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Detection of Pb in Whitening Creams via Laser Induced Breakdown Spectroscopy

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ABSTRACT

Recently whitening creams have been widely used to protect UV light exposure due to the depletion of ozone layer. The demand attracts the rapid growth of various whitening creams in the market. The detection is required in order to determine the constituent of the whitening cream, whether it contains dangerous element like heavy metal (Pb, Hg or Cr).In this attempt, laser induced breakdown spectroscopy (LIBS) technique was deployed to analyse the existence of heavy metal. Several whitening creams available in retail shop and open market were investigated. Cryogenically frozen technique was utilized to convert the emulsion into solid form. Lead Pb was detected in all the tested samples in the range of 2 – 5 ppm. The LIBS results were validated by Inductive Couple Plasma Mass Spectroscopy (ICP-MS) technique. The high sensitivity, portable and in-situ LIBS system allow simple, faster and easy heavy metal detection. This enhances the procedure of inspection in cosmetic industries.

Keywords: LIBS, Whitening Cream, Lead, ICP-MS, concentration.

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1. Introduction

In recent years, the depletion of ozone layer makes the ultraviolet rays become stronger than ever. Excessive exposure to ultraviolet rays leads to human health, especially skin problem including sunburns, skin cancer, skin ageing and pigmentation [1]. Hence, whitening cream is widely used for skin treatment. Various kind of white creams are commercially available either in supermarket to the retail store with different range of prices. Whitening cream contains ingredients that might be harmful to health and cause permanent skin damage. Generally preferable creams in the society, those are offered faster and cheaper product especially among the young ones for seeks of beauty and confident, without concerning much on the side effect. There is blooming demand on skin lightening products that are toxic-free. However, they are more costly due to their expensive ingredients. Japan and Pacific are big markets for high quality skin lightening products imported from Europe. The publics especially the young ones, may not afford to purchase the high quality cream. Thus they prefer to buy in retail outlet and open market which are not provable and controlled by any health agency.

Normally, to be more effective and aggressive results the white creams are added with various chemical compound including heavy metals (Hg, Pb, Fe, Al, Cr, Cd, Zn, Co, Cu, Snand Ag). The element of heavy metal can easily cause health problems. In addition, long term use of any skin whiteners can cause increase pigmentation in joints of the fingers, toes, buttocks and ears. Also the skin of the face can become thinned and the area around the eyes can have increased pigmentation leading to bleach panda effect [2].

Lead (Pb) for example affects virtually every system in the body such as the reproductive, neurological, hematopoietic, hepatic, and renal systems [3]. More than 90% of the lead in the body burden is localized in bone with an average half-life of more than 20 years [4]. Bone releases lead during periods of increased bone turnover in women's liver, like pregnancy, lactation, and menopause [5]. Lead can also cross the placenta during pregnancy and can cause intrauterine fetal death, premature delivery and low birth weight [6]. Furthermore, the consequences of accelerated bone loss during menopause due to decrease in oestrogen production may place women at increased risk for high of lead levels [7].

More than 2,000 years, lead poisoning has been a recognized health hazard. Lead toxicity including anaemia, colic, neuropathy, nephropathy, sterility and coma. Exposure to low levels of lead has also been associated with behavioural abnormalities, learning impairment, decreased hearing, and impaired cognitive functions in humans [8]. Although FDA does monitor lead levels in consumer products, the levels of lead above FDA limits can have injurious effects, especially in sensitive populations like infants, children, pregnant women, and women of child bearing age. Lead is most dangerous to foetuses, babies and children, whose nervous systems are still developing. Lead is absorbed slowly into body, its rate excretion is even slower. Thus, with constant exposure, lead can be accumulated gradually in the body. It is absorbed by the red blood cells and is circulated through the body where it becomes concentrated in soft tissues, especially in the liver and kidneys [9].

There are numerous researches have been conducted in analysing the cosmetic products like whitening cream using different techniques [3-9]. In conventional techniques normally are expensive and required long procedure for sample preparation. Thus alternative approaches are needed to overcome the drawback. In this attempt, a new technique is introduced to analyse heavy metal in whitening cream. Laser induced optical breakdown spectroscopy LIBS is conducted to detect one of the toxic element such lead in whitening cream.

LIBS is a widely used as an analysing technique for the elemental composition of materials in solid, liquid and gaseous state [10]. Moreover, LIBS can be developed as a field-portable technology that can be applied for in-situ characterization which is direct detection to the samples [11]. LIBS is a technology in which a laser beam is directed at a sample surface to create a high-temperature plasma and a detector used to collect the spectrum of light emission from plasma and record its intensity at specific wavelength [12]. On the other hand, LIBS is a direct analysis technique for solid samples that does not require time-consuming pre-treatment of samples [13]. These advantages make the LIBS technique particularly interesting for cosmetics analysis.

Laser induced breakdown spectrometer (LIBS) was developed for detection of hazardous contaminants in whitening creams such as lead in this study. LIBS is a powerful analytical technique that can be used for the characterization and detection of materials. In LIBS, a focused laser beam is used to create a plasma plume on the surface of solid and liquid samples or inside the sample volume of gases, liquids, and aerosols. Each excited atom in the plasma emits a unique set of spectral lines, especially in the optical region of the spectrum. Therefore, this optical emission can be collected and analysed to determine the chemical composition in the sample. A LIBS plasma can be generated as a single event using only one laser pulse or using repetitive laser pulses [14]. There are many processes that occur when a pulsed laser beam interacts with any solid material resulting in intense plasma, like phase change, thermo ionic emission, sample heating, melting, ionization, atomization, and excitation [9].

2. Experimental

A schematic diagram of a single pulse LIBS spectrometer is presented in Figure 1. A Q-switched Nd:YAG laser manufactured by FP Medical Technology Co., Ltd. (Hong Kong) was employed as a source of plasma. The laser was focused using a lens of 80 mm focal length to create an optical breakdown and plasma formation. The fluorescence of plasma radiation was collected via a collimated lens and sends the light signal through 2 m glass optical fiber with 600 µm in diameter. The light signal was detected by CCD camera provided in a MAYA 2000PRO Spectrometer manufactured by Ocean Optics with resolution of 0.2 nm. The spectrometer detected in the range of 200 to 700 nm of UV-Visible range. All

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the spectral lines were used to identify the elements by comparing them with NIST database. The spectrometer was coupled to a personnel computer and analysed the signal via Spectra Suite software.

The Q-switched Nd:YAG laser was operating at a fundamental wavelength of1064 nm with pulse duration of 10 ns. The laser is running in repetitive mode at the rate of 1 Hz. The output energy of the laser is remained constant at 97 mJ. A target is placed at defocused distance of 2 cm away from the focal point. In such position the beam size is enlarged to avoid thermal damage. The whole experimental set-up is shown in Figure 1.

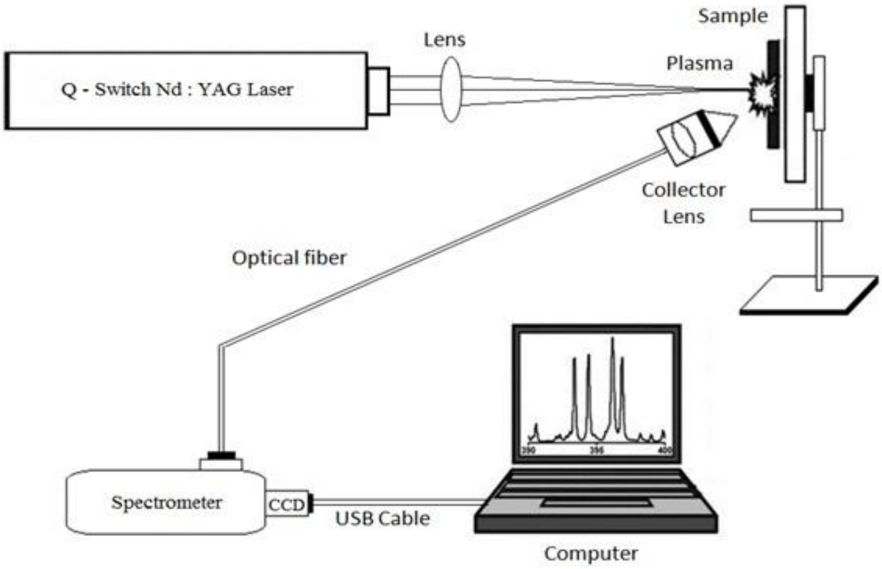

Fig. 1: Experimental setup for recording the LIBS spectra of cream sample

2.1 Samples preparation and the reagents used for LIBS and ICP-MS analysis

Six whitening creams were obtained from various retail shops and open market in Johor Malaysia. The brand name is blinded and labelling as A, B, C, D, E and F respectively. The whitening cream is in the form of an emulsion. It required preparation prior to analyse using LIBS technique. The sample of cream was painted on a glass slide and cryogenically frozen in refrigerator at temperature of -5°C for overnight. The cryogenic frozen sample was then immediately irradiated with laser light at 5 different positions on the same target. This is accomplished in order to get an average of spectral lines produced from each sample. The number of accumulated laser pulses of each sampling spot was optimized. The spectral lines of the six cream samples were identified using NIST Atomic Spectra Database.

A conventional method using ICP-MS was also conducted for comparison purposed. In this technique, 0.1g of contaminated whitening cream sample was digested in 0.2 ml sulphuric acid of 99.99% purity to get the lowest concentration. The digestion was reduced in volume while heating at 80°C for 15 minutes and then diluted to a final volume by top-up with ultra-pure water until 50 ml. The resulting solution of the sample was analysed for various metals using ICP-MS calibrated by using reference standards.

In preparation a standard curve for LIBS system, Pb powder was deposited into whitening cream matrix. The lowest Pb contained from the tested cream (which identified based on ICP-MS technique) was chosen as a matrix cream. Various concentrations were prepared by weighting the mass of Pb powder in the range of 20-100 μg and mixed into 1 g of cream matrix in order to provide the concentration in the range of 20-100 ppm. The same procedure of cryogenically frozen was followed for converting the emulsion into solid sample.

3. Results and discussion

Typical emission spectra for all brands of whitening cream sample are shown in Figure 2. The LIBS spectra of the whitening cream samples were recorded to identify each element present in it. In this experiment only lead line was studied. The most sensitive lines for identification of lead elements were found between 240 – 520 nm regions using NIST database. In this study Pb line at 310.2 nm was selected.

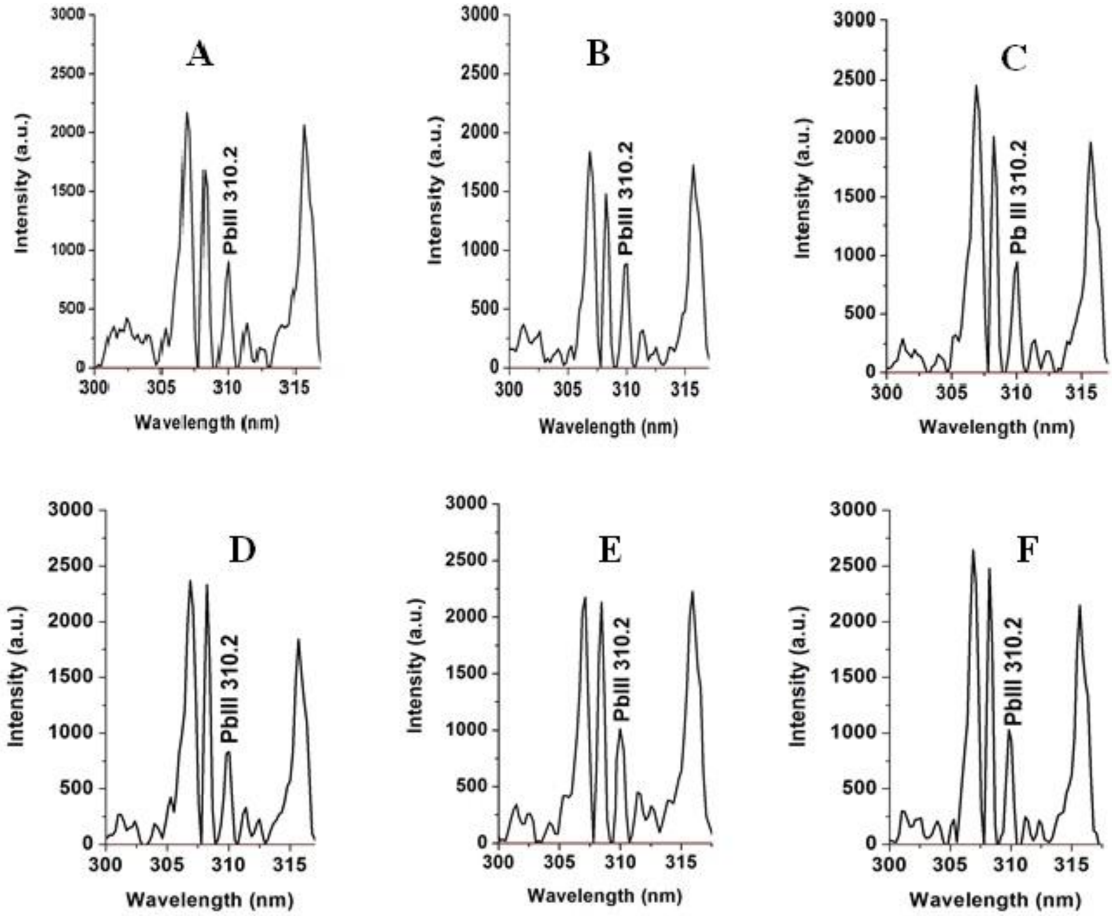

Fig 2: LIBS spectrum of the whitening cream sample A - F.

3.1 Calibration curve for lead elements

In this experimental work, six samples of known Pb concentration in weight percent were prepared in selected whitening cream matrix. The Pb powder was mixed to have homogenous distribution in the emulsion prior to cryogenically frozen in refrigerator. Harden whitening cream samples were focused by Q-switched Nd:YAG laser. The high energy density of the focused beam is energetic enough to excite and cause plasma formation. The fluorescence of plasma radiation is collected by collimated lens and cascading into CCD camera provided in the spectrometer. Each spectra-line is a finger print for each constitute element of the interaction target, in this case the frozen whitening cream. The intensity of the spectral line is found proportional with the Pb concentration. Thus the larger the concentration of Pb in whitening cream matrix, the higher is the intensity of the spectrum line. The calibration curve for lead element in different concentration is presented in Fig 3.Such calibration curve is used to determine the concentration of Pb for unknown whitening cream.

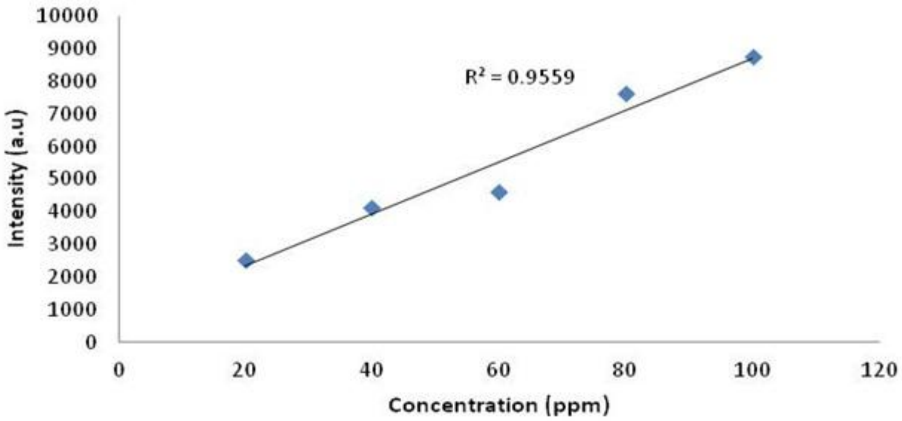

Fig 3: Calibration curve for Pb obtained by using standard samples of Lead in whitening cream with known concentration.

3.2 Comparison LIBS and ICP-MS technique

The laser induced breakdown spectroscopy technique was employed to determine the Pb concentration in various whitening creams. The spectrum each of the sample is shown previously in Fig 2. The intensity of Pb spectrum at line 310.2 nm for each sample was measured. The calibration curve (Fig 3) is utilized to identify the Pb concentration in each sample based on its intensity. The same sample of whitening creams were also analysed using ICP-MS technique. Both results from LIBS and ICP-MS are presented in histogram of Fig 4. The comparison between the two results has clearly shown the similarity. This is also indicated that the LIBS result is validated by the standard technique using ICP-MS.

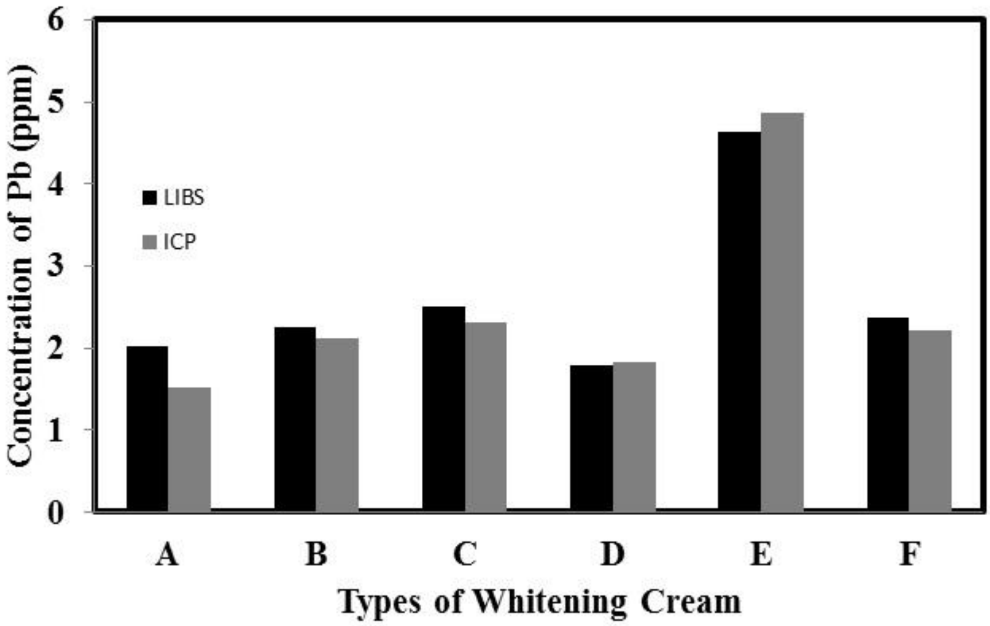

Fig 4: Comparison of concentration of lead detected with LIBS and ICP-MS technique

The concentration of Pb measured by LIBS technique is found to be in the range of 2.0 –5.0 ppm. The highest Pb concentration of 4.64 ppm is obtained from Sample E. According to Malaysia standard MS 526-2009 Act 1983 and Food Regulation 1985 the minimum Pb contaminant is allowable to be provided in any colouring food is < 2 mg/kg (20 ppm) based on report by International life Science Institute Southern Asia Region for Malaysia [15]. Thus the Pb concentrations in all the tested creams according to Malaysia standard are under permissible limits.

Other country like Sri Lanka, under the Sri Lanka standard SLS report that for Skin creams and lotions, the maximum permissible level of Pb in pigments and color additives given under SLS457: Part 1 (coloring agents, pigments and color additives generally recognized as safe) is 20 mg/kg (20 ppm or 0.002 percent) [2]. This is the same as Malaysia standard. On the other hand, World Health Organization WHO in 1972 has set even lower limit for tolerable daily intake is only allow 5µg/kg (0.05 ppm or 0.0005 percent) of body weight/day for total Pb which is the toxic heavy metal included in whitening cream.

Overall Pb was detected in all tested samples in this study with concentration found to be in the range of 2 to 5 ppm which above limit set by WHO but still safe regarding the Malaysia and Sri Lanka Standard. These are considered low level of contamination, comparing to the maximum permissible level for colouring agents in externally applied cosmetics as set by MS 526. However since Pb is toxicity, is better to take precaution not to continuously use these cosmetics. The health implications of the use of these cosmetics can only be properly assessed by monitoring the levels of these toxic metals in the blood and urine samples of the group engaged in the practice [16].

The present study indicate that the use of facial cosmetics exposes users to low levels of heavy metals of which Pb is of most toxicological concern. Understanding the consequences of low-level human Pb poisoning will depend upon an accurate assessment of the pervasiveness of toxicity in the global population. This will require that toxicity thresholds be determined as well as an understanding of the mechanisms underlying toxicity [17]. Education of parents and childcare workers regarding the risks of administering lead-based substances to mankind needs to be incorporated into health and healthcare framework systems in developing nations.

In conclusions, this study has revealed that continuous use of these cosmetics could result in an increase in the trace metal levels in human body beyond acceptable limits. Efforts should be made at enlightening the users and the general public on the dangers involved.

4. Conclusions

The determination of heavy metal like Pb in whitening cream obtained from retail shop and open market in Johor Malaysia was carried out by using Laser Induced Breakdown Spectroscopy (LIBS) technique. Six different of whitening creams were analysed and found that the Pb concentration in the range of 2 – 5 ppm. The LIBS results are validated by the ICP-MS technique. The high sensitivity and simplicity of the technique might open opportunity to consider LIBS system as heavy metal detection in cosmetic industry. The detection of Pb in the tested creams is under permissible limit as set by Malaysia standard. However, the limitation is over as set by WHO (0.05 ppm) for daily used. So it is better to take precaution because continuously applied such creams may lead to accumulative toxicity in the body beyond the acceptable limit.

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