

Short Communication

Chromium Quantification in a Leather Tanning Industrial Area Using Laser Induced Breakdown Spectroscopy

Shakeel Ahmad Khan^{1*}, Muhammad Ibrahim¹, Yasir Jamil^{2**},
Nasir Amin³, Saif Ullah⁴, Farhat Abbas¹

¹Department of Environmental Sciences, Government College University, Faisalabad (38000), Pakistan

²Laser Spectroscopy Laboratory, Department of Physics, University of Agriculture, Faisalabad (38040), Pakistan

³Department of Physics, Government College University, Faisalabad (38040), Pakistan

⁴Department of Physics, The Islamia University of Bahawalpur (63100), Pakistan

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Abstract

We report the use of laser-induced breakdown spectroscopy (LIBS) for determination of soil contamination due to effluents from the leather tanning industry in Kasur district of Punjab in Pakistan. The quantitative analysis was performed by making a calibration curve for Cr using LIBS spectral line at 427.48 nm. Chromium concentration of 839 mg·kg⁻¹ in the vicinity of an effluent drain and 1,829 mg·kg⁻¹ in the area of an old stagnant pool was found. The leaching of Cr due to seepage of industrial effluents from deteriorating brick-lined drains in horizontal direction also was observed.

Keywords: Cr contamination, laser-induced breakdown spectroscopy (LIBS), *in situ* analysis, online environmental monitoring system, soil degradation by leather tanning industry

Introduction

Management of industrial waste is a major concern, especially in developing countries. Due to rapid growth of industry, huge amounts of industrial waste are being dumped on the soil surface, resulting in eco-damaging effects. Due to ignorance about environmental hazards, the high cost of treatment plants, and lack of effective enforcement of environmental control laws, very little attention is being given to proper disposal of industrial waste [1]. Throwing waste water and dumping solid waste is causing serious health and environmental problems.

In developing countries like Pakistan, very little work has been done for effective environmental monitoring

methods despite the urgency of the matter. There have been very few reports in literature about environmental studies in the region. Mubin et al. [2] analyzed 10 main industries of Karachi (Pakistan) and found that the leather industry was the major contributor toward damaging the environment due to toxicity in untreated industrial waste water. Forcing this industry to have treatment plants could reduce problems associated with industrial effluents up to 25%.

Industrial waste contains a large amount of contaminants like heavy metals, which may enter into the food chain through vegetation in dumping areas and the areas being irrigated by the untreated/semi-treated waste water from the industry [3]. Chromium is a pollutant that is being disposed of due to several industrial processes like chromium plating, stainless steel manufacturing, wood treatment, paint industry, and tanning industry. The chromium containing effluents from the tannery industry may cause seri-

*e-mail: shakeel890@yahoo.com

**e-mail: yasirjamil@yahoo.com

ous environmental problems. The U.S. Environmental Protection Agency has designated Chromium (Cr) as a priority pollutant due to its adverse effects on human health [4]. Although Cr-III is an essential dietary mineral [5], Cr-VI is a toxic form of the element found mostly in compound forms made artificially for use in different industries. Exposure to hexavalent chromium can cause adverse effects on warm-blooded organisms [6]. The Occupational Safety and Health Administration (OSHA) [7] has reported lung cancer; irritation or damage in the nose, throat, and respiratory tract due to breathing in a chromium-polluted environment; and eye and skin rashes, which may all be the result of direct contact with chromium. The maximum dose limit set in a workplace for eight hours in the form of dust or particles is $5 \mu\text{g}\cdot\text{m}^{-3}$. Cr-VI depresses biological activity and the enzymatic activity of microorganisms by modifying their living environments [8]. Soil dying out by tanning industrial waste can contain chromium concentrations much higher than safe limits. This chromium can be retrieved from industrial waste for reuse. Malek et al. [9] studied different mechanisms for removal of Cr from solid industrial waste from the leather tanning industry for its reuse and reported 95% extraction capability.

The monitoring of inclusion of contaminants like Cr to soil requires a rapid analytical technique that can be used both *in situ* or in laboratory to comprehend environmental degradation due to different sources. Laser-induced breakdown spectroscopy (LIBS) can serve the purpose. It is an atomic emission spectroscopic technique in that a laser beam is focused on the target material that ablates some material (hundreds of nanograms to a few micrograms) from the target surface, producing high temperature microplasma. This plasma atomizes, ionizes, and excites the species present in the plasma plume. On cooling, in a few microseconds the atoms return to their ground state by emitting characteristic radiations of the atoms [10]. The emitted radiations are analyzed by spectrometer for elemental detection. Due to simple arrangement, almost no sample preparation, rapid analysis, and capability of analyzing all states of matter (solid, liquid, or gaseous). LIBS is rapidly finding its niche among the modern spectroscopic techniques. The emission spectrum can be used both for qualitative and quantitative analysis [11]. Rai and Rai [12] studied Cr concentration in liquid effluents from the Chromium electroplating industry using LIBS.

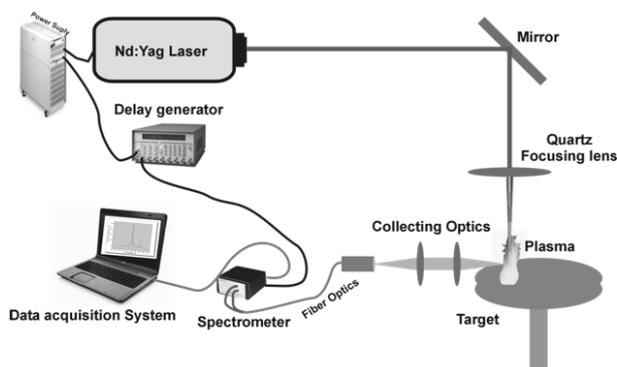


Fig. 1. Experimental setup.

LIBS is one of those spectroscopic techniques that are considered to have the capability of determining elements down to trace levels [12, 13]. It is non-destructive because it uses a very small amount of material to be analyzed and is also suitable for multi-elemental analysis simultaneously. Only optical access is required for producing plasma and collection of signals from the sample so LIBS that can be used to study samples in hazardous environments from which carrying a sample to a laboratory is difficult, and so remote analysis is possible [10].

Materials and Methods

The experimental set-up for analysis of a soil sample by LIBS is shown in Fig. 1. A short pulsed (5 ns) Q-switched Nd:YAG laser operating at the fundamental mode (1,064 nm) having 10 Hz repetition rate was used. A quartz biconvex lens of focal length 10 cm was used for focusing the laser beam on a pelletized sample. The sample was mounted on a rotating stage to provide a fresh surface for each laser pulse. The focal point of the laser beam was kept slightly inside the sample to avoid air breakdown in front of the sample surface. The light emitted by the plasma was fed to a spectrometer (Avantes; AvaSpec-3648 USB 2 Dual channel) through collecting optics, including a collecting lens and fiber optics. It covers the spectral range from 300 nm to 750 nm with spectral resolution of 0.07 nm. The acquisition of data by spectrometer is synchronized with Q-switch output of laser system with a time delay (2 μs) with the help of a digital delay generator (DG-535 of Stanford Research System). The spectrometer was operated by Avasoft[®] software to record spectrum. The data were analyzed using Origin[®] software. Peaks were identified and compared with the NIST (National Institute of Standards and Technology) atomic emission spectral database [14] for elemental detection.

Samples of soil were collected from an industrial area of Kasur (+31°6' 23.21", +74°27' 16.29"), a district of Punjab, Pakistan. Twenty-four samples were collected from different locations in the area. The first set of six samples was collected in the vicinity of discharge, the other three sets each of six samples were collected from 20 m, 50 m, and 200 m from the main drain. Each sample was packed in polythene bags. Samples were dried at 60°C for 6 hour in an oven (Shell Down Manufacturing, Inc., Portland, Oregon). The samples were ground in an agate mortar and pestle and then palletized at 4,000 bar pressure by hydraulic press for 2 minutes by adding poly vinyl alcohol (PVA).

Standard samples for constructing calibration curves were prepared by the addition of known masses of potassium chromate (K_2CrO_4 >99% pure 194.19 molecular weight) in chromium-free soil (confirmed by ICP-OES) obtained from the Institute of Soil and Environmental Sciences UAF. Standard procedure described in detail by Khan et al. [15] was adopted for constructing the calibration curve of Cr shown in Fig. 2. The limit of detection for our LIBS was found by using equation (1) [16].

$$LOD = \frac{\sqrt[3]{S^2 + s_a^2 + (a/b)^2 * s_b^2}}{b} \tag{1}$$

...where *S* is the standard deviation of calibration data, *a* is the intercept of the calibration curve at zero analyte concentration, *s_a* is the standard deviation on the intercept, and *s_b* is the indetermination on the slope of the calibration curve. The limit of detection for the above-described setup was found to be 23.71 mg·kg⁻¹ for chromium.

Results and Discussion

Typical LIBS spectra are shown in Figs 3a and b from unpolluted and polluted soil samples. The emission lines of chromium (427.48 nm), sodium (588.97 nm), chlorine (499.57 nm), and other elements listed in Table 1 can be identified in spectrum 3b. Chromium (Cr) is found in tanning industry effluents due to the use of chrome alum and chromium (III) sulphate in chrome tanning of leather. Due to its solubility it is mixed with waste water and is flushed out mostly without any effort of chrome recovery. The concentration of Cr was determined using the calibration curve shown in Fig. 2. The linear regression line fit of the experimental data points showed linear dependence of analyte signal with intensity. The deviation of data points from linear fit line at high analyte concentration is due to saturation of the spectrometer. The concentration of Cr found in the area was found in the range of 128 mg·kg⁻¹ to 1,829 mg·kg⁻¹, with mean value of 468 mg·kg⁻¹ and range of 1,701 mg·kg⁻¹. Its concentration varies randomly from place to place. There were two sampling points where the concentration of the Cr is very high (up to 1,829 mg·kg⁻¹). Those were in the area of a stagnant pool where Cr concentration was still very high. The random distribution of Cr (Fig. 4) in soil in the area is due to unplanned distribution of the tanneries in the area and due to deteriorating brick lining of the drains and texture of the soil causing seepage of polluted water. The major industry in the sampling area was tanning, which uses chromium compounds for processing raw hides to fin-

ished leather. UNDP initiated the Kasur Tanneries Pollution Control Project (a water treatment plant and solid waste treatment plant) in collaboration with the government of Pakistan, the provincial government, and the operators of tanneries. Due to these facilities, stagnant pools have van-

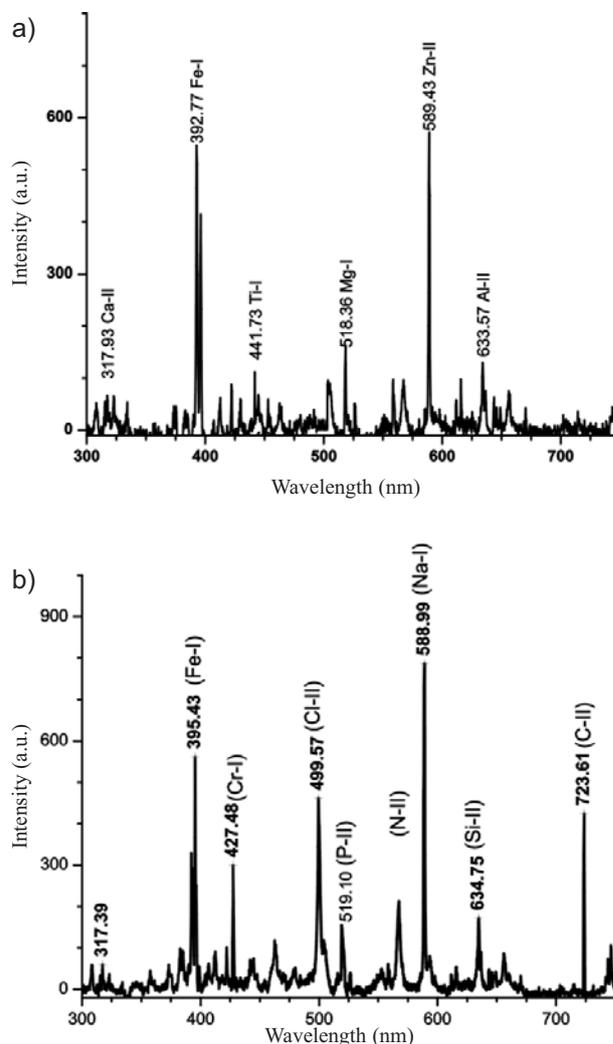


Fig. 3. a) Chromium-free soil spectrum from the Institute of Soil and Environmental Sciences UAF, b) typical spectrum of polluted soil from sampling area.

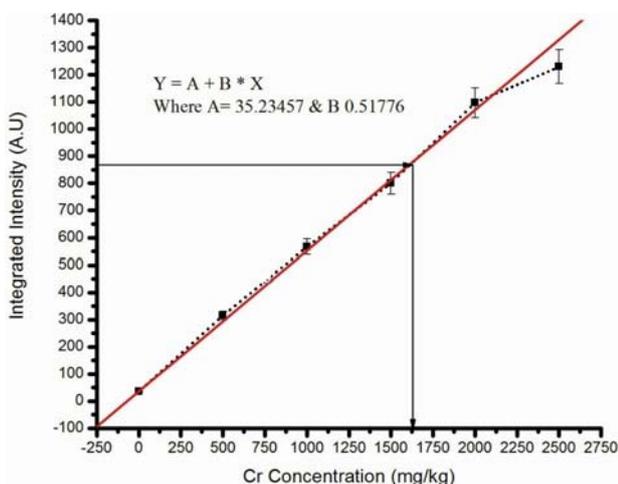


Fig. 2. Calibration curve for Cr in soil.

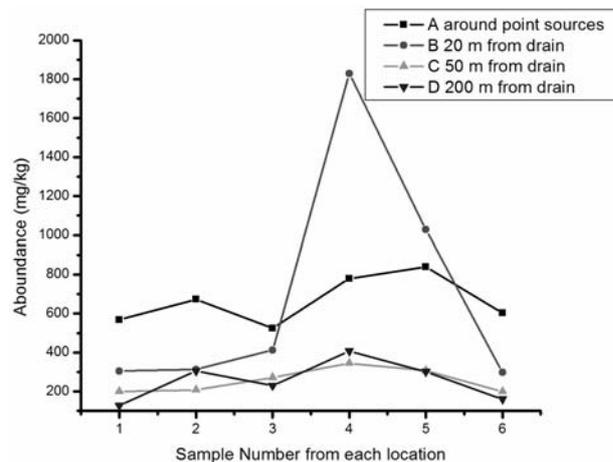


Fig. 4. Variation of Cr concentrations with distance for different samples.

Table 1. Important elements found in different samples with their possible transitions.

Element symbol	Wavelength (nm)	Configuration
Na II	313.548	$2s^2 2p^5 3s - 2s^2 2p^5 3p$
Fe I	395.465	$3p^6 4f - 3p^6 6f$
Cr I	427.48	$3d^5(6S)4s - 3d^5(6S)4p$
Cr II	462.617	$3d^4 4s^2 - 3d^4(^6D)4s4p(^6P^o)$
Hg I	498.064	$5d^{10} 6s^7 s - 5d^{10} 6s^1 2p$
Cl II	499.547	$3s^2 3p^3(^3D^o)3d - 3s^2 3p^3(^3D^o)4p$
P II	519.141	$3s^2 3p^4 s - 3s^2 3p^4 p$
N II	567.38	$2s^2 2p^3 p - 2s^2 2p^3 d$
Cr I	578.799	$3d^3(^6S)4p - 3d^3(^6S)4d$
Na I	588.995	$2p^6 3s - 2p^6 3p$
Na I	616.074	$2p^6 3p - 2p^6 5s$
Si II	634.71	$1s^2 2p^4 p - 1s^2 2p^4 d$

ished from the area, reducing hazardous materials in the surroundings.

Other elements found in the soil samples given in Table 1 add up the threats faced by the community living around these industries. The chromium from soil may include the food chain due to uptake of Cr by plants and vegetation in the polluted area.

The sodium and chlorine found in the soil showing high peaks in the spectra are due to excessive use of sodium chloride (NaCl) for skin preservation or the pickling process of leather. Since it is highly soluble and stable and even effluent treatment does not much reduce its concentration, it remains in the effluent from which it is leached into the soil to a reasonable distance. Increased salt concentrations in the water and soil are a serious issue for the environment. Chlorides have adverse effects on the growth of plants, bacteria, and fish in surface water. When this saline water is used for irrigation purposes soil salinity increases and crop yield decreases. According to Rahim et al. [17], soil with a high concentration of sodium, known as sodic soil, soluble calcium levels decrease, causing decreased growth of plants due to loss of favorable structural properties. A plant's ability to extract water from saline soil lessens. Sodium salts are critically important because they have the potential to spoil soil structure and often lower soluble salts. It has been observed that in the presence of organic acids (citric and oxalic), uptake of Cr by plants may increase [18] and can be toxic for the community.

Conclusions

The present study shows the LIBS application in monitoring soil degradation due to industrial effluents. The calibration curves made in this study showed a reasonable lin-

ear relationship between analyte concentration and signal intensity. It depicted a high concentration of Cr with random distribution in the area with mean of 468 mg·kg⁻¹. Since the areas around tannery industries are highly contaminated by chromium, it can contaminate vegetation that is being irrigated by the waste water from these industries. The salinity of the soil is also increasing due to dissolved salts in the effluents, causing reduced crop yield. LIBS can be used to monitor the variation of salt and mineral contents of the soil rapidly without much sample preparation, so it can be used for monitoring the remedial process more effectively. The *in situ* analytical capability and rapidity make LIBS a star among other spectroscopic techniques.

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