

# Detection of highly toxic elements (lead and chromium) in commercially available eyeliner (kohl) using laser induced break down spectroscopy



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## ABSTRACT

A sensitive laser induced breakdown spectroscopic system was developed and optimized for using it as a sensor for the detection of trace levels of lead and chromium present in the cosmetic eyeliner (kohl) of different price ranges (brands) available in the local market. Kohl is widely used in developing countries for babies as well adults for beautification as well eyes protection. The atomic transition lines at 405.7 nm and 425.4 nm were used as the marker lines for the detection of lead and chromium respectively. The detection system was optimized by finding the appropriate gate delay between the laser excitation and the data acquisition system and also by achieving optically thin plasma near the target by establishing the local thermodynamic equilibrium condition. The detection system was calibrated for these two hazardous elements and the kohl samples under investigation showed 8–15 ppm by mass of lead and 4–9 ppm by mass of Chromium, which are higher than the safe permissible levels of these elements. The limits of detection of the LIBS system for lead and chromium were found to be 1 and 2 ppm respectively.

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## 1. Introduction

The use of kohl as a cosmetic for the eye makeup is more of a tradition in the East, particularly in the Indian sub continent, the Arabian Peninsula and the North Africa and the people of all age group including very young children use this material [1,2]. Kohl is also used as a home remedy to treat many ocular discomforts like conjunctivitis, eye soreness and light sensitivity. Naturally the major chemical component of kohl is lead (II) sulfide (galena) and in addition to this, many elements are added to it for coloring and softness during the manufacturing and chromium is one of the most common coloring agents added to the commercially available kohl [3–7]. Although the health hazards of lead had been known for centuries, only recently the steps were taken to restrict its use in our day to day products. The use of lead has been increasingly banned or phased out from the very common products like paint, gasoline and hundreds of other products in many countries. Excessive use of lead causes physical, mental and behavioral problems in human and is injurious to the nervous system, red blood cells, bones, kidney and even affect human reproduction [8–12]. Exposure to chromium beyond the permissible level can cause respiratory irritation, cancer, liver damage and pulmonary

congestion [13–15]. These toxic metals can easily enter the human body through inhalation, ingestion, and skin exposure, and the children are more prone to absorption by gastrointestinal tracts [16]. It is worth mentioning that safe maximum permissible limits for lead and chromium are 0.5 ppm and 1 ppm respectively [17].

Several analytical techniques such as energy dispersive X-ray fluorescence [6], Atomic absorption spectrometry [2], Neutron Activation Analysis, Inductively Coupled Plasma (ICP), microwave induced plasma (MIP) etc have been applied to study the elemental composition of cosmetic products. All these analytical techniques require tedious sample preparation methods and while doing so, the actual chemical composition of the sample is often lost, and particularly when we are interested in the trace level of contaminant in any sample, the results become quite unreliable. Laser Induced Breakdown Spectroscopy (LIBS) is a versatile method capable of analyzing sample in its original form and thereby catching up from their point of limitations of other techniques in terms of prolonged sample preparation that could lead to the modification of chemical composition of the original sample. LIBS is basically an atomic emission spectroscopy, capable of characterizing the elemental composition of a sample by recording the atomic transition lines of neutral and ionized atomic species. Plasma plume on the sample surface is created by a high power pulsed laser, and at the very initial stage after the laser excitation, the plasma is said to be hot, as it contains all the components of a

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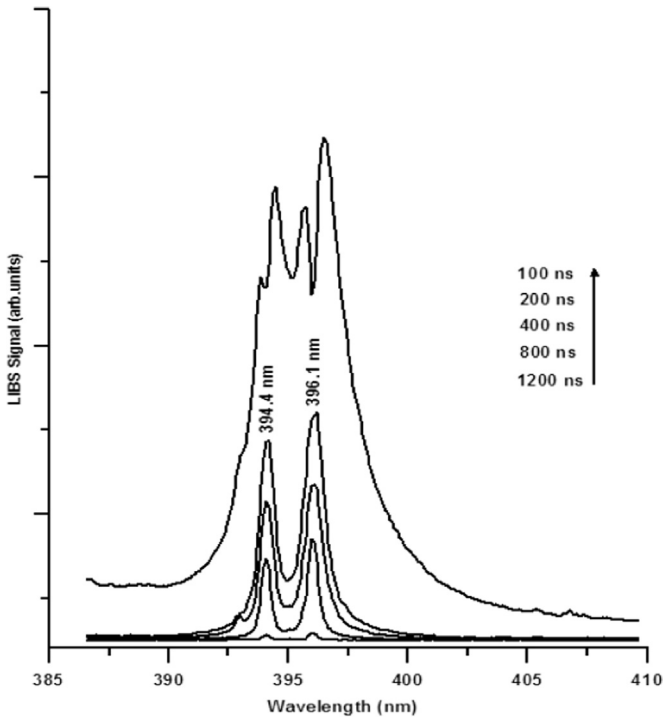


Fig. 1. LIBS signal of Al-I 394.4 nm and Al-I 396.1 nm with various time delays between the laser excitation and signal acquisition.

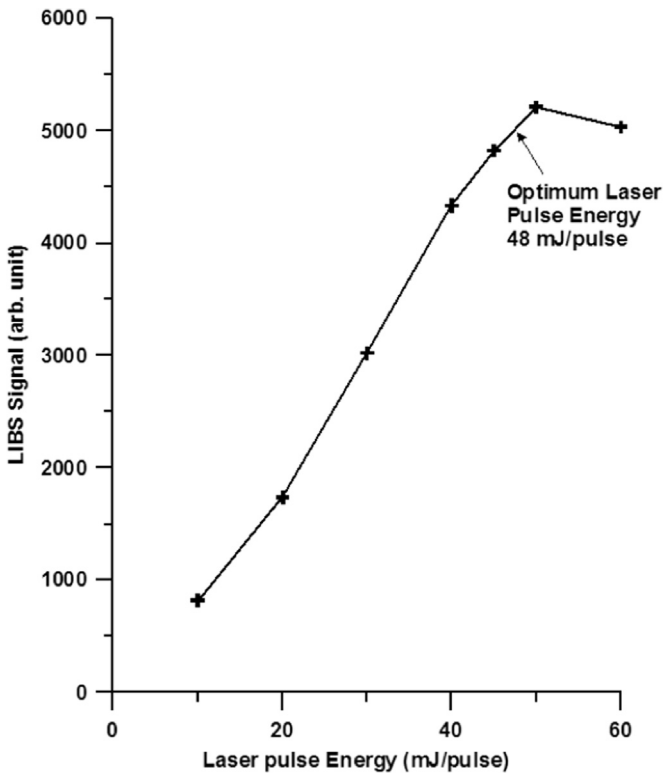


Fig. 2. LIBS signal intensity versus Laser pulse energy for Pb-I 405.7 nm atomic transition line.

typical plasma giving rise to an undecipherable broad continuum emission. In order to avoid this, in LIBS, we let the plasma cool down and start characterizing the sample after few micro seconds and record emissions only from the neutral, and sometimes from the ionized atoms.

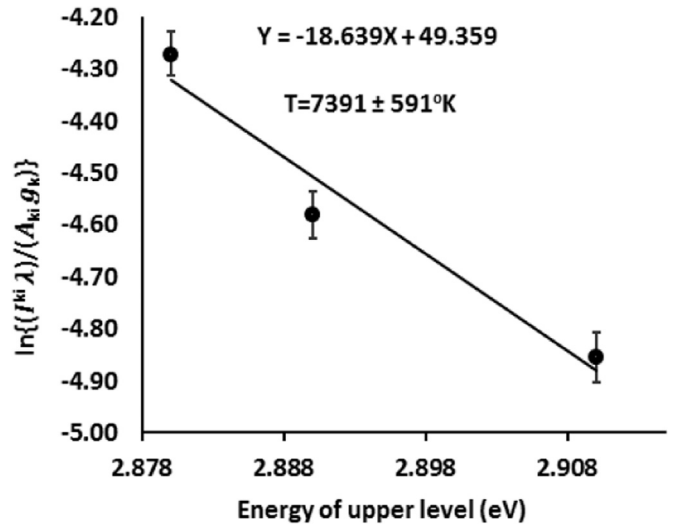


Fig. 3. Boltzmann plot for calculating the plasma temperature of electron.

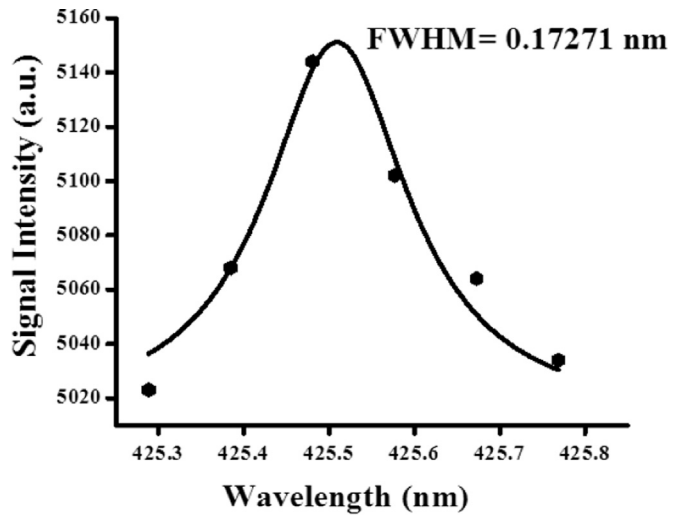


Fig. 4. Stark broadened profile of Cr I (425.4 nm) used for electron number density calculation.

In this study, we developed a sensitive LIBS system capable of detecting trace levels of lead and chromium present in the kohl of different price ranges available in the local market. For ethical reasons, the brand names of the product are kept anonymous and instead, the samples are labeled with numbers. A strong persistent atomic transition line of neutral lead (Pb I) at 405.7 nm and a strong persistent transition line of neutral chromium (Cr I) at 425 nm were used as the marker atomic transition lines to detect and quantify lead and chromium. The sensitivity and the accuracy of the LIBS detector were insured by achieving optically thin plasma by establishing the local thermodynamic equilibrium (LTE) condition of the plasma plume [18]. The LIBS system was calibrated for lead and chromium and the limit of detection of the system was found to be 1 ppm and 2 ppm respectively. Using the LIBS system and the calibration curves for lead and chromium, we found that in the random kohl samples purchased from the local market, the levels of lead ranges between 8–15 ppm and the levels of chromium are in 4–9 ppm range.

## 2. Experimental methods

The laser wavelength of 266 nm from a frequency quadrupled Nd: YAG laser with 8 ns pulse duration and 20 Hz pulse repetition

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