

# Detection of Nutrient Elements and Contamination by Pesticides in Spinach and Rice Samples Using Laser-Induced Breakdown Spectroscopy (LIBS)

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**ABSTRACT:** The laser-induced breakdown spectroscopy (LIBS) technique was applied to quantify nutrients (Mg, Ca, Na, and K) in spinach and rice and to discriminate pesticide-contaminated products in a rapid manner. Standard reference materials (spinach leaves and unpolished rice flour) were used to establish a relationship between LIBS intensity and the concentration of each element (Mg, Ca, Na, and K) (i.e., calibration line). The limits of detection (LODs) for Mg, Ca, Na, and K were found to be 29.63, 102.65, 36.36, and 44.46 mg/kg in spinach and 7.54, 1.76, 4.19, and 6.70 mg/kg in unpolished rice, respectively. Concentrations of those nutrient elements present in spinach and unpolished rice from a local market were determined by using the calibration lines and compared with those measured with ICP-OES, showing good agreement. The data also suggested that the LIBS technique with the chemometric method (PLS-DA) could be a great tool to distinguish pesticide-contaminated samples from pesticide-free samples in a rapid manner even though they have similar elemental compositions. Misclassification rates were found to be 0 and 2% for clean spinach and pesticide-contaminated spinach, respectively, by applying the PLS-DA model established from the training set of data to predict the classes of test samples.

**KEYWORDS:** *laser-induced breakdown spectroscopy (LIBS), nutrient elements, pesticide, agricultural products, internal standardization, partial least squares-discriminant analysis (PLS-DA)*

## ■ INTRODUCTION

Elemental analysis of agricultural products has been conducted due to the importance of food security as well as nutritional status.<sup>1–3</sup> It is well-known that insufficient inputs of macronutrients and/or micronutrients degrade the quality of the product and can also adversely affect plant growth, thereby reducing crop yields. Mg deficiency can cause chlorosis and impair shoot and root growth. Na is essential for some plant species due to its role in preventing damage to mesophyll chloroplasts.<sup>4</sup> In some cases, it can be used as a substitute for K, which is used for cell expansion.<sup>4</sup> K plays an important role in resistance to drought. Moreover, plants suffering from K deficiency showed chlorosis and necrosis. Ca is an important element used to deliver nutrients into the plant. Ca deficiency results in deformation and chlorosis of leaves. In the worst case, even necrosis can be observed. Although symptoms caused by Ca deficiency were not easily visible, it can be inferred from declined growth at the beginning and chlorosis and necrosis at later stages.<sup>5</sup>

In addition, agricultural products can be contaminated by pesticides, which can adversely affect human health. Pesticides are known to be carcinogenic and toxic, and the endocrine system can be disturbed by pesticides.<sup>6</sup> The use of pesticides has increased, especially in developing countries.<sup>7</sup> Once a pesticide is introduced into the ecosystem, it can be found in various environments such as surface and ground waters, soils, and atmosphere.<sup>6,8,9</sup> Thus, detection of pesticide-contaminated products is also important to protect human health and the ecosystem.<sup>10</sup>

Conventional methods such as inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and atomic absorption spectrometry (AAS) have been used to determine elemental composition of agricultural products after a series of extractions of their bulk samples. Those techniques are relatively time-consuming (not real-time measurement), and complex sample preparation steps are required.<sup>11,12</sup> Also, detection of pesticide-contaminated products by such methods has been difficult because the measured elements were often overlapped with those existing in products. The laser-induced breakdown spectroscopy (LIBS) technique has emerged as an alternative method for the rapid elemental analysis of various samples such as gas, solid, liquid, aerosol, and biological substances and for discrimination or classification of samples using elemental distribution.<sup>11–19</sup>

The main objective of this study is to evaluate the feasibility of the LIBS technique for the rapid quantitative analysis of nutrient elements in spinach and rice and for the discrimination of pesticide-contaminated products from clean ones in a rapid manner. Standard spinach leaves and unpolished rice flour samples and their mixtures with lactose anhydrous having various amounts of nutrient elements were used for establishing a relationship between LIBS intensity and the concentration of

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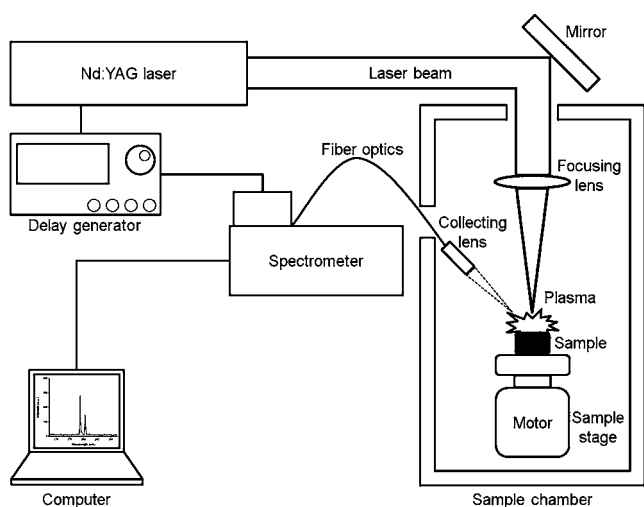
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major elements (Mg, Ca, Na, and K) (i.e., calibration line). To minimize shot-to-shot variation of the LIBS emission lines and matrix effect of products, the emission line of interest was typically normalized by the intensity of a specific element (i.e., standard normalization method), which often results in improvement of linearity of the calibration line.<sup>16</sup> Then, concentrations of nutrient elements present in spinach and rice from a local market were determined by the LIBS and compared with those measured with ICP-OES. Also, LIBS emission spectra of pesticide-contaminated spinach were measured, and a chemometric method (e.g., partial least squares-discriminant analysis (PLS-DA)) was applied to discriminate the contaminated sample from a clean sample.

## MATERIALS AND METHODS

A schematic diagram of the LIBS system used in this work is shown in Figure 1. It mainly consists of a pulsed laser, optics, a delay generator,



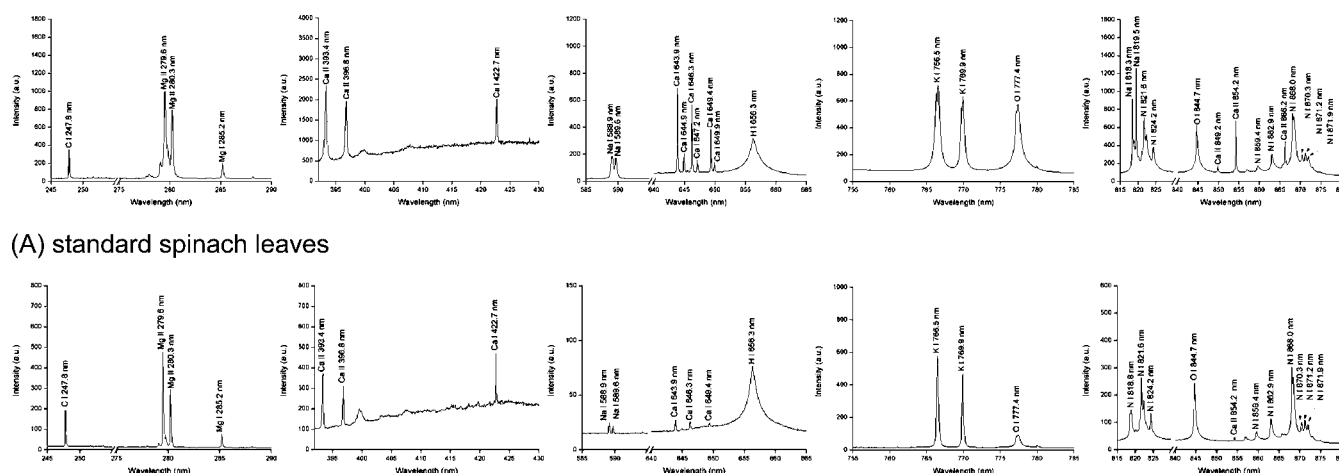
**Figure 1.** Schematic of the current LIBS system.

a spectrometer, and a solid sample chamber equipped with a rotating sample holder. The Q-switched Nd:YAG laser, which can deliver a maximum pulse energy of 650 mJ with a pulse width of 7 ns at a wavelength of 1064 nm and a repetition rate of 10 Hz (Surelite II-10,

Continuum Inc.), was used as an excitation source. In this study, spinach and unpolished rice samples were analyzed using laser pulse energies of 80–140 mJ. The laser beam was focused by a 90 mm focal length plano-convex lens. The emitted light from plasma was collected by a collimating lens and was transferred to a broadband spectrometer measuring emission lines from 200 to 980 nm with a spectral resolution of 0.1 nm (LIBS 2000+, Ocean Optics). During measurements, the sample holder was automatically rotated to provide a fresh surface of a pellet sample to minimize any crater effect.<sup>20,21</sup> Fifty spectra per sample were collected. An internal standard method,<sup>16</sup> which is often used for correction of nonlinear calibration curves by normalizing LIBS signal of the target element by that of an internal standard element in a sample, was applied to minimize shot-to-shot variations and matrix effects.

Powders of spinach leaves (NIST SRM 1570a) (Mg, 8900 mg/kg; Ca, 15270 mg/kg; Na, 18180 mg/kg; and K, 29030 mg/kg) and unpolished rice flour (NIES CRM 10-c) (Mg, 1250 mg/kg; Ca, 95 mg/kg; Na, 14 mg/kg; and K, 2750 mg/kg) were used as standard samples to obtain a calibration line for quantification of their constituent elements by LIBS. Those samples were usually mixed with lactose anhydrous (Fluka, Germany) having only C, H, and O constituents. The lactose was used only to dilute standard samples to obtain calibration curves for quantification of nutrients. This was done to obtain a range of mass concentrations of nutrient elements by diluting standard samples with the lactose anhydrous. The standard material and mixture were made as pressed pellets under a pressure of 40 kN for 3 min. The powder was pelletized to provide a more uniform sample surface to obtain more stable LIBS emissions.<sup>22</sup> To prepare a contaminated sample by pesticide, the standard spinach powder or rice flour was mixed with parathion ( $C_{10}H_{14}NO_5PS$ ), which has been used for the agricultural farming of fruits, wheat, and vegetables. It was banned in several countries due to its high toxicity.<sup>23–25</sup> Ten parts per million of the parathion solution was made by using a mixture of ethanol and deionized (DI) water (1:1, v/v) and spiked in the test samples. The spiked sample was dried for 48 h so that the parathion was sufficiently penetrated into the standard spinach powder prior to preparation of pellet sample. In addition, the spinach sample was spiked with 10 ppm of the fosetyl-aluminum ( $C_6H_{18}O_9P_3Al$ ) solution in DI water in a similar way.

For test samples, spinach and unpolished rice were obtained from a local market. Both samples were washed using a DI water to remove soil and dust from the surface and then dried at a temperature of 110 °C in an oven. After samples were completely dried, they were ground into powder, which is similar to the standard samples described above. The ground samples were filtered through 50 and 200 mesh screens to achieve a similar homogeneity in terms of particle size to the standard



**Figure 2.** LIBS spectra of standard samples of (A) spinach leaves (SRM 1570a) and (B) unpolished rice flour (CRM 10-c).

samples.<sup>22</sup> Note that this sample preparation step is much simpler (i.e., no sample extraction steps) than that employed in the traditional ICP-OES method. ICP-OES (Optima 5300 DV, PerkinElmer Inc.) was used to determine the elemental composition of spinach and unpolished rice. The samples were extracted using 2 mL of HNO<sub>3</sub> (60%) for 24 h. After that, 2 mL of H<sub>2</sub>O<sub>2</sub> (30%) was added, and the samples were heated at 100 °C for 1 h. After that, samples were centrifuged and diluted with deionized water and then analyzed with ICP-OES. Standard reference samples were also analyzed with ICP-OES under the same conditions as a quality control. All reagents used were of analytical grade, and all procedures were repeated in duplicate.

A chemometric method (i.e., PLS-DA) was applied to discriminate samples by using various LIBS emission lines. In PLS-DA, two matrices were used. The X matrix consists of LIBS spectral data, whereas the Y matrix contains the class information that was assigned as either 0 or 1 (binary).<sup>26</sup> The relationship between the two matrices was then determined to develop the PLS-DA model allowing the maximum separation of classes and to predict the class of unknown samples.<sup>27</sup>

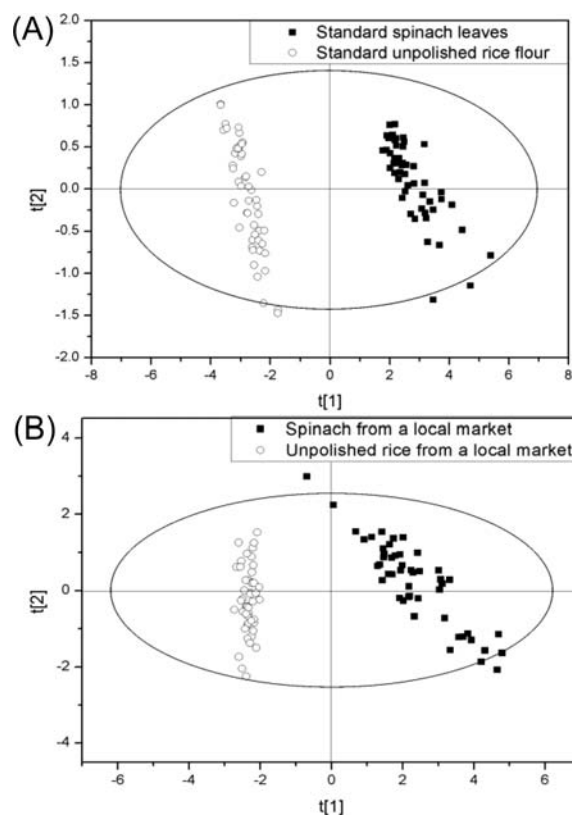
## RESULTS AND DISCUSSION

Figure 2 shows LIBS spectra (50 shot average) of standard samples of spinach leaves and unpolished rice, respectively. As shown, C, H, O, N, Mg, Ca, Na, and K emission lines are identified in both standard samples. Due to higher concentrations of Mg, Ca, Na, and K elements in the spinach sample (Mg, 8900 mg/kg; Ca, 15270 mg/kg; Na, 18180 mg/kg; and K, 29030 mg/kg) than in the rice sample (Mg, 1250 mg/kg; Ca, 95 mg/kg; Na, 14 mg/kg; and K, 2750 mg/kg), their LIBS intensity was much higher than that from the rice sample.

Because both samples have similar elemental components, the detection of specific elements cannot be used to differentiate them. Thus, the distribution of elements in each sample (i.e., multiple LIBS emission lines) was analyzed by using the PLS-DA method to discriminate our samples. Figure 3A shows that spinach and rice samples were clearly separated due to their different distributions of elements, although they had similar elements. The LIBS measurements were also conducted for spinach and rice samples purchased from a local market as shown in Figure 3B. Both samples were also clearly separated, suggesting that the LIBS data for spinach and rice can be used to discriminate them even though they have similar elemental compositions.

For quantification of nutrients of interest, the relationship between the LIBS emission line of a specific nutrient and its concentration must first be determined. The most appropriate LIBS emission lines (i.e., wavelength) for Mg, Ca, Na, and K were selected having highest linearity and sensitivity. For example, LIBS emission lines of Ca at 393.4, 396.8, 422.7, 854.2, and 866.2 nm in the spinach sample tended to be quickly saturated as their concentrations increased, affecting the linearity of the calibration line, and Na at 588.9 and 589.6 nm had low sensitivity. Thus, the 643.9 nm line was selected for Ca, and 819.5 nm was selected for Na. The selected emission lines for quantification of Mg, Ca, Na, and K in spinach and rice samples are summarized in Table 1.

Figure 4 shows the relationship between LIBS signal intensity and concentration for Mg, Ca, Na, and K in spinach samples. With increasing concentration, the LIBS signal intensity increased with a correlation coefficient of 0.88–0.97. The Na line was saturated above 8000 mg/kg (we used the Na calibration line only in the linear range). C, H, O, and N elements, which are elements typically existing in agricultural products, were used to normalize the elements of interest. We found that the normalization of Mg, Ca, and Na elements by O



**Figure 3.** PLS-DA score plots for (A) standard samples of spinach and unpolished rice and (B) spinach and unpolished rice samples from a local market.

in the spinach sample led to improved correlation. One example (i.e., normalization of Mg by O in the spinach sample) is shown in Figure 5A (compare it with Figure 4A). In the case of rice sample, we found that the normalization of elements by C led to improved linearity of the calibration line as shown in Figure 5B. The data suggest that internal standardization with an appropriate selection of normalizing element can be helpful in improving the linearity of the calibration curve.

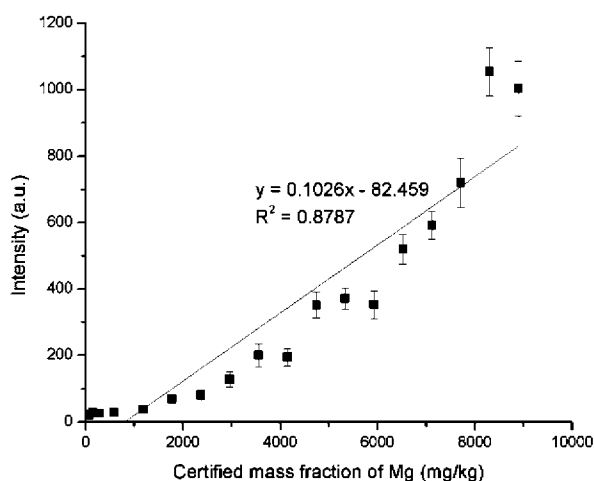
LOD values of those nutrient elements in spinach and rice samples were also determined according to the equation defined as  $2\sigma/S$ , where  $\sigma$  is the standard deviation of the least concentrated sample and  $S$  is the slope of the calibration curve.<sup>28,29</sup> The LOD values of Mg, Ca, Na, and K in spinach samples were found to be 29.63, 102.65, 36.36, and 44.46 mg/kg, respectively, whereas the LOD values of Mg, Ca, Na, and K in rice samples were 7.54, 1.76, 4.19, and 6.70 mg/kg, respectively, as summarized in Table 1. The LOD of elements in spinach samples can be further lowered by using standard samples having much wider concentrations and a similar matrix to test samples. Note that the current standard samples with dilution method were limited to obtain a wide range of concentrations of such elements.

Quantification of Mg, Ca, Na, and K elements in spinach and unpolished rice samples purchased from a local market was conducted with the LIBS technique. However, concentrations of Mg, Ca, Na, and K elements in rice samples and K in spinach samples from a local market were much higher than the linear concentration range in current calibration lines obtained above. Thus, those elements were excluded in the determination of their concentrations. Figure 6 shows concentrations of Mg, Ca, and Na in spinach sample determined by using the calibration

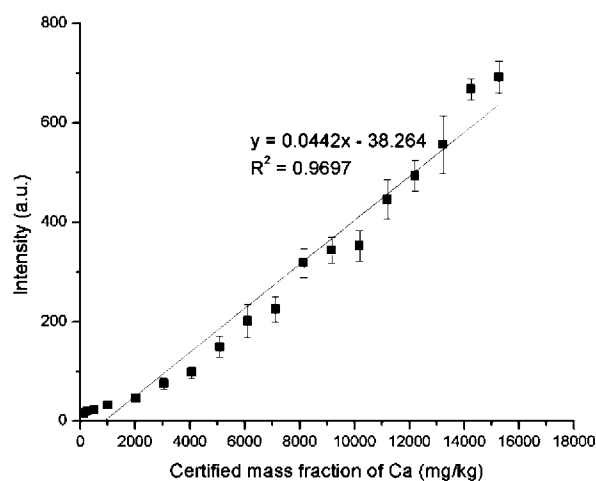
Table 1. Selected Emission Lines for Mg, Ca, Na, and K in Spinach and Unpolished Rice (I, Atomic; II, Ionic)

spinach				unpolished rice			
element	wavelength (nm)	LOD (mg/kg)	SD	element	wavelength (nm)	LOD (mg/kg)	SD
Mg II	279.6	29.63	1.52	Mg II	279.6	7.54	1.66
Ca I	643.9	102.65	2.27	Ca I	422.7	1.76	3.98
Na I	819.5	36.36	5.90	Na I	588.9	4.19	2.01
K I	766.5	44.46	3.25	K I	766.5	6.70	0.74

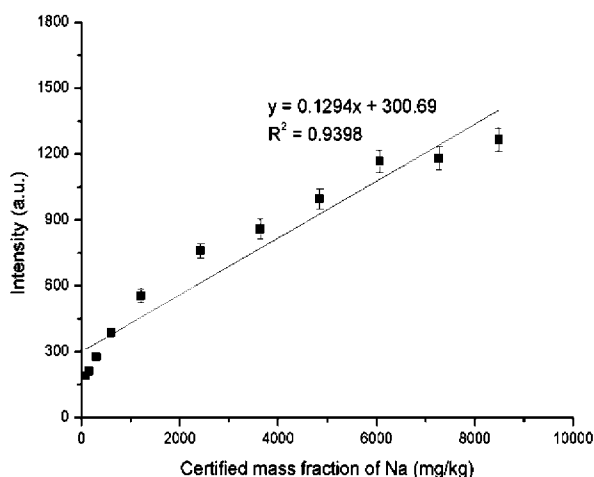
(A) Mg



(B) Ca



(C) Na



(D) K

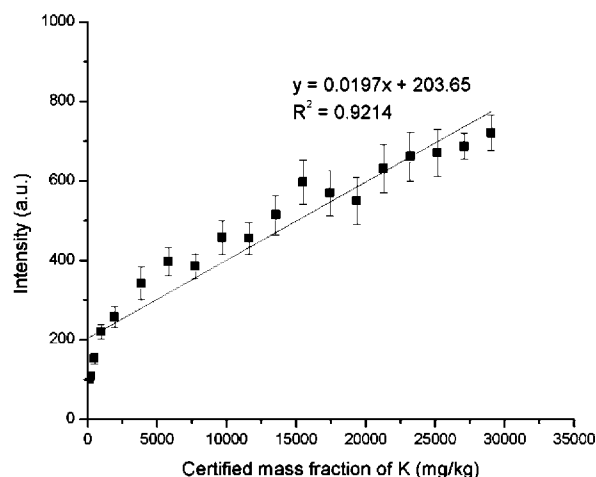


Figure 4. Calibration curves for (A) Mg at 279.6 nm, (B) Ca at 643.9 nm, (C) Na at 819.5 nm, and (D) K at 766.5 nm in spinach samples.

curves obtained above. We also compared their concentrations with values measured with ICP-OES. A reasonable agreement was found between the LIBS and ICP-OES concentrations. ICP-OES was based on bulk analysis of solutions extracted from samples, whereas LIBS detected metals on the sample surface, which might cause disagreements between two independent measurements. By using standard samples having wider concentration ranges and matrices similar to those from a local market to derive calibration lines, the agreement between LIBS and ICP-OES as well as the LODs of each element determined by LIBS will be improved.

LIBS measurements were also conducted for spinach samples contaminated with pesticide (i.e., parathion or fosetyl-aluminum). Because the existing elements in the pesticide

were typically overlapped with the elements in spinach or rice, the detection of new elements cannot be used to identify the existence of pesticide. Instead, the distribution of elements (i.e., the distribution of multiemission lines in the LIBS spectra) could be analyzed for the discrimination of contaminated spinach from clean spinach. The PLS-DA method was applied to discriminate pesticide-contaminated spinach (10 ppm parathion or fosetyl-aluminum-spiked spinach) from clean spinach (nonspiked spinach). The PLS-DA model was developed using 100 spectra of known samples as a training set as illustrated in Figure 7. As shown in Figure 7A, 50 spectra from a spinach sample spiked with parathion and 50 spectra from a nonspiked one were clearly separated. Also, clean spinach and spinach spiked with fosetyl-aluminum were

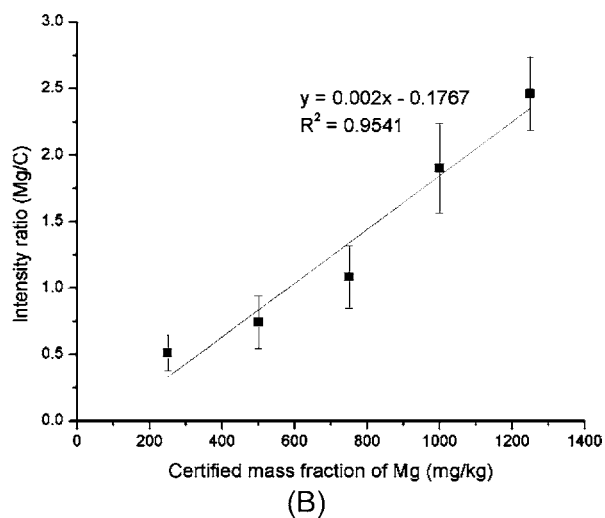
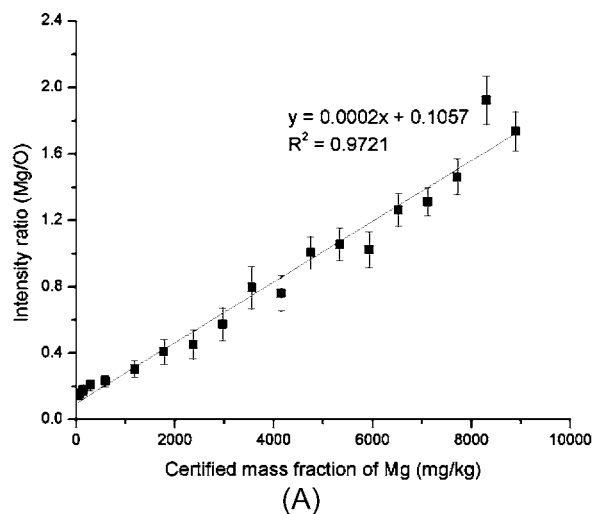


Figure 5. Calibration curves for (A) Mg normalized by O in spinach samples and (B) Mg normalized by C in rice samples.

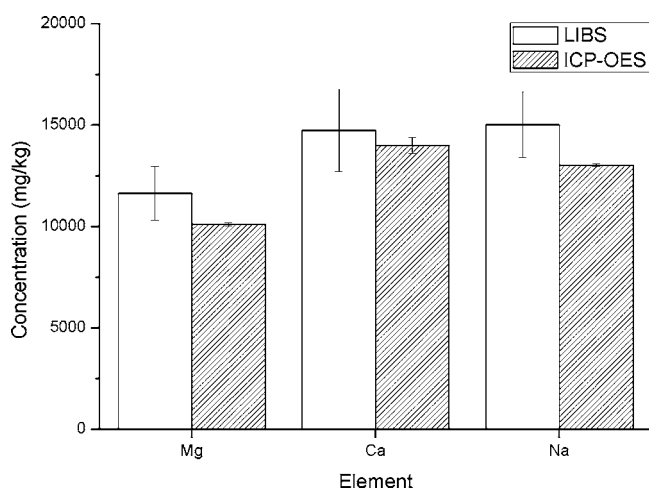


Figure 6. Comparison of Mg, Ca, and Na concentrations in spinach samples from a local market determined by LIBS with those by ICP-OES.

separated as shown in Figure 7B. Data for rice samples with and without parathion are shown in Figure 7C. A clear discrimination of two data sets suggests that the LIBS spectral data are useful to detect pesticide-contaminated spinach. The

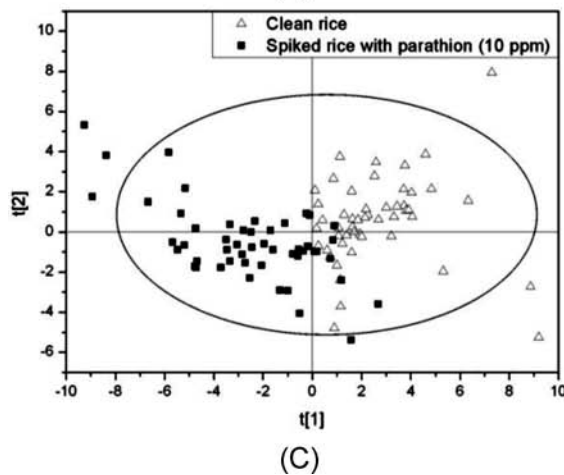
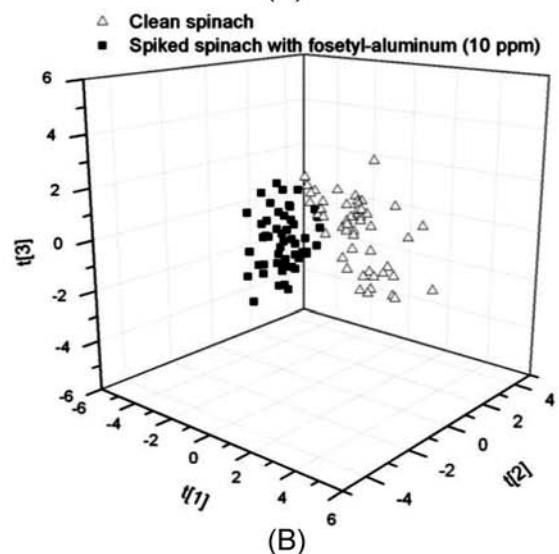
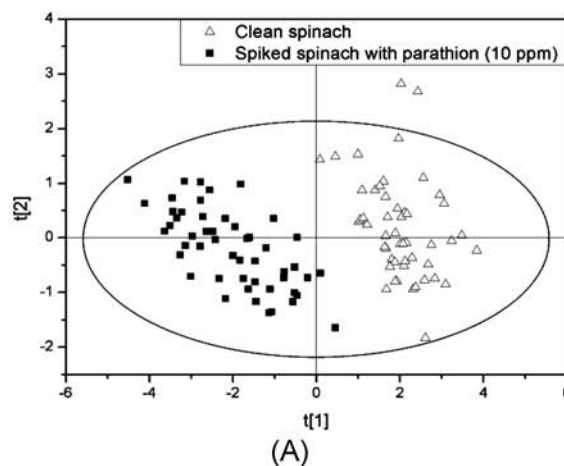
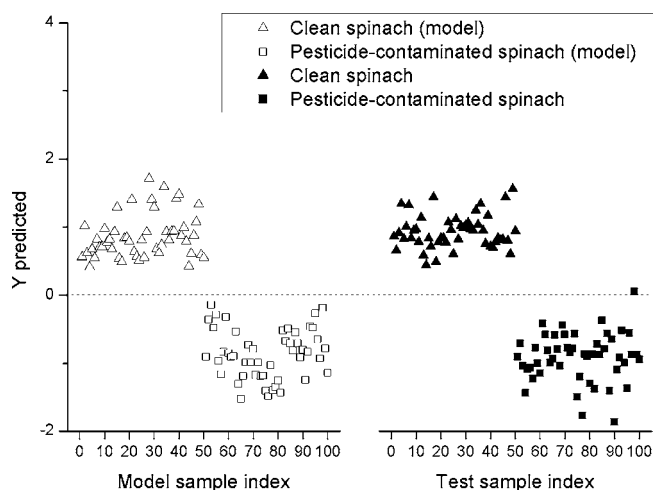


Figure 7. PLS-DA score plots for (A) clean spinach and spinach spiked with parathion, (B) clean spinach and spinach spiked with fosetyl-aluminum, and (C) clean rice and rice spiked with parathion.

established PLS-DA model using the training set of data was then applied to predict the classes of test samples, as shown in Figure 8. It shows predicted scores for nonspiked (pesticide-free) spinach and spinach spiked with 10 ppm of parathion. Except one sample, the model predicted the pesticide-contaminated spinach very well. Misclassification rates were 0 and 2% for clean spinach and pesticide-contaminated spinach, respectively.



**Figure 8.** Predicted scores for nonspiked (pesticide-free) spinach and spinach spiked with 10 ppm parathion obtained by the PLS-DA method.

In conclusion, the results presented in this paper demonstrated the feasibility of the LIBS technique for the quantitative analysis of nutrient elements in agricultural products and rapid detection of pesticide-contaminated products. Mixtures of standard samples with a binding material were used to obtain various concentration ranges of standard samples to determine a relationship between LIBS intensity and concentration of major elements (Mg, Ca, Na, and K) (i.e., calibration line). A reasonable agreement was found between the LIBS and ICP-OES concentrations. Standard samples with much wider concentration ranges and matrices similar to test samples should be required to more accurately determine the concentration of major elements in spinach and rice samples purchased from a local market. The usefulness of an internal standardization was demonstrated by showing that the relatively poor linear behavior of some calibration curves was improved as a result of internal standardization. Our data also showed that the LIBS technique with the chemometric method (PLS-DA) should be a promising tool to rapidly distinguish pesticide-contaminated samples from pesticide-free samples even though they have similar elemental compositions.

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