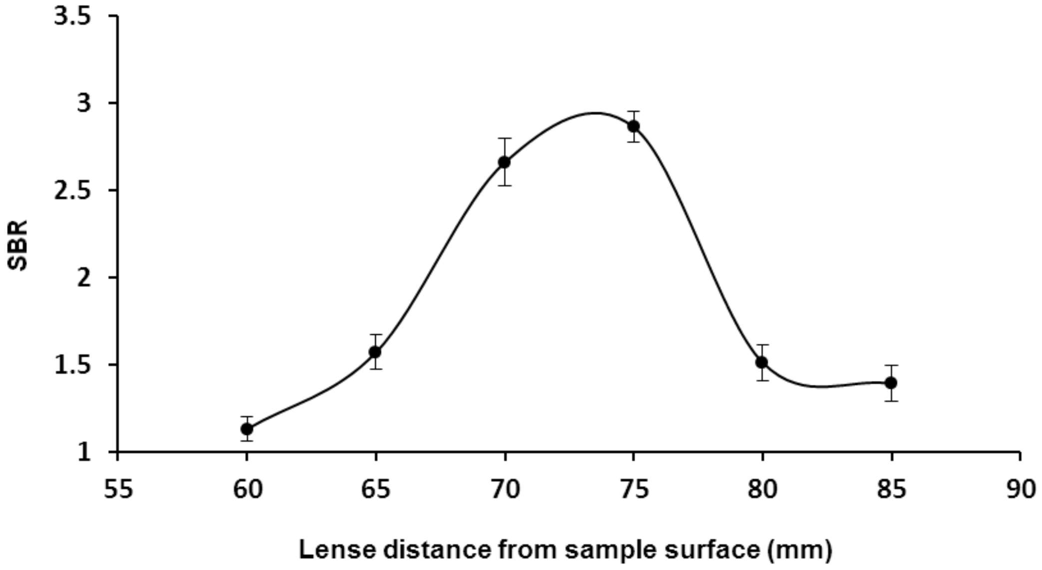


Figure 4.5. Effect of focusing lens distance on LIBS signal intensity (SBR)

4.2.4. Light Collection System (Fiber Optic) to Sample Surface Distance

Distance of light collection system (fiber optic) from sample surface was also optimized to ensure the appropriate collection of emission lines from the sample plasma because a change in the distance between the fiber and the plasma (sample surface) might affect the LIBS signal intensity. The optical fiber is pointed at angle 45° relative to sample surface. Figure 4.6 shows signal intensity (SBR) versus the distance from sample surface to fiber optic for both metal standards. The optimized value was found to be 7 mm for both metals.

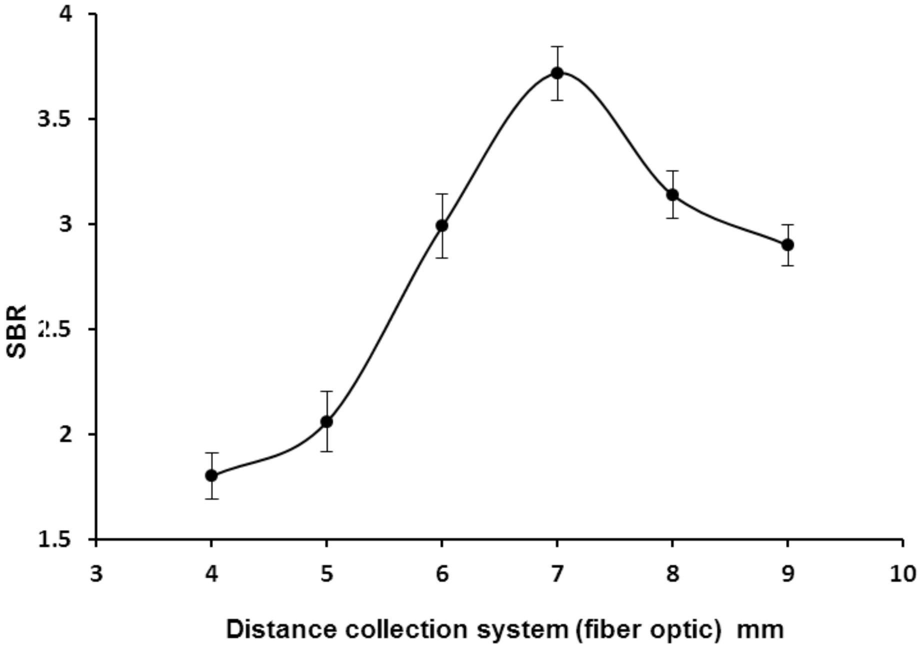


Figure 4.6: Effect of collection system (fiber optic) distance on LIBS signal intensity (SBR)

4.3. CALIBRATION CURVES (STUDY-3)

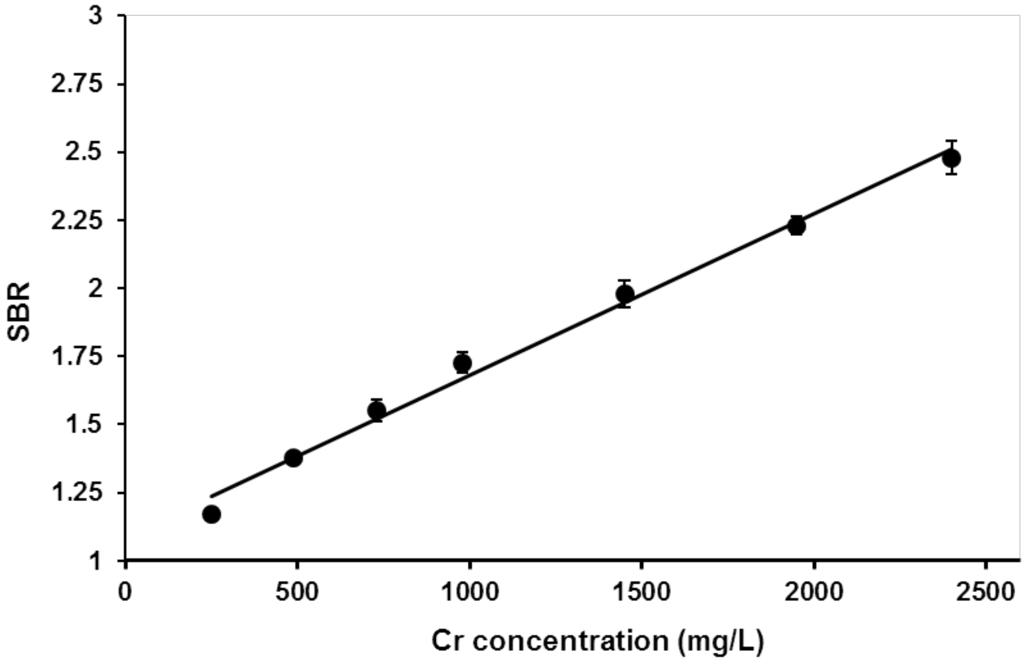
Conducting a calibration study before quantitative analysis is a pre requisite for any analytical technique including LIBS. A calibration curve is developed using a certain set of standards having a close composition to the unknown sample. The signal intensity of an atomic line of any element is proportional to the amount of the elements present in the sample. The use of clear and powerful lines is necessary in order to achieve the lowest detection limits while analyzing environmental samples (Díaz *et al*., 2006).

Calibration curves were obtained from chromium and cadmium standards ranging from 250 mg/L to 2400 mg/L at the wavelength of 427.481 nm (Cr), and from 50 mg/L to 900 mg/L at the wavelength of 226.502 nm (Cd) respectively. Each standard reading was taken as an average of ten shots (Figure 4.7). This reduces the background noise to a minimal when compared to a single shot. Precision is actually the measure of the degree of reproducibility of a measured data (signal intensities). The precision among the values of each calibration data point (replicate SBR) was calculated with the help of 95% confidence intervals (95% CI) using equation 4.1 (Christian, 2004); also denoted by the error bars in figure-4.7.

$$Confidence \quad \lim it = \bar{x} \pm \frac{ts}{\sqrt{N}} \qquad 4.1$$

Where $\bar{x}$ is the mean of 6 replicate signal intensities, N is number of measurements (6) and s is standard deviation for 5 degree of freedom & 95% CI t = 2.571.

A linear regression approach was used to fit the appropriate trend-lines to LIBS data obtained. All calibration curves demonstrated good linearity with correlation coefficients, R^2 of 0.992 for Cr and 0.997 for Cd respectively.


SBR
3
2.75
2.5
2.25
2
1.75
1.5
1.25
1
0
500
1000
1500
2000
2500
Cr concentration (mg/L)

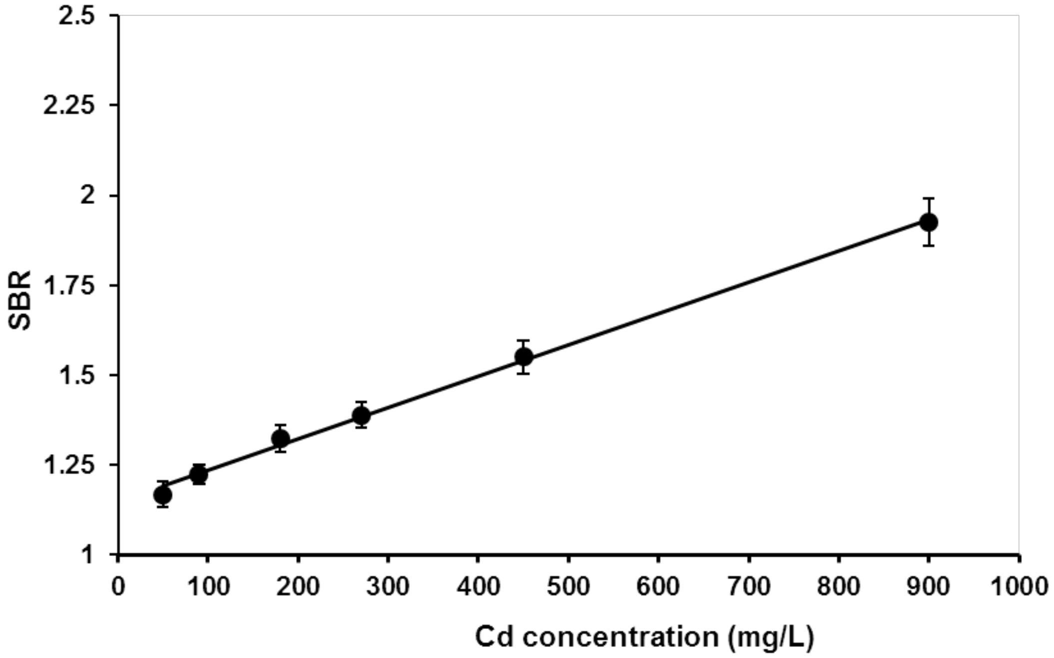

SBR
2.5
2.25
2
1.75
1.5
1.25
1
0
100
200
300
400
500
600
700
800
900
1000
Cd concentration (mg/L)

Figure 4.7. Calibration curve; concentration vs. signal intensity (SBR) for Cr (427.481 nm) and Cd (226.502 nm). Error bars denote the 95% CI and are based on replicate (10) measurements.

4.3.1. Limit of Detection (LOD)

The calculation of the Limit of Detection (LOD) is an important part of any calibration study. LOD is the lowest concentration that can be detected by an analytical method. In this study the LODs of two metals were determined by using the calibration data; *y*-intercept and standard deviation of the regression, (Miller and Miller, 2000), see equation below.

$$y_{LOD} = y_{\text{intercept}} + 3\left[\frac{\sum(y_i - \bar{y}_i)}{n-2}\right]^{\frac{1}{2}}$$

Where $(y_i - \bar{y}_i)$ is linear regression y-residual and *n* is the number of calibration data points. The calibration curve equations were then used to convert the signal y_{LOD} to LODs in concentration units. The values of LOD for Chromium and Cadmium were 230 mg/L and 46 mg/L respectively and are comparable with reported values (Cremers and Radziemski, 2006).

Elements	**Wavelength**	**Calibration**	**R²**	**Calculated LOD**
Chromium	427.481	y = 0.0006x +	0.992	230
Cadmium	226.502	y = 0.0009x +	0.997	46

Table 4.1. LOD determined for each metal

Though the LODs determined by the developed method look high but still these are appropriate for the analysis of thick industrial effluents**.**

4.4. FIELD SAMPLING (STUDY-4)

4.4.1. Tannery wastewater analysis

The tannery wastewater samples were collected from the areas containing a bulk of tannery industries in Lahore and Sambrial regions (Table 3.4). The calibration equations obtained by the LIBS developed method were used to estimate the levels of chromium and cadmium in tannery wastewater samples. For quantification purposes, average spectra of 10 laser shots were recorded for each metal present in the sample under optimized LIBS parameters, in order to reduce background noise to the minimal. The experimental conditions were identical to those used in calibration study and were kept constant throughout the procedure. Laser pulse energy was fixed at 146.7 mJ for chromium and 89.5 mJ for cadmium, whereas delay time between laser trigger and the opening of shutter of CCD detector, lens to surface distance and light collection system to sample distance were maintained at 4.5μs, 75mm, and 7mm respectively.

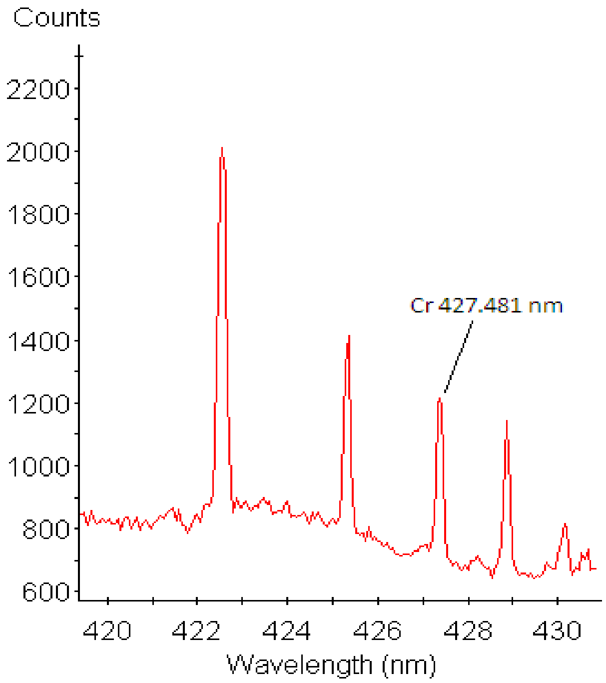
The metals concentrations were determined in units of mg/L in order to have a comparative analysis with atomic absorption spectrophotometry. The calibration curves obtained were then used to estimate the concentrations of selected heavy metals in the samples.

4.4.1.a. Chromium

As shown in Table 4.2 the concentration of chromium in Samples 1 and 2 was above 2000 mg/L because these two samples were collected directly from the tanning drums during the tanning process. The concentration of chromium in other three samples was comparatively low due to dilution of the tanning wastewater in the main and side drains. The levels of chromium observed using the developed LIBS method were found to be comparable with the reported concentration levels; 1003-1619 mg/L for the chrome tanning effluent (Tahir and Naseem, 2007).

4.4.1.b. Cadmium

The concentration of cadmium in all samples (except Sample-4) was around 500 mg/L. The probable reason of somewhat uniform levels of cadmium in all samples might be the addition of effluents from leather dying sections into the same main and side drains. Such effluents carry cadmium containing dyes and pigments hence its level remains high in all the samples.



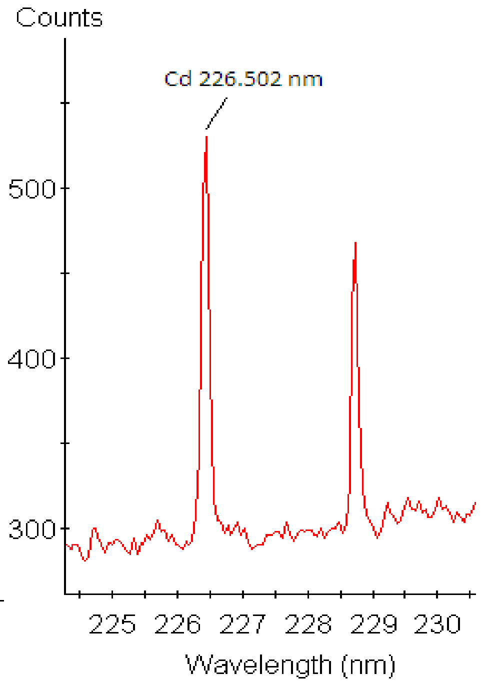


Figure 4.8. LIBS spectra showing Chromium and Cadmium lines in Sialkot tannery wastewater sample

4.5. COMPARATIVE ANALYSIS: ATOMIC ABSORPTION SPECTROSCOPY (AAS)

In order to authenticate the above results for LIBS, a comparative study was carried out using the conventional analytical technique of flame atomic absorption spectroscopy (FAAS). Table 4.2 gives a comparison of the quantitative analysis made both by the developed LIBS method and FAAS.

Sample	Cr ppm ± SD		Cd ppm ± SD	
	LIBS	FAAS	LIBS	FAAS
S-1	2192 ± 37	2245 ± 1.1	519 ± 15	533 ± 0.5
S-2	2225 ± 29	2269 ± 1.4	563 ± 17	575 ± 0.3
S-3	495 ± 13	459 ± 0.4	590 ± 12	530 ± 0.2
S-4	249 ± 7	278 ± 0.2	867 ± 13	832 ± 0.4
S-5	331 ± 9	304 ± 0.4	591 ± 7	570 ± 0.3

Table 4.2. Comparison of Chromium and Cadmium concentrations determined both by LIBS and FAAS in selected Tannery wastewater samples

Figure 4.9.a and b exhibit the FAAS calibration curves for chromium and cadmium used in this study.

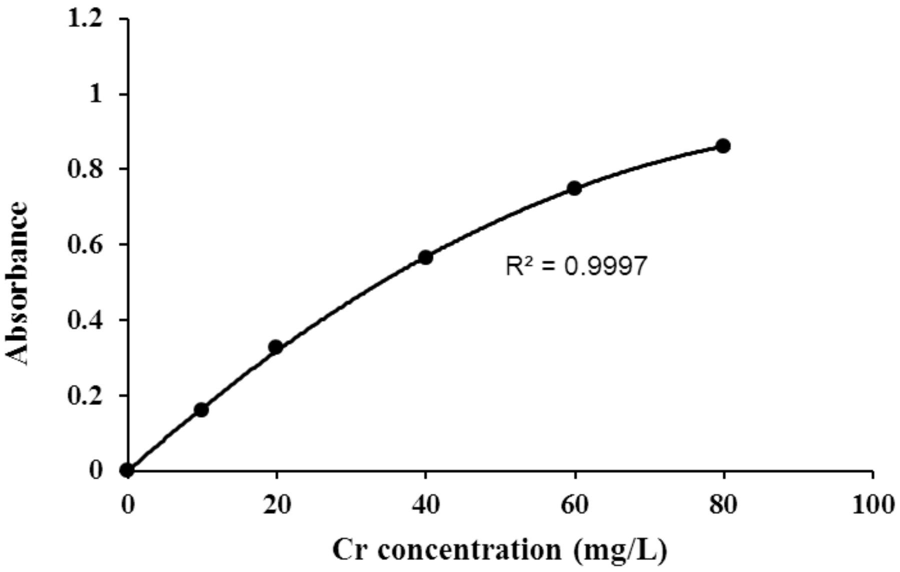


Figure 4.9.a. FAAS calibration curve for chromium

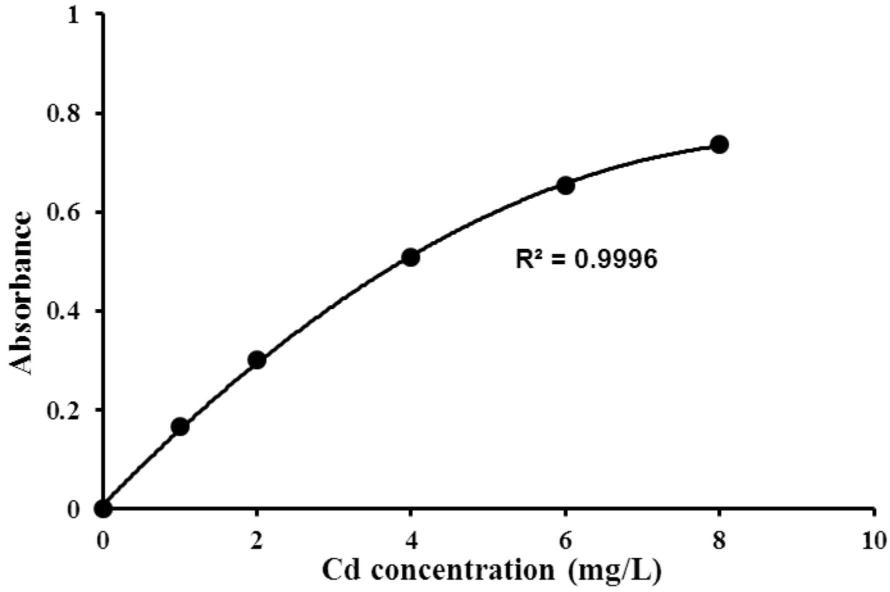


Figure 4.9.b. FAAS calibration curve for cadmium

It is evident that there is a good correlation between the results of these two different analytical techniques. Values of the concentrations of chromium and cadmium, obtained by LIBS were in good agreement with those obtained by AAS. This indicates that our developed LIBS method could be effectively used for the rapid analysis of chromium and cadmium in general and tannery effluent in particular.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

The research has shown that:

- A convenient LIBS method that has been developed for the detection of heavy metals (chromium and cadmium) in tannery wastewater samples does not involve time consuming multi-step and expensive sample preparation processes.
- The method was based on the absorption of the liquid samples on the absorbent papers resulting in homogeneous spread of metal standards and samples leading to precise results.
- The use of methanol as a solvent for the solid phase chromium and cadmium standards provided not only homogeneous mixing but a very rapid drying method for the development of calibration curves.
- The analytical method shows good linearity over a large concentration range with correlation coefficients (R^2) in the range of 0.992 to 0.997.
- The validity of the developed LIBS method was proved by comparison with the established metal analysis technique of Atomic Absorption Spectroscopy.
- The optimized values of LIBS parameters were 89.5 mJ (laser pulse energy), 4.5 µs (delay time), 75 mm (lens to sample surface distance) and 7mm (light collection system to sample surface distant).

5.2. RECOMMENDATIONS

After concluding the results of the present study, the recommendations for future work are as follows:

- The developed method may be used to detect traces of other metals in tannery wastewater.
- The developed method may be validated for metallic contaminants in other matrices as well.
- Emphasis should still be given to improve limit of detection, accuracy, calibration and precision for more work on LIBS.

The extensive and systematic research has finally helped in extending analytical capacity of the ‘Ocean Optics LIBS2500 plus Laser-induced Breakdown Spectrometer’ to liquid (industrial wastewater) samples by developing rapid methodology for heavy metal analysis without undergoing time consuming multi-step and expensive sample preparation processes.

Chapter 6

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