

Detection of hazardous pollutants in chrome-tanned leather using locally developed laser-induced breakdown spectrometer

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Abstract Highly toxic contaminants like Cr, As, and Pb were detected in chrome-tanning process of animal skin to produce leather by applying locally developed laser-induced breakdown spectrometer. An Nd–YAG laser with 1,064 nm wavelength was focused on the surface of leather samples (natural and manufactured) to generate a plasma spark and spectrally resolved spectra were used for identification and quantification of contaminants. The leather samples were collected from a tannery located in industrial cities of Riyadh and Jeddah, Saudi Arabia. The study was carried out on fully, half manufactured (wet blue leather), and natural hide (skin). To the best of our knowledge, this is the first attempt where laser-induced breakdown spectroscopy (LIBS) technique has been applied for the analysis of leather before and after

tanning process. The maximum concentration of different elements of environmental significance like chromium, lead, arsenic, sulfur, magnesium were 199, 289, 31, 38, and 39 ppm, respectively, in one of the manufactured leather samples. The limit of detection (LOD) of our LIBS system for chromium, lead, arsenic, sulfur, and magnesium were 2, 3, 1.5, 7, and 3 ppm, respectively. The safe permissible limit for tanned leather for highly toxic elements like chromium, lead, and arsenic are 1, 0.5, 0.01 ppm, respectively, as prescribed in Environmental Regulation Standards for Saudi Industries set by Royal Commission Jubail, Saudi Arabia. The LIBS technique is superior to other conventional techniques like ICP or atomic absorption that a little or no sample preparation is required, no chemicals are needed, multi-elemental analysis is possible for all kinds of samples (natural and anthropogenic materials), microgram of sample is essential, and LIBS could be applied for remote analysis. It is highly selective and sensitivity higher than ICP, and as no sample and chemicals are required, it is cost effective for multi-sample analysis per unit time as compared with other conventional techniques. The concentration of some toxic elements (Cr, Pb, As) is much higher than the safe permissible limits set by Occupational Safety and Health Administration in USA or Saudi environmental regulatory agencies. Results obtained with our LIBS systems were in close agreement with the results obtained

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using other standard analytical technique such as the inductively coupled plasma atomic emission spectroscopy.

Keywords Laser-induced breakdown spectroscopy · Chromium · Lead · Arsenic · Toxic elements detection

Introduction

Leather processing is one of the earliest industrial activities carried out by humans due to protection of their feet from harsh environment. Around 3000 A.D., ancient Egyptians were the first who were applying mineral tanning for leather processing. There are different methods of leather tanning (Josep et al. 2008; Agrawal et al. 2008). One of the effective and widely used methods is chrome tanning which was developed in the USA by Augustus Schultz in 1884. The main problem in this method is the huge amount of pollutants of waste water posing great threat to the clean environment (Wenjie et al. 2008; Amoozegar et al. 2007). In addition, it adds hazardous pollutants to the leather which is produced. The hazards effect of leather chrome-tanned shoes allergy inflammation on foot and other organs that contained contaminated leather chrome-tanned causes dermatitis. The studies using conventional analytical methods have revealed that exposure to such processed leather could expose to both Cr (III) and Cr (VI). It has been reported that Cr plays an important role in chromium allergy, because Cr is capable of eliciting eczema at low concentrations (Süreyya et al. 2005; Loveren et al. 2008). Although Cr is natural and essential for human and shortage may cause heart conditions, disruptions of metabolisms, and diabetes, its uptake caused dangerous defects like alteration of genetic material skin rashes and many kinds of other allergies. The toxic effect of arsenic is that it can cause skin disturbances, declined resistance to infections, heart disruptions, and brain damage for both men and women. Finally, inorganic arsenic can damage even DNA structure. A lethal dose of arsenic oxide, such as 100 mg if accumulated in kidneys, could damage the filtering mechanism of

human body. This causes the excretion of essential proteins and sugars from the body which could cause further damage to kidney.

Previous studies demonstrated that chromium, arsenic, and lead were most abundant in the wastewater generated by a tannery (Wenjie et al. 2008; Amoozegar-et al. 2007). Very little work has been reported on detection of these hazardous pollutants in the leather samples using laser-induced breakdown spectroscopy (LIBS) (Jerschow et al. 2001; Gondal et al. 2007a, b; Gondal and Hussain 2007; Gondal and Siddiqui 2007; Hussain and Gondal 2008; Siddiqui et al. 2008; Laserna 2005; Ferrero and Laserna 2008; Wu et al. 2007; Giacomo et al. 2007; Seong et al. 2008; Shuya and Kazuaki 2007; Shaikh et al. 2007), and this work is of its first kind on detection of various poisonous elements which exist in the full, half (wet blue), and natural hide/skin of animals. The basic principal of LIBS is based on the spectral analysis of radiation emitted from a plasma generated by focusing a high power pulsed laser beam on to the surface of the test sample. The characteristic emission from plasma provides information about the elements present in the target material. The unique features of LIBS (Jerschow et al. 2001; Gondal et al. 2007a, b; Gondal and Hussain 2007; Gondal and Siddiqui 2007; Hussain and Gondal 2008; Siddiqui et al. 2008; Laserna 2005; Ferrero and Laserna 2008; Wu 2007; Giacomo et al. 2007; Seong et al. 2008; Shuya and Kazuaki 2007; Shaikh et al. 2007) technique are that it requires no sample preparation and is capable of remote and in situ analysis of materials in any phase (solid, liquid, or gas). This is in contrast with conventional analytical techniques that require time-consuming sample preparation and can be employed only in well-equipped laboratory. Laser-produced plasma of solid and liquid materials are also of great interest, especially for laser diagnostic, thin film growth, and trace elemental analysis.

This study was carried out on fully manufactured, half manufactured (wet blue leather) and natural hide (skin) to detect hazardous elements like Cr, As, and Pb. LIBS results were compared with the results obtained using other analytical techniques such as the inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Materials and methods

Details of sample preparation for ICP and LIBS analysis

The leather samples were collected from a tannery located in the industrial area of Riyadh and Jeddah, Saudi Arabia. These samples were fully manufactured, half manufactured (wet blue leather), and of natural hide (skin) of lamb. For calibration purposes of LIBS spectrometer, the metals used are Cr, As, and Pb of high purity grade (99.99%).

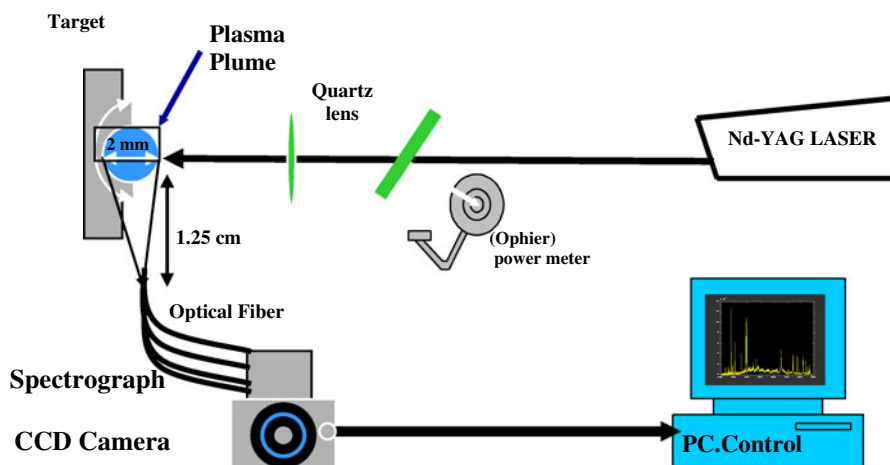
For the analysis of lipstick samples using ICP technique, standard preparation method 3050B as recommended by EPA for ICP analysis was adopted [<http://www.epa.gov/waste/hazard/testmethods>: Sample collection, preservation, and handling methods for ICP analysis]. For this purpose, the contaminated leather samples were digested in 5% nitric acid of 99.99% purity supplied by Fisher Scientific, USA. For the digestion of samples, a representative 1 g of leather contaminated sample was digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2). The resultant digestate is reduced in volume while heating at 95°C for 6 h and then diluted to a final volume. The resulting solution of the sample was analyzed for various metals using inductively coupled plasma spectrometer calibrated using reference standards. In order to test the homogeneity of our samples, several LIBS measurements were performed at different loca-

tions on the surface of Cr-contaminated leather samples. Analytical-reagent grade chemicals without further purification were used for the calibration and analysis of lipstick samples by ICP and LIBS method. For laser-induced breakdown spectroscopy, leather samples under investigation were placed into LIBS ablation chamber with out any pre-chemical treatment.

Development of LIBS system

The schematic diagram of our LIBS experimental setup for detection of toxic elements present in leather samples is depicted in Fig. 1. The LIBS setup applied in this work has been described in detail in our previous publications and briefly described here (Gondal et al. 2007a, b; Gondal and Hussain 2007; Gondal and Siddiqui 2007; Hussain and Gondal 2008; Siddiqui et al. 2008). The light emitted from the plasma spark is collected by a collimating lens using UV-graded fused silica 1 m, multimode sampling fiber with SMA connector is transferred to LIB2000+ Spectrometer (Ocean Optics). Our LIBS 2000+ has four spectrometer modules to provide high resolution (FWHM 0.1 nm) in the 200- to 620-nm wavelength region. The detector has a gated CCD camera having 14,336 pixels. The LIBS emission spectra are recorded at a 45° angle to the direction of incident laser pulse. Software built in the spectrometer read the data from the chip and reconstruct the spectrum. This makes it possible to measure a

Fig. 1 Schematic diagram of the LIBS setup applied for the detection of contaminants in leather samples



large wavelength range (200–620 nm) simultaneously with high spectral resolution (0.1 nm). The software provides element identification through a spectral database for qualitative measurements. Samples can be quickly measured and saved to log-file. Options allow customization of spectral search algorithms. Custom compound element libraries can be created or searched using LIBS 2000+ spectrometer.

A Q-switched Nd–YAG laser (Spectra physics Model GCR 100) operating at 1,064 nm wavelength was employed as an excitation sources. It can deliver maximum pulse energy of 1 J with a pulse width of 8 ns and operates at a 10-Hz pulse repetition rate. The collimated beam at 1,064 nm is tightly focused on the target sample using a convex lens to create a spark or breakdown in the sample.

Optimization of our LIBS system

In order to optimize the sensitivity of our LIBS system, laser energy dependence of the LIBS signal intensity on incident laser energy was conducted on the finger print wavelength of the elements under consideration in this study (Cr, Pb, As). For this purpose, the laser energy was measured with a calibrated energy meter (ophir model 300). In this experiment, we placed a 2-mm diameter aperture inside the path of laser beam in order to get a uniform laser beam shape. In this experiment, the pulse energy was varied in the range of 25–120 mJ. A lens of 25 mm diameter and 35 mm focal length was used to focus the laser beam on the pellets sample under investigation. The exposed area on the sample was about 150 μm in diameter and rotated with a constant speed motor to avoid leaser ablation on the sample's surface. The LIBS signal intensity was recorded for different laser energies and plotted versus incident laser energy. The trend of LIBS signal intensity showed linear dependence on the incident laser energy.

Calibration of the LIBS system

Laser-induced breakdown spectroscopy is emission spectroscopy in which emission intensity is monitored for the analysis and quantification. The

intensity of emission line I_{ji} of an element for transition from energy level j to i is given by

$$I_{nm} = n_n (hc/\lambda_{nm}) \{g_n/Q(T)\} A_{nm} \exp(-E_n/kT) \quad (1)$$

Where n_n is the concentration of element under investigation in n state, λ_{nm} is the emission wavelength, Q is partition function, T is the electron temperature in laser produced plasma, A_{nm} is the transition probability for the transition n to m , h is planks constant, c is speed of light, and g_n and E_n are the degeneracy and energy of level n , respectively. A plot of intensity I_{nm} as a function of elemental concentration n_j yields the calibration curve. If the dependence of LIBS signal intensity on the elemental concentration is linear, then one can determine the unknown concentration of particular element at any LIBS signal intensity I_{nm} provided that the same experimental parameters (time delay, incident laser energy, collecting fiber optics and incident focusing optics distance, target rotation speed, atmospheric pressure) are selected.

For calibration of our LIBS spectrometer, four samples of known concentration of 10, 1, 0.1, and 0.01 wt.% of elements under investigation were prepared in the matrix of leather. The LIBS spectra were recorded for these four (10, 1, 0.1, and 0.01 wt.%) concentrations of each element. All these spectra were recorded with an average of 20 laser shots, at three different locations on the sample surface. The calibration curve for each element under investigation was established by plotting the LIBS signal intensity of specific transition of each element as a function of the wt. %.

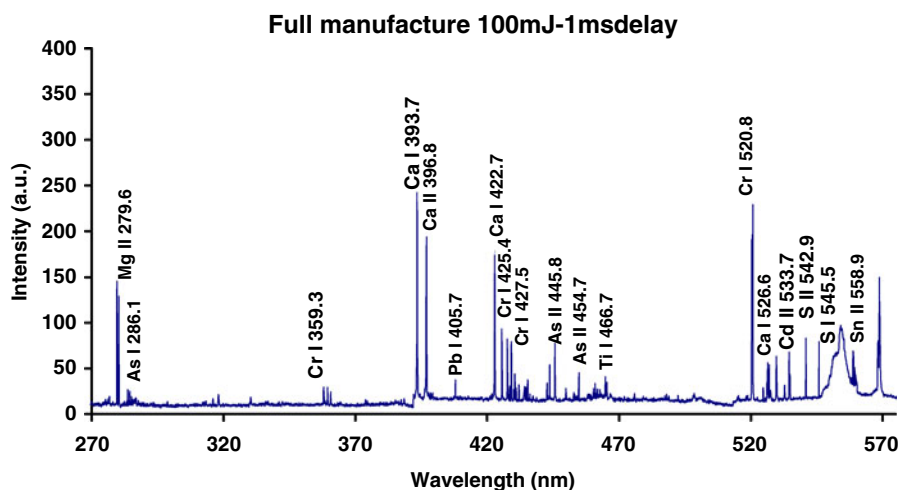
Limit of detection

The estimation of detection limit is very important for samples under investigation. Detection limit here means the lowest concentration that can be detected with LIBS. The LOD can be estimated using the equation

$$\text{LOD} = \frac{2\sigma_B}{S} \quad (2)$$

Where σ_B is the standard deviation of the background and S is the sensitivity which is given by

Fig. 2 Typical LIBS Spectra of fully manufactured leather sample in the region of 270 to 575 nm recorded at delay time of 1.0 μ s and laser pulse energy = 100 mJ



the ratio of the intensity to the concentration. The detection limit for LIBS analysis of leather samples under investigation was calculated by using the above mentioned equation. The relative standard deviation (RSD) is given by the equation

$$RSD = \frac{\text{Standard deviation}}{\text{Mean}} \quad (3)$$

The relative standard deviation decreased with the number of shots but no improvement in RSD after 20 shots. The RSD Value in our case was 2.6%. The leather samples results were comparable to the results obtained by ICP-AES. The LOD of our LIBS system for chromium, lead, arsenic, sulfur, magnesium were 2, 3, 1.5, 7, and 3 ppm, respectively.

Results and discussion

Before testing our LIBS spectrometer on actual leather samples, experiments were performed to find the optimal conditions for its performance by finding the best settings of temporal delay, incident laser energy, optical components (focusing lens for irradiation and collection of plasma light) location for the maximum LIBS signal intensity for different leather samples under investigation. After the LIBS parametric optimization, spectra of different leather samples were recorded over a 200–650-nm wavelength range for qualitative and quantitative analysis under these optimum experimental conditions. The LIBS spectra of natural, full-manufactured, and wet blue leather samples

Fig. 3 Typical LIBS Spectra of wet blue leather sample in the region of 270 to 575 nm recorded at delay time of 1.0 μ s and laser pulse energy = 100 mJ

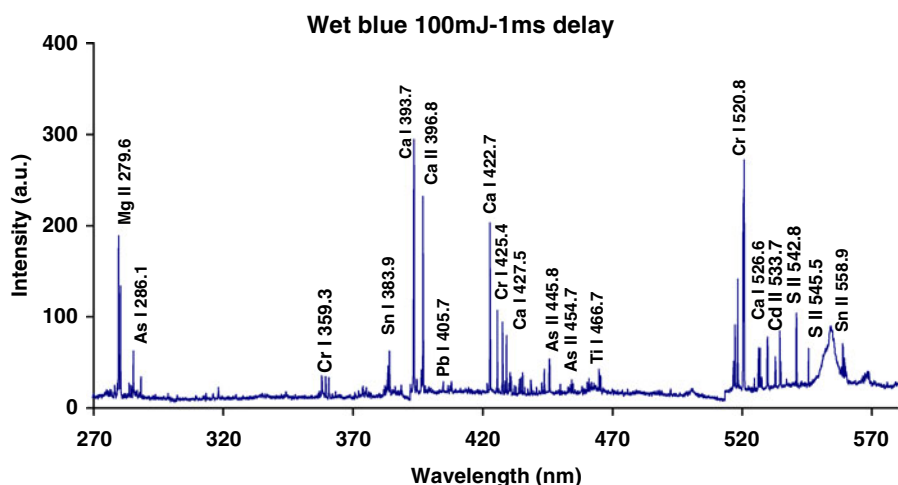
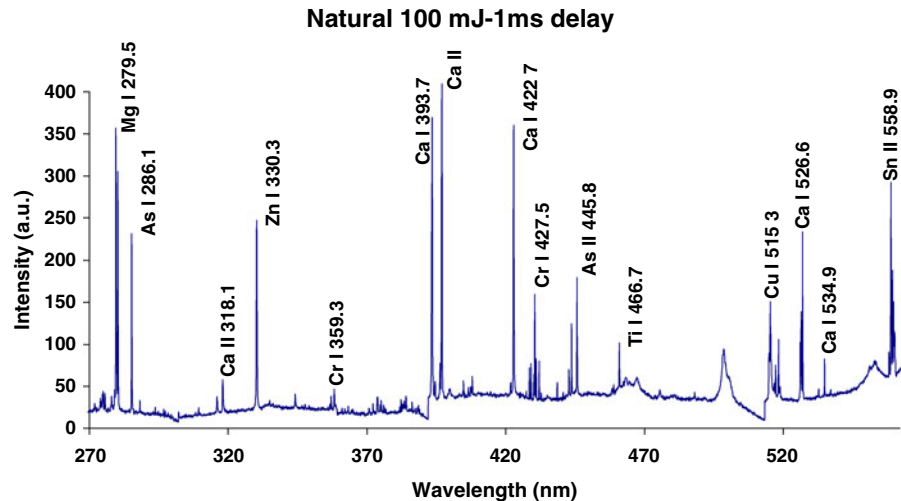


Fig. 4 Typical LIBS Spectra of natural leather sample in the region of 270 to 575 nm recorded at delay time of 1.0 μ s and laser pulse energy = 100 mJ



were plotted and are depicted in Figs. 2, 3, and 4. The emission spectra of the leather samples for spectral region of 270 to 585 nm. The laser pulse energy was fixed at 100 mJ for recording of all these spectra. The distance between the optical fiber and the plasma was 10 mm. Here, the LIBS spectra of elements under investigation were recorded in the abovementioned spectral region to find the most sensitive lines of each element. The major elements detected in these samples are of toxic nature like chromium, arsenic, lead, sulfur, and some trace elements such as manganese were also present in appreciable amount. All the elements present in these leather samples along with their concentration detected with our LIBS spectrometer and with standard method such as ICP are listed in Table 1, and the finger print wavelengths for the elements depicted along with transitions and concentrations detected with our LIBS system are listed in Table 2. The

spectra of full-manufactured leather samples manufacturing plants were depicted in Fig. 2. One can notice that the contaminations of hazardous contaminants like Cr, Pb, and As are found to be close to that in the wet blue as presented in Fig. 3. It is worth mentioning that the concentration of these toxic elements detected in this work exceed the safe permissible exposure limits set by Occupational Safety and Health Administration (OSHA) and Saudi Environmental Regulatory Agency.

In order to apply the LIBS spectrometer for quantitative analysis to measure the unknown concentration in the leather samples, the LIBS spectrometer was calibrated as described under experimental section.

A plot of intensity I_{mn} as a function of elemental concentration n_m yields the calibration curve. If the dependence of LIBS signal intensity on the elemental concentration is linear, then one can determine the unknown concentration of particular

Table 1 List of elements detected in leather samples collected from local Saudi industries and comparison of LIBS with standard conventional technique (ICP)

Element	Finger print wavelength	Full manufactured sample 1		Wet blue sample 2		Natural sample 3	
		LIBS ppm	ICP ppm	LIBS ppm	ICP ppm	LIBS ppm	ICP ppm
Ca	422.7	12.4	13.0	12.3	13.1	8.4	9.2
Cr	427.5	135.5	136.8	198.8	199.1	4.6	5.2
Pb	405.8	148.1	150.2	288.4	289.2	27.2	28.9
As	445.8	27.1	27.1	29.7	31.4	2.7	2.9
S	542.9	38.2	38.2	23.2	23.2	20.7	21.2
Mg	279.5	26.4	25.1	28.2	27.8	39.0	38.2

Table 2 List of elements detected in different leather samples along with their fingerprint wavelengths and the transition probability

Element	Wavelength (nm)	Intensity (a.u.)	Spectral transition	Ground state energy (eV)	Transition probability
Mg	279.5	354.7	$2p^6 3s \rightarrow 2p^6 3p$	4.4	$3.8E - 03$
Ca	422.7	359.9	$3p^6 4s^2 \rightarrow 3p^6 4s 4p$	2.9	$2.18E + 08$
Cr	427.5	94.5	$3d^5 4s \rightarrow 3d^5 4p$	2.9	$3.07E + 07$
Pb	405.8	25.9	$6s^2 6p^2 \rightarrow 6p_{1/2} 6p_{3/2}$	9.2	$8.9E + 07$
As	445.8	76.7	$4p^3 4s_{3/2} \rightarrow 4p^3 2D$	5.2	$0.55E + 08$
S	542.9	29.8	$(^3P)4s \rightarrow (^3P) 4p$	15.86	$4.2E + 07$

element at any LIBS signal intensity I_{mn} provided that the same experimental parameters (time delay, incident laser energy, collecting fiber optics and incident focusing optics distance, target rotation speed, atmospheric pressure) are selected.

In this experimental work, four samples of known concentration of 10, 1, 0.1, and 0.01 wt.% of elements under investigation were prepared in the matrix of leather. The LIBS spectra were recorded for these four (10, 1, 0.1, and 0.01 wt.%) concentrations of each element. All these spectra were recorded with an average of 20 laser shots, at three different locations on the sample surface. The calibration curve for each element under investigation was established by plotting the LIBS signal intensity of specific transition of each element as a function of the wt.%. The LIBS signal intensity showed linear dependence on the concentration of Cr in the standard sample as predicted by Eq. 1. For calibrations, the line interference is the most sever problem for emission identification; thus, we choose those lines for analysis which are free from interference or those

which have minimal effect are selected to get better results. The safe permissible exposure limits of Cr is $5 \mu\text{g}/\text{m}^3$ according to OSHA as studies showed that higher concentrations cause cancer; for the safe permissible exposure limits for lead, OSHA set it to be $19 \mu\text{g}/\text{dL}$. Typical calibrations curves for Cr and Pb are present in Figs. 5 and 6, respectively, which were obtained after irradiating cylindrical pellets of 1 cm diameter and 0.5 cm height pressed from crust dry powder of leather-tanned mixed with Cr and Pb in different concentrations.

Chromium toxicity among workers in tanneries and other chromium-based industries have been known for a long time. The workers are reported to suffer from ulcers, allergic dermatitis, lung cancer, renal insufficiency, and liver necrosis. In 1960, the famous catastrophic incidence of lung cancer due to inhaling of dust containing Cr (VI) was reported from the Kiryama factory of the Nippon-Denko concern on the island of Hokkaido, Japan (Förstner and Wittmann 1979). Chromium pollution in groundwater as a result of leaching of

Fig. 5 Calibration curve for Cr in leather sample

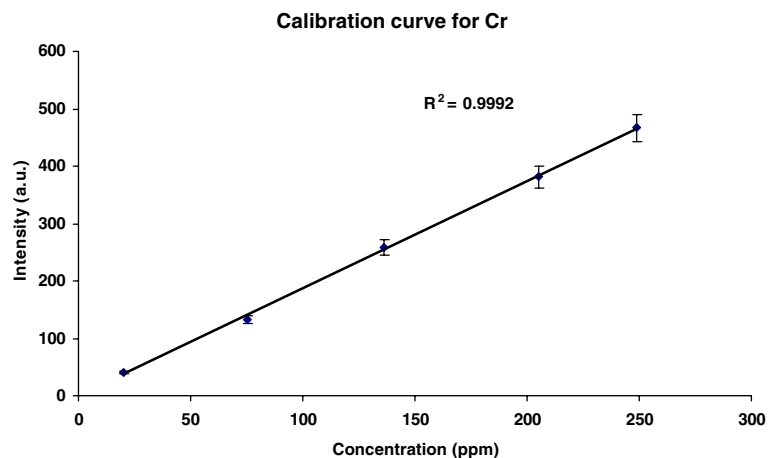
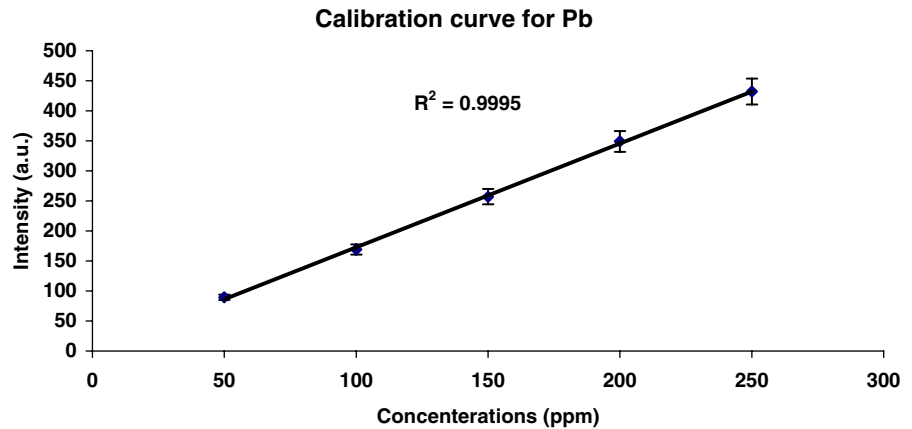


Fig. 6 Calibration curve for Pb in leather sample



Cr (VI) from spent solid and liquid wastes at chromium-based industries has currently become a serious problem at the global level. In August 1975, it was found that underground drinking water in Tokyo near the Cr (VI)—containing spoil heaps contained chromium more than 2,000 times the permissible limit. In Ludhiana and Chennai, India, chromium levels in underground waters have been recorded at more than 12 mg/L and 550–1,500 ppm Cr/L, respectively (Sujana et al. 1997).

Precision and accuracy of LIBS analysis

The precision of any analytical instrument is defined as the accuracy in repeatability of the analytic measurement and is usually estimated in LIBS by the RSD as follow

$$\text{RSD} = \text{standard deviation} / \text{mean}$$

For leather samples, the precision of LIBS measurements depend on the complexity and homogeneity of the sample and the reproducibility of the laser shots. Typical values for LIBS analysis for various samples are in the range 1–7%. For precision of our results regarding leather samples presented in this work, the same method was adopted as applied for the analysis of ore and other samples (Gondal and Hussain 2007; Gondal et al. 2007b), and the precision was found to be 2–4% as indicated. Hence, LIBS spectrometer built in our laboratory is robust in nature, and results are precise, highly repeatable, and comparable

with the results achieved by standard method like ICP.

In addition, the LIBS signal intensity showed linear dependence on the concentration of the element present in the tested sample. The finger print wavelength selected for the analysis was in the wavelength region which is free from any interference by other elements present in the tested sample. The response of CCD detector is very fast (ns); therefore, the waiting period (recovery time) between consecutive measurements is not an issue like other conventional sensors such as thin film sensors. Due to these reasons, LIBS system is ideal for in situ or online monitoring.

Conclusion

In this study, a new rapid technique was developed based on LIBS which can be applied in situ to detect the contaminations in leather finishing process. This technique has the advantages that it is fast, in situ, and more accurate without any lengthy sample preparation procedure. The sensitive lines for the abovementioned contaminants were identified using standard data published by NIST for the elemental analysis. This study reveals that leather produced by chrome-tanning method is contaminated by several toxic elements like lead, chromium, and arsenic. Most of these elements are considered highly toxic and carcinogens. They could cause a lot of problems for heart

and lungs diseases. In addition, they could cause allergy so it is recommended that more effective methods should be adapted for decontaminations of toxic substances in leather-tanning process.

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