Detection of Harmful Metal Elements in Rice Using Laser Induced Breakdown Spectroscopy

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Abstract. Transportation of toxic elements from air, water and soil is the main reason for agriculture crops pollution. Therefore, fast detection of heavy metals is very important for ensuring the quality and safety of crops. Laser-induced breakdown spectroscopy (LIBS), coupled with univariate and multivariate analysis, was applied for quantitative analysis of Cr, Pb, Cu and Cd in twelve kinds of rice available in local markets. Qualitative and quantitative analysis of the samples were achieved by using the locally developed LIBS set up equipped with Q-switched Nd: YAG laser and optical spectrum analyzer. Atomic absorption spectrometry (AAS) was used not only to validate the analysis results but also to establish the essential calibration curves. Distribution pattern of detected metals and possible contamination sources were analyzed by radar plot and multivariate statistics including PCA. In this study, harmful metals have been analyzed in all samples. The average content for harmful metals were 0.040 mg/kg for chromium (VI), 0.051 mg/kg for lead, and 0.041 mg/kg for copper and 0.043 mg/kg for cadmium.

Keywords Harmful metals, Laser based spectroscopy, Rice analysis.

1. Introduction

Minerals and other chemical elements present in food affect human health, some of which have a useful and known biological function, while others have indefinite biological function and may be harmful to human health [1, 2]. Human exposure to heavy metals (HMs) in general is more through food and water, due to their transmission through the food chain [3]. It has been found that these minerals accumulate in the body at rates related to the amount of contaminated food consumption. Therefore, food safety has become a critical issue in both public opinion and scholarly research [4, 5]. As a main food around the world, Rice considered an important route of toxic elements exposure to human, leading to a high probable health risk [5]. It has been reported that the irrigation water system, soil, pesticides and factory waste are the major sources of rice contamination [6]. Surely, knowledge of the
percentages of containing this crop of heavy elements, especially cadmium, lead, chrome, cobalt, nickel, arsenic and mercury may contribute to hazard detection and control [7]. Although, the most common approach for the investigation of elemental composition of food are atomic absorption spectroscopy AAS and induced couple plasma ICP [8, 9], laser based technique has been recently proven to be pioneer method for qualitative and quantitative analysis for all substances [10]–[12]. In this context, Kim et al [13] applied LIBS to quantify nutrients (Mg, Ca, Na, and K) in spinach and rice and to discriminate pesticide-contaminated products in a rapid manner Kabir et al [14].

Detection of Harmful Metal Elements in Rice Using Laser Induced Breakdown Spectroscopy 3 investigated Laser induced breakdown spectroscopy (LIBS) method to determine the elemental content of rice and husk which were collected from the agricultural land in Gazipur in Bangladesh. While, Wahid et al [15] used LIBS for fast detection of calcium in rice. This study aimed at introducing a novel analytical approach using laser based spectroscopy for rice elemental analysis. Rapid quantitative determination of harmful metals was performed for some types of locally growing rice with respect to some imported rice. LIBS data will be utilized to establish a relationship between LIBS intensity and the concentration of metals and to classify the different types of rice also.

2. Materials and Methods

Twelve samples locally growing and imported rice were collected from markets. They have differences in rice varieties, grain size, and country of origin as shown in Table 1.

At first rice samples were grounded and sieved before they were pressed into pellets. With no binding agent, 5 grams of each sample was weighed, put into the circular iron die with 1.0 cm and transformed into pellets by applying 7 MPa pressure for 3 minutes. The ground rice and the produced pellet are shown in Fig 1. An atomic absorption spectrometer (model: PerkinElmer Analyst 400 was used for quantitate analysis of samples.

![Rice samples](image)

**Figure 1.** Rice sample, Basmati Thailand (R<sub>1</sub>) and Nasiriyah anber Iraq (R<sub>3</sub>).

**Table 1.** Types of rice samples examined in this work.

| Sample | Varieties of rice | Country of origin |
|--------|-------------------|-------------------|
| R<sub>1</sub> | TH Basmati | Thailand |
| R<sub>2</sub> | Gold Basmati | Thailand |
| R<sub>3</sub> | Nasiriyah anber | Iraq |
| R<sub>4</sub> | Babylon anber | Iraq |
| R<sub>5</sub> | Najaf anber | Iraq |
| R<sub>6</sub> | Maysan anber | Iraq |
| R<sub>7</sub> | Kalat | Iran |
| R<sub>8</sub> | Stara | Iran |
| R<sub>9</sub> | Krdea | Iran |
| R<sub>10</sub> | Aklemia | Iran |
| R<sub>11</sub> | Basmati rice | India |
| R<sub>12</sub> | Indian Basmati | India |
A schematic diagram of the LIBS system used in this work is shown in Fig 2. This setup consists of Nd:YAG laser (pulse energy of 150 mJ with a pulse width of 9 ns at a wavelength of 1064 nm), multimode fiber optics, focusing lens and a spectrometer (Model: HR4000, Ocean Optics) having a spectral resolution of 0.1 nm FWHM and working at spectral region from 200 nm to 600 nm.

![LIBS Experimental Setup](image)

**Figure 2.** LIBS Experimental Setup.

### 3. Results and Discussion

LIBS spectra of twelve rice samples were acquired in the UV to Visible region (200 to 600nm) after adjusting the LIBS setup for maximum signal intensity. Six of these spectra were used to construct calibration curves according to spectral intensities of Pb, Cd, Cr and Cu emission lines and their concentrations in rice sample previously measured by AAS. Fig. 3 shows the LIBS spectra where different emission lines are considered and labeled by comparison atomic translations of the assigned emission lines with that of NIST universal data base [16]. Regarding each specific spectrum, there was different relative emission intensities from these elements. Table 2 presents the specific wavelengths and spectral intensity for each detected elements in two samples R₁ and R₃.

**Table 2.** Wavelengths and spectral intensity of heavy metals found in rice samples R₁ and R₃.

| Sample | Wavelengths (nm) | Average Spectral Intensity (a.u) |
|--------|------------------|----------------------------------|
|        |                  | R₁    | R₃    |
| Pb     | 373.99           | 70    | 100   |
| Cd     | 346.60           | 80    | 190   |
| Cr     | 534.50           | 95    | 99    |
| Cu     | 450.59           | 220   | 150   |
Fig. 3 presents calibration curves (C.C) for detected elements. In these curves LIBS intensity of Pb, Cd, Cr and Cu in different rice six rice samples are plotted versus element concentrations that previously measured by AAS analysis. The particular emission lines used were: Pb @ 373.99nm, Cd@ 346.6nm, Cr@ 534.5nm and Cu@450.59nm. For quantitative analysis, the unknown concentration of heavy metals in rice samples can be detected by utilizing the linear correlation of C.C [17]. The results of detected elements present in six examined samples at particular wavelengths, the concentration detected with LIBS set up and with standard method AAS are tabulated in Table 3.
Figure 4. Calibration curves (C.C): the intensity of emission lines of (a) Pb at 373.99 nm (b) Cd at 346.6 nm (c) Cr at 534.5 nm (d) Cu at 450.59 nm presented in six samples versus AAS concentration in ppm of these samples.

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### Table 3 List of detected elements in examined rice samples.

| Element | Sample | Fingerprint wavelength (nm) | AAS (ppm) | LIBS (ppm) | Error % |
|---------|--------|-----------------------------|-----------|-------------|---------|
| Pb      | R1     | 373.99                      | 0.013     | 0.012       | 4.00    |
|         | R2     |                             | 0.015     | 0.016       | 6.66    |
|         | R3     |                             | 0.022     | 0.020       | 2.20    |
|         | R4     |                             | 0.024     | 0.023       | 4.16    |
|         | R5     |                             | 0.029     | 0.031       | 6.80    |
|         | R6     |                             | 0.036     | 0.035       | 2.77    |
|         | R7     |                             | 0.063     | 0.060       | 6.30    |
|         | R8     |                             | 0.075     | 0.070       | 6.66    |
|         | R9     |                             | 0.082     | 0.085       | 3.52    |
|         | R10    |                             | 0.077     | 0.080       | 3.80    |
|         | R11    |                             | 0.028     | 0.030       | 7.10    |
|         | R12    |                             | 0.019     | 0.020       | 5.26    |
| Cd      | R1     | 346.60                      | 0.024     | 0.025       | 2.88    |
|         | R2     |                             | 0.031     | 0.030       | 3.22    |
|         | R3     |                             | 0.072     | 0.070       | 2.77    |
|         | R4     |                             | 0.079     | 0.080       | 1.25    |
|         | R5     |                             | 0.083     | 0.088       | 6.02    |
|         | R6     |                             | 0.071     | 0.070       | 1.40    |
|         | R7     |                             | 0.059     | 0.052       | 11.8    |
|         | R8     |                             | 0.053     | 0.050       | 5.66    |
|         | R9     |                             | 0.039     | 0.040       | 2.50    |
|         | R10    |                             | 0.041     | 0.045       | 8.88    |
|         | R11    |                             | 0.032     | 0.035       | 9.30    |
|         | R12    |                             | 0.028     | 0.030       | 7.14    |
| Cr      | R1     | 534.50                      | 0.049     | 0.045       | 8.10    |
|         | R2     |                             | 0.038     | 0.040       | 5.26    |
|         | R3     |                             | 0.085     | 0.088       | 8.50    |
|         | R4     |                             | 0.086     | 0.088       | 2.32    |
|         | R5     |                             | 0.063     | 0.061       | 3.10    |
|         | R6     |                             | 0.063     | 0.065       | 3.17    |
|         | R7     |                             | 0.011     | 0.010       | 9.00    |
|         | R8     |                             | 0.021     | 0.020       | 4.76    |
|         | R9     |                             | 0.020     | 0.022       | 10.0    |
|         | R10    |                             | 0.019     | 0.020       | 5.25    |
|         | R11    |                             | 0.019     | 0.020       | 5.20    |
|         | R12    |                             | 0.011     | 0.010       | 9.09    |
| Cu      | R1     | 450.59                      | 0.082     | 0.088       | 7.31    |
|         | R2     |                             | 0.088     | 0.090       | 2.27    |
|         | R3     |                             | 0.010     | 0.011       | 10.0    |
|         | R4     |                             | 0.011     | 0.010       | 10.0    |
|         | R5     |                             | 0.012     | 0.011       | 8.30    |
|         | R6     |                             | 0.019     | 0.017       | 10.5    |
|         | R7     |                             | 0.016     | 0.017       | 9.60    |
|         | R8     |                             | 0.039     | 0.038       | 2.25    |
|         | R9     |                             | 0.039     | 0.037       | 5.10    |
|         | R10    |                             | 0.035     | 0.037       | 5.57    |
|         | R11    |                             | 0.093     | 0.090       | 3.20    |
|         | R12    |                             | 0.083     | 0.080       | 3.36    |

The average content for harmful metals detected by LIBS were 0.04 mg/kg for chromium, 0.051 mg/kg for lead, 0.041 mg/kg for copper and 0.043 mg/kg for cadmium. These values were quite comparable to that measured by AAS with slight relative errors in the range of (1.25-11.8%). This point out the potential of LIBS method for multipurpose analysis. It is
important to refer that the concentration of these harmful elements detected in this work were within the safe permissible exposure limits [18].

In Fig. 5 Radar plots are constructed based on the concentrations of Pb, Cd, Cr, and Cu to display a fingerprint on the distribution of these metals at different geographical sites [19].

![Radar plots obtained using the total concentration.](image)

**Figure 5.** Radar plots obtained using the total concentration.

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It is difficult to use only one variable to differentiate the rice origin. Therefore, in this study a radar plot was applied to classify the geographical origins of rice. From distribution of elemental pattern in Figs.5 (a, d) there is a clear increase in the copper concentration in both Thai and Indian rice. While, there was an increase in the elements of cadmium and chromium in the Iraqi rice as shown Fig.5 (b). Lastly, a strong increase in lead levels were revealed in the Iranian rice as shown in Fig.5 (c).

Concerning multivariate analysis based on PCA [20], the first two components are taken into account that represent about 90% of the variance, HMs correlated along the sample set which illustrate that their concentrations varied similarly. In Fig. 6, it is noticed that there are three distinctive groups based on metal concentrations. In first group (R1, R2, R11 and R12) was depended on high copper concentrations, similar trend showed from radar plot explained above. Moreover the second group (R7, R8, R9 and R10) concerning Iranian rice showed high levels of lead. The last group (R3, R4, R5 and R6) represent the local rice growing in various regions showed a high levels of cadmium and chromium. The observations relevant to local rice are consistent with our previous findings reported by Ghazai et al. [21] and Hamad et al. [22] in which higher concentration of heavy metals in soil was owing to emission of dust and gases during combustion process in gas station and cement factories located near cultivated rice regions. Although it is difficult to determine the reasons that lead to contamination with the heavy elements of rice, the data obtained from this research would be useful in distinguishing the sorts rice of from each other and furthermore valuable in knowing the new rice from that old or stock badly.
Figure 6. The PCA results for heavy metal concentrations in the 12 different rice samples.

4. Conclusion:

The concentrations of Cr, Pb, Cu and Cd in 12 rice samples collected from local markets were analyzed by a lab built laser induced spectroscopy LIBS technique. The obtained LIBS data was verified by using Atomic absorption spectrometry (AAS). A strong correlation calibration curves was established and utilized in rapid and accurate quantitative analysis of all samples. Based on elevated levels of HMs, notable differences were observed between Iraqi rice and imported rice. Multivariate analysis were able to characterize the contamination resources and classification in different origin. The results indicated that HMs levels of all studied rice samples were within the permission limits and safe for food consumption.

Detection of Harmful Metal Elements in Rice Using Laser Induced Breakdown Spectroscopy 1.

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