

# Detection of lead in paint samples synthesized locally using-laser-induced breakdown spectroscopy

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**Q3:** Au: Is "ns fs" correct in reference [29].

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**Detection of lead in paint samples synthesized locally using-laser-induced breakdown spectroscopy**

*Mohammed A.Gondal, Mohamed M.Nasr, Mubarak M. Ahmed, Zain H. Yamani and M. S. Alsalhi*

# Detection of lead in paint samples synthesized locally using-laser-induced breakdown spectroscopy

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10 A laser-induced breakdown spectroscopy (LIBS) setup was developed to detect lead and other toxic contaminants such as chromium in paint emulsion samples manufactured in Saudi Arabia. The lead concentration detected in these samples was in the 327.2–755.3 ppm range, which is much higher than the safe permissible limit set by Saudi regulatory agencies. Similarly chromium concentration (98.1–149.5 ppm) was found in high concentrations as well. The results obtained with our LIBS setup are comparable with the sample analysis utilizing a standard technique such as ICP and Our LIBS results are comparable to ICP with in an accuracy limit of 2–4 %.

15 **Keywords:** LIBS, lead, chromium, paint, hazardous effects of lead.

## Introduction

Lead-based paint is being preferred by paint companies not only due to its impact on color shining quality but also to make it durable, corrosion resistant, and to improve in fast drying processes. Also paint coatings in toys, pen, pencil and children painting materials are also considered as a great hazard to human being (adults as well as children). The main material used in paint pigments is lead chromate, which increases the chances of not only lead contamination but also chromium, which is carcinogenic as well. Children with high levels of lead in their bodies can suffer from damage to their brain and nervous system behavior and learning problems. In addition, hyperactivity, slowed growth, hearing problems and headaches are common symptoms of lead poisoning.<sup>[1–4]</sup> Lead is also harmful to adults.<sup>[5–8]</sup> Adults can suffer from reproductive problems (both men and women), high blood pressure and hypertension, nerve disorders, memory concentration problems, muscle and joint pain. Symptoms of lead poisoning include loss of appetite, weakness, anemia, vomiting, and convul-

sions, sometimes leading to permanent brain damage or even death.<sup>[9–12]</sup> This is why use of lead in paint has been banned in many advanced countries. The present study was aimed to evaluate lead content and some other toxic elements like chromium and arsenic in 5 paint samples manufactured in 3 different plants in Saudi Arabia by applying Laser-Induced Breakdown Spectroscopy (LIBS). Nd: YAG laser at 1064 nm was employed as a radiation source to generate a plume for LIBS to determine the concentration of these trace elements present in these paint samples. The concentrations of hazardous elements such as Pb, Cr and As determined with our LIBS setup was compared with standard technique such as ICP and results achieved with our LIBS setup are in close agreement with ICP analysis of these samples. The unique features of LIBS are that they have little sample preparation requirement and fast and rapid analysis and in-situ detection ability, which are lacking in the conventional analytical techniques such as Atomic Absorption and Inductively Coupled Plasma.<sup>[13–33]</sup>

## Materials and methods

### *Sample preparation and reagent used for LIBS and ICP analysis*

The 5 paint samples were obtained from 3 different companies in the Kingdom of Saudi Arabia. These samples were

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Received June 25, 2010.

of a different nature due to use of various ingredients such as base from raw emulsion to final and colored emulsion. As we know that the paint is in the form of a fluid that needs extra treatment to analyze by the LIBS technique. The samples were therefore heated first for any water contamination at 105°C, and then were cut into small circular pieces of 1 cm diameter so that they fit into the sample disk holder. This holder was mounted on the rotating motor inside the LIBS chamber to avoid the ablation of the samples from same spot. The emitted spectra were then recorded from these 5 samples. For the analysis of paint samples using the ICP technique, standard preparation method 3050B as recommended by EPA for ICP analysis was adopted.

For this purpose, the contaminated paint samples were digested in 5 % nitric acid of 99.99 % purity supplied by Fisher Scientific, USA.

For the digestion of samples, a representative 1 gram (dry weight) of paint contaminated sample was digested with repeated additions of nitric acid (HNO<sub>3</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). 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 of three levels of accuracy. To test the homogeneity of our samples, several LIBS measurements were performed at different locations on the surface of the contaminated paint samples.

Analytical-reagent grade chemicals without further purification were used for the calibration and analysis of paint samples by ICP and LIBS method. For calibration purposes, the metals used are lead and chromium. These metals in powder forms were of high purity (99.99%) and procured from Fisher Scientific USA. For the construction of the calibration curves, different samples comprising these metals were prepared in paint. For this purpose, pure metals in

powder form were mixed with in the paint matrix melted at 124 °C to ensure good mixing and homogeneity.

### Experimental setup details

In our study, laser-induced breakdown spectrometer (LIBS) was developed for the detection of hazardous contaminants in paint samples such as lead, chromium and Arsenic. LIBS technology provides a rapid elemental analysis of solids, liquids or slurries, and gases with little or no sample preparation.<sup>[15–18]</sup> In LIBS technique, a strong laser pulse evaporates a small amount of material (typically a few micrograms) under the test by creating a plasma plume. The light emitted by plasma is spectrally resolved to determine the chemical composition of the sample material. There are many processes that occur when a pulsed laser beam interacts with any solid material, resulting in intense plasma, such as thermo ionic emission, sample heating, phase change, melting, atomization, excitation and ionization.<sup>[15–18]</sup> This study was focused on the analysis of paint samples utilizing our LIBS system for environmental and other analytical applications which is a continuity of our group activities for development of laser based pollution monitoring systems.<sup>[16–22]</sup> The schematic diagram of our LIBS experimental setup for detection of hazardous elements in paint samples is depicted in Figure 1. The LIBS setup applied in this work has been described in detail in our previous publications and is briefly described here.<sup>[16–22]</sup> The light from the plasma spark is collected by a collimating lens using UV graded fused silica 1 meter, multimode sampling fiber with SMA connector is transferred to LIB2000 + Spectrometer (Ocean Optics). Our LIBS 2000 + has 4 spectrometer modules to provide high resolution (FWHM 0.1 nm) in the 200 nm to 620 nm wavelength region. The detector has a gated CCD camera with

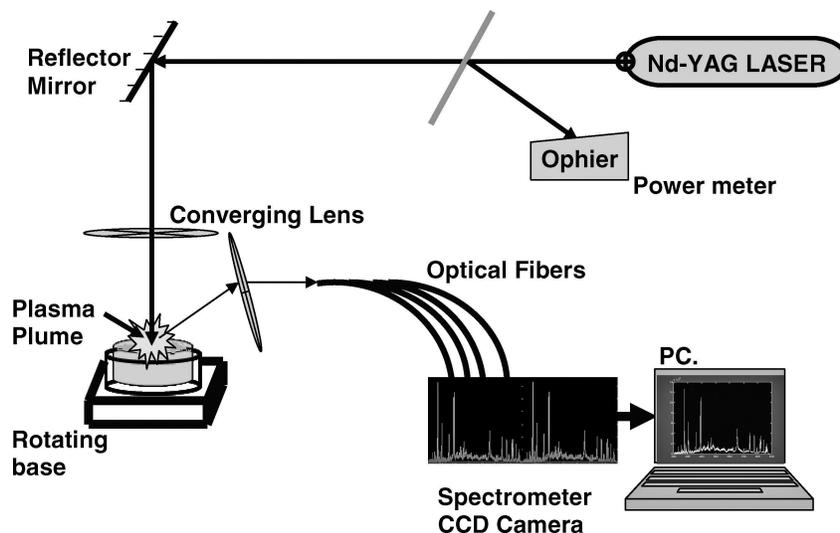


Fig. 1. Schematic diagram of the experimental setup applied for the analysis of paint samples.

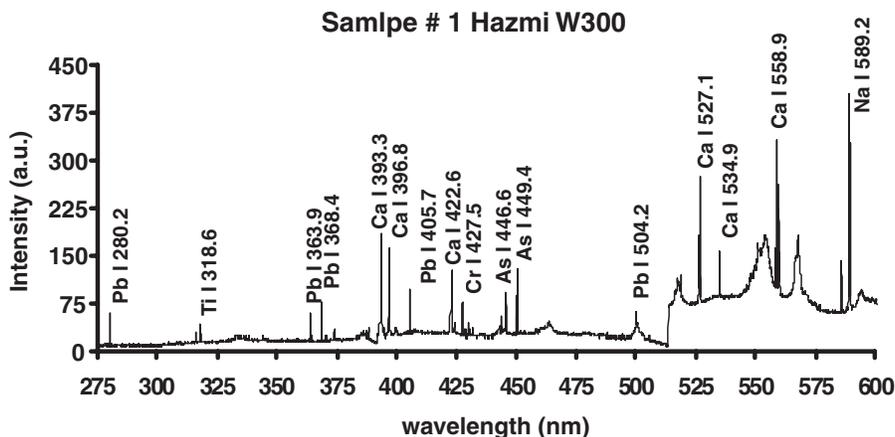


Fig. 2. Typical LIBS Spectra of paint sample # 1 manufactured in local Saudi plant in the region of 275 to 600 nm recorded at delay time of 2.0  $\mu$ s and laser pulse energy 80 mJ.

130 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 reads the data from the chip and  
 reconstructs the spectrum. This makes it possible to mea-  
 135 sure a large wavelength range (200–620 nm) simultaneously  
 with high spectral resolution (0.1 nm). The software pro-  
 vides elements identification through a spectral database  
 for qualitative measurements. Samples can be quickly mea-  
 sured and saved to log-file. Options allow customization of  
 spectral search algorithms.  
 140 Custom compound element libraries can be created or  
 searched using LIBS 2000+ spectrometer. A Q-switched  
 Nd-YAG laser (Spectra Physics Model GCR 100) operat-  
 ing at 1064 nm wavelength was employed as an excitation

source. 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 1064 nm is tightly focused on  
 the target sample using a convex lens to create a spark or  
 breakdown in the sample. The laser energy was measured  
 with a calibrated energy meter (Ophir model 300) for the  
 study of dependence of LIBS signal on incident laser energy.  
 In this experiment, we placed a 2 mm diameter aperture in-  
 side the path of laser beam in order to get a uniform beam  
 shape. The pulse energy utilized in this experiment was in  
 the range of 50 mJ–125 mJ. A lens of 25 mm diameter and  
 35 mm focal length was used to focus the laser beam on the  
 155 pellet samples under investigation. The exposed area on the  
 sample was about 150  $\mu$ m in diameter.

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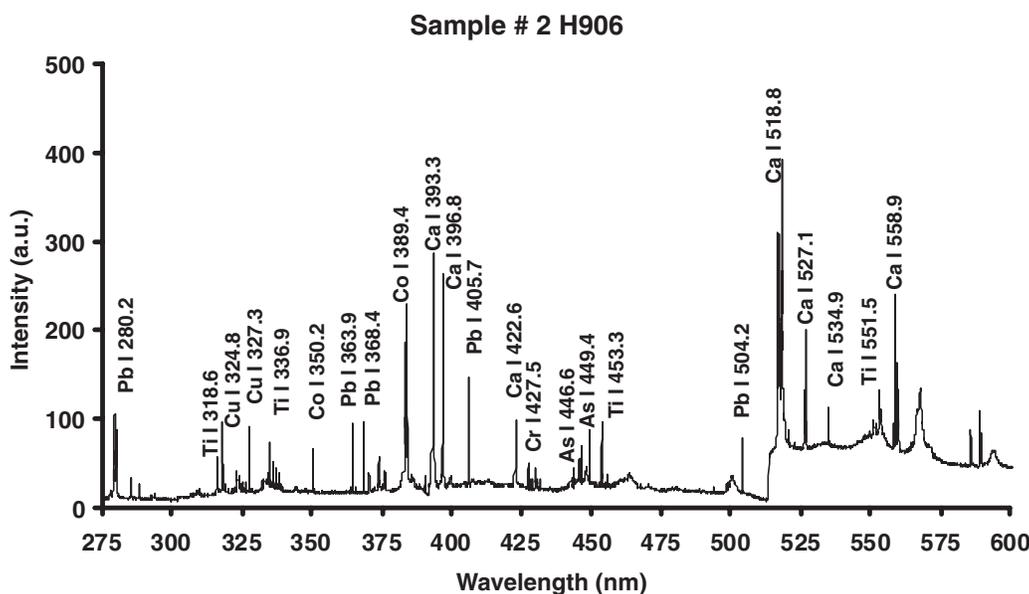
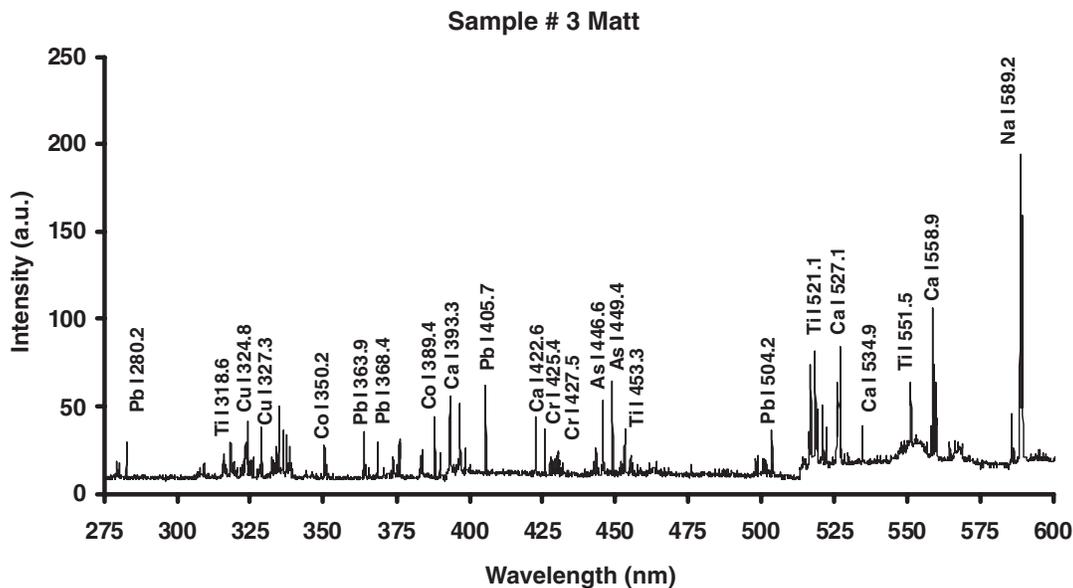


Fig. 3. Typical LIBS Spectra of paint sample # 2 manufactured in local Saudi plant in the region of 275 to 600 nm recorded at delay time of 2.0  $\mu$ s and laser pulse energy 80 mJ.



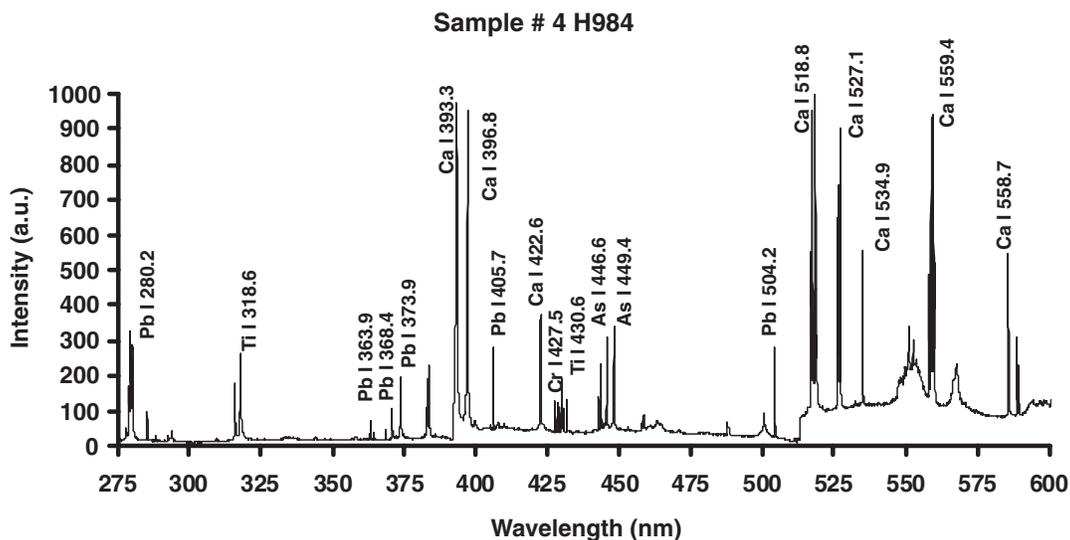
**Fig. 4.** Typical LIBS Spectra of paint sample # 3 manufactured in local Saudi plant in the region of 275 to 600 nm recorded at delay time of 2.0  $\mu$ s and laser pulse energy 80 mJ.

## Results and discussion

160 The detection limit of any analytical instrument should  
 165 be enough to detect the trace amounts of individual elements present in the sample. This detection limit can vary greatly, according to the transitional strength of the elemental line, delay time (time between the firing of the laser pulse and the opening of the camera shutter) and the gate width (time for which the shutter is open) selected during the measurements, the sample matrix, and collection optic geometry, etc. Experiments were performed to find

optimal conditions of temporal delay, incident laser energy to achieve best detection limit prior to the analysis of different paint samples under investigation. LIBS spectra of  
 170 different paint samples were recorded over a 240–620 nm wavelength range for qualitative and quantitative analysis. The laser pulse energy was fixed at 130 mJ.

The distance between the optical fiber and the plasma  
 175 was 10 mm. The LIBS spectra of the paint samples were recorded to identify each element present in paint sample. The most sensitive lines (finger print wavelength) for identification of elements were found between 275–600 nm



**Fig. 5.** Typical LIBS Spectra of paint sample # 4 produced in local Saudi plant in the region of 275 to 600 nm recorded at delay time of 2.0  $\mu$ s and laser pulse energy 80 mJ.

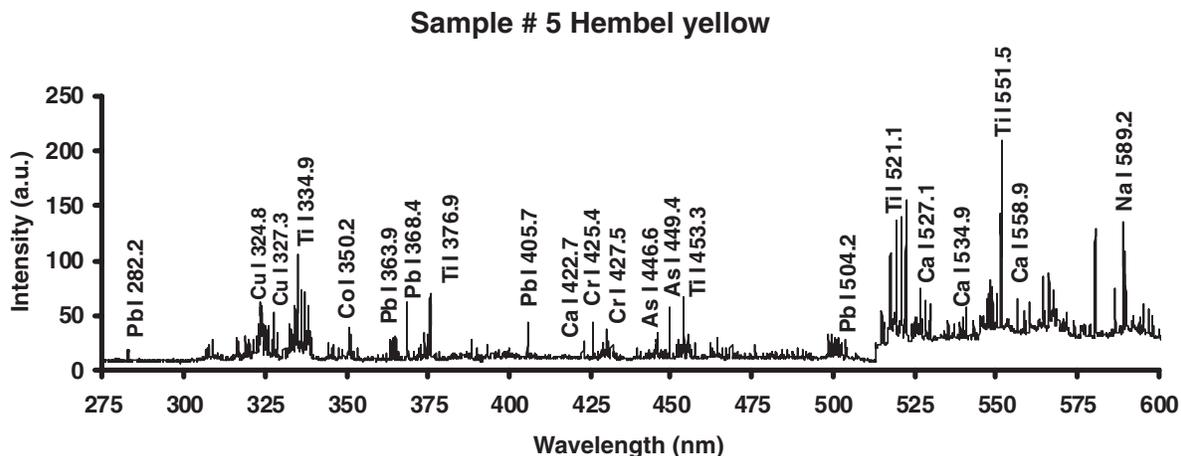


Fig. 6. Typical LIBS Spectra of paint sample # 5 produced in local Saudi plant in the region of 275 to 600 nm recorded at delay time of 2.0  $\mu$ s and laser pulse energy 80 mJ.

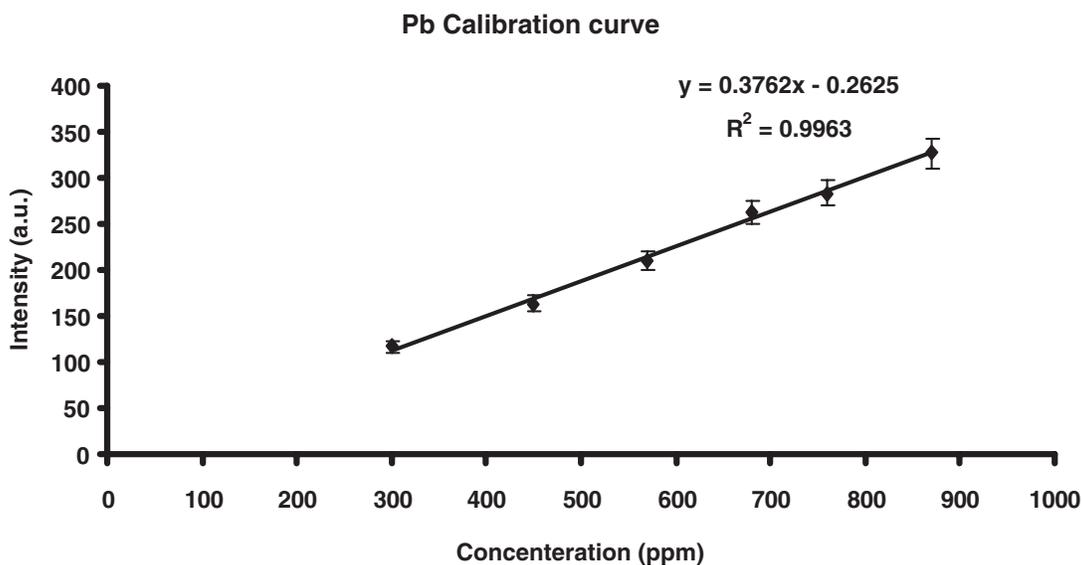


Fig. 7. Calibration curve for lead concentrations in paint samples.

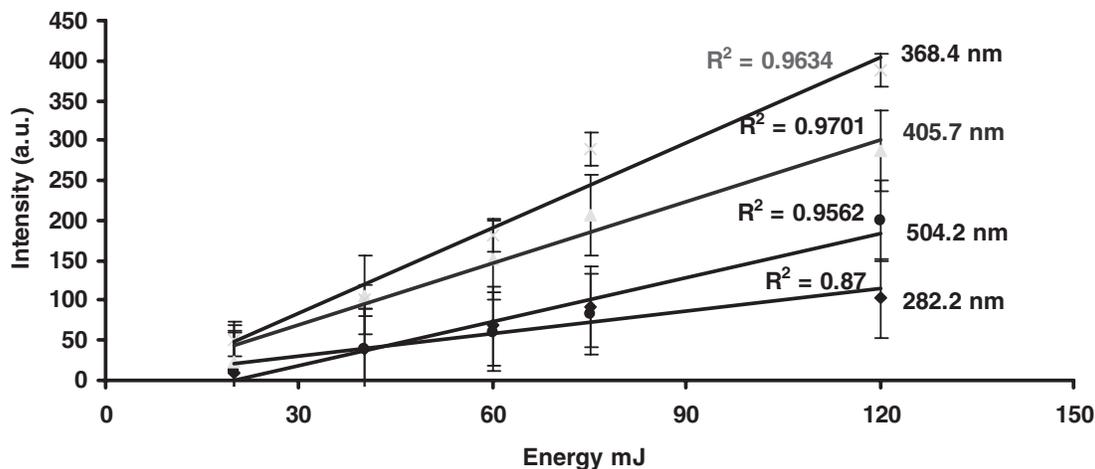


Fig. 8. Energy dependence for lead lines.

**Table 1.** Elements detected in paint samples along with their wavelengths and transition probability.

Element	Wavelength (nm)	Intensity (a.u.)	Transition	E.	Transition probability
Pb	405.8	252.7	$6s^2 6p^2 \rightarrow 6p_{1/2} 6p_{3/2}$	9.2	8.9E+07
As	449.4	339.8	$4p^3 4s_{3/2} \rightarrow 4p^3 2D$	5.2	0.55E+08
Cr	427.5	124.9	$3d^5 4s \rightarrow 3d^5 4p$	2.9	3.07E+07
Ti	318.6	114.6	$3d^2 4s^2 \rightarrow 3d^3 ({}^4F) 4p$	3.89	8.0 E+07
Ca	422.7	371.3	$3p^6 4s^2 \rightarrow 3p^6 4s 4p$	2.9	2.18E+08

180 region using NIST database and reference.<sup>[34]</sup> The finger-  
 185 print wavelength (as specified in Table 1) for each element  
 of interest was selected to study the effect of different exper-  
 imental parameters. These selected finger print wavelengths  
 for analysis purpose were 428.9 nm for chromium, 405.8 nm  
 for lead, 449.4 nm for arsenic and 318.6 nm for titanium  
 190 respectively. The wavelengths for all these elements are in-  
 dicated on the spectrum (Figs. 2–6) and are listed in Table 1  
 with their wavelengths and transition probability. For each  
 data point, an average spectrum for 20 laser pulses was  
 recorded. The energy dependence of four lines for lead is  
 depicted in Figure 8. The recording of the averaged spectra  
 reduces the background noise to a great extent as compared  
 to the single-shot spectrum of the sample. (Figs. 2–6) depict  
 the typical spectrum recorded with our setup for the paint  
 samples no 1, 2, 3, 4 and 5 in the 275–600 nm region.

#### 195 *Calibration curves for lead in samples under investigation*

In order to draw a calibration curve for our LIBS system  
 following procedure was adopted. Six samples of known  
 concentration in different weight percents (wt. %) of lead  
 under investigation were prepared in the matrix of paint  
 200 by adding the known concentration of lead and they were  
 mixed to be homogenous and dried in a pallet form. The  
 LIBS spectra were recorded for these 6 concentrations of  
 each element. All these spectra were recorded with an aver-  
 age of 20 laser shots at 3 different locations on the sample  
 205 surface. The calibration curve for lead under investigation  
 was established by plotting the LIBS signal intensity of  
 specific transition of lead (405.7 nm) as a function of the  
 lead concentration. A typical calibration curve for Pb in-  
 side paint matrix is presented in Figure 7. The LIBS signal

intensity showed linear dependence ( $R^2 \geq 0.998$ ) on the  
 concentration of Pb in the standard samples as predicted  
 theoretically.<sup>[17–22]</sup>

The line interference is the most problem for emission  
 identification, thus we chose those lines for analysis that  
 are free from interference or those which have minimal  
 215 effects to get better results.

#### *Concentration of different toxic contaminants detected with LIBS and ICP in paint samples*

After calibration of our LIBS spectrometer, the concentra-  
 tion of each element was determined with our LIBS setup,  
 which is also listed in Table 3 and has been confirmed by  
 the analysis using standard analytical technique such as  
 ICP. The values obtained with our LIBS setup are well in  
 agreement with the ICP results. The concentration of lead  
 measured with our system is in the range of 327.2–755.3  
 225 ppm, which is quite high as compared with the standard  
 permissible safe limit of 600 ppm set by the EPA and other  
 regulatory authorities. The highest value of Pb = 755.3 ppm  
 was detected in the yellowish colored sample of paint. Lead  
 could be found in the paint due to the use of lead chromate  
 in the paint production process for pigment purposes.

Lead could be found in the effluent in the following forms  
 such as:  $Pb^{2+}$ ,  $PbCr_2O_7$  (the solubility of lead dichromate is  
 very high),  $PbCrO_4$  (pigment, the solubility of lead Chromate  
 is low, about  $7 \times 10^{-6}$  g/100 g water) and  $Pb(Ac)_2$   
 235 (the solubility of lead acetate is very high and is about  
 55 g/100 g water). However LIBS system cannot distin-  
 guish between these different forms of lead and could de-  
 tect only the elemental compositions of trace metals present  
 in the test sample. Similarly, for chromium; the maximum  
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**Table 2.** Elements detected in paint sample1 with the limit of detection and maximum detected concentrations and the permissible safe limit set by the US FDA and EPA.

Elements detected in paint samples	Wavelength (nm) <sup>a</sup>	Comparison of LIBS and ICP and relative accuracy (RA)			Standard deviation (S.D.) LIBS	Limit of detection LOD of LIBS (ppm)	Maximum detected concentration in LIBS (ppm)	Safe Permissible limits (ppm)
		LIBS (ppm)	ICP (ppm)	RA				
Pb	405.7	634.6	633.78	0.08	0.99	2.55	755.3	600
As	449.4	258.1	256.61	0.18	0.97	3.7	258.1	10
Cr	428.9	98.1	97.5	0.10	0.99	3.9	149.5	1
Ti	318.6	80.5	81.73	0.12	0.98	4.6	287.2	—
Ca	422.5	1181.5	1182.25	0.19	1.12	5	1181.5	—

**Table 3.** Toxic elements detected in paint samples collected from local Saudi market and comparison of LIBS with ICP results.

Element	Wavelength (nm)	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
		LIBS ppm	ICP ppm								
Pb	405.7	634.6	633.78	349.3	348.57	527.2	526.48	455.3	454.52	671.7	670.28
Cr	427.48	98.1	97.5	123.1	122.4	120	119.7	149.5	148.6	136.8	135.8
As	449.4	258.1	256.61	72.2	70.13	57.6	56.51	39.2	38.56	53.3	52.37
Ca	422.6	981.5	982.25	930.1	930.8	916.1	915.2	995.2	994	967.3	965.8
Ti	318.6	79.8	81.73	56.8	57.72	43.3	42.08	187.2	188.5	188.5	189.83

permissible limit is 1 ppm and the detected value in the paint samples was ranging 98.1–149.5 ppm. In summary this high concentration of chromium in the paint is found due to the manufacturing of lead chromate which is used

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Although chromium, in limited amounts, is an essential nutrient that helps the body use sugar, protein, and fat, breathing high levels of chromium, however, can cause irritation to the nose, and cause runny nose, nosebleeds, ulcers and perforations in the nasal septum. Ingesting large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage, even death. Skin contact with certain chromium compounds can cause skin ulcers. For people who are extremely sensitive to chromium, allergic reactions consisting of severe redness and swelling of the skin have been noted.<sup>[30,31]</sup> The safe permissible limits for Pb and Cr for water and other food products are 5, 15 and 100 parts per billions while the concentration detected in this study in various paint samples listed in Table 1 is much higher than these safe permissible limits which is a matter of great concern. It is worth mentioning that LIBS spectrometer developed at our laboratory and the standard method like ICP applied for comparative study are both elemental analysis techniques and one could not predict the complex nature of these metals present in paint matrix. For such studies other different spectroscopic techniques are already available that are not the purpose of this study.

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The precision of any analytical instrument is defined as the repeatability of the analyte measurement, and is usually estimated in LIBS with the relative standard deviation (RSD) as follows:<sup>[31,32]</sup>

$$\text{RSD} = \frac{\text{standard deviation}}{\text{mean}} \quad (1)$$

For paint samples, the precision of LIBS measurements depends on the complexity and homogeneity of the sample, and the reproducibility of the laser shots. Typical values for LIBS are in the range of 1–7%.<sup>[23–31]</sup> For precision of our results for the 5 paint samples, the same method was adopted as applied for the analysis of samples like lipstick and ore samples; the precision was found to be 2–5%.<sup>[10–14]</sup>

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The accuracy of an analytical method is defined as the measured experimental values that are true or close to the accepted “actual” values. Generally speaking, the accuracy

of any measurement or analytical technique is defined as the percentage difference between the experimental values measured with LIBS and the actual values measured with a standard method like ICP.

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The details of the method applied for determination of accuracy of our results regarding concentration of toxic contaminants and other trace elements is discussed in depth in our earlier publications using crude oil, different binding materials and plastic samples.<sup>[16–22]</sup> For the 5 paint samples studied in this work, the transition probabilities, intensities and energy levels for each fingerprint wavelength of each element detected are depicted in Table 1 and the values obtained by 2 methods (ICP and LIBS as presented in Table 3 are in good agreement with in the 5–6% error limit.

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## Conclusions

This study demonstrated that despite large efforts to reduce the lead concentration in paints for housing units, the lead concentration detected in 5 paint samples of 3 different brands synthesized locally was as high as 755.3 ppm, which exceeded the safe permissible limit (600 ppm) set by the Environmental Protection Agency (EPA). Exposure to leaded paint is a great threat to children, especially when the paint is deteriorated and leaded dust is created. Children could eat paint chips directly or indirectly ingest lead-contaminated house dust or soil through normal hand-to-mouth contact.<sup>[35–38]</sup> The U.S. government has recently put the lead-based paint on the first place as a source for children lead poisoning (Seaqert et al., 2003) and introduced a series of regulations by Federal or State Governments.<sup>[38]</sup> The numbers of samples that exceeded the limit of 600 ppm were three out of five samples under investigation samples.

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## Acknowledgments

The support by the Physics Departments and King Fahd University of Petroleum and Minerals is gratefully acknowledged though project IN 080410. One of the author (M.N) is thankful to KFUPM for its hospitality and permission to work at its research facilities also the team is

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315 thankful to KACST and prince Dr. Turkey Al-Saud for his support in ICP analysis at KACST Laboratories.

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