

DETECTION OF MINERALS IN GREEN LEAFY VEGETABLES USING LASER INDUCED BREAKDOWN SPECTROSCOPY

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The distribution of minerals in different green leafy vegetables, such as spinach, chenopodium, chickpea, mustard, and fenugreek, was calculated using laser induced breakdown spectroscopy (LIBS). LIBS can provide an easy, reliable, efficient, low-cost, and in situ chemical analysis with a reasonable precision. In situ LIBS spectra in the range 200–500 nm were carried out using fresh leaves and leaves in the pellet form. As the spectra suggest, magnesium and calcium are present in each vegetable; however, the amount of them varies. It is observed that the amount of iron is maximal in spinach. The nutrition value of the plants was analyzed, and it was revealed that they are low in calories and fat and high in protein, fiber, iron, calcium, and phytochemicals.

Keywords: laser induced spectroscopy, in situ, leafy vegetable, mineral.

Introduction. Green leafy vegetables are not only the most nutritious but also the most productive plants [1–3]. They are rich in fiber and can stimulate weight loss. Moreover, they are an excellent source of vitamins, phytochemicals, and minerals. As natural minerals play a vital role in the normal functioning of the human body [4], it is necessary to perform an analysis of green leafy vegetables. Five green leafy vegetables frequently used in Indian, Chinese, and Japanese cuisines are chosen for the analysis: spinach, mustard, chenopodium, fenugreek, and chickpea. They are all considered to be rich in iron. Red blood cells use iron to transport oxygen through the body [5–7]. According to the report of the United States Department of Agriculture, the iron content is 6.43 mg in 180 mg of boiled spinach [8]. Mustard leaves contain large amounts of phytonutrients, minerals, vitamins, and fiber, which helps to maintain the level of cholesterol [9]. Fenugreek seeds are widely used in folk medicine as diuretic, hypotensive, hypoglycemic, and hypolipidemic cures [10].

In the present paper, we have used LIBS to perform *in situ* analysis of minerals present in these vegetables. We have evaluated the levels of magnesium, calcium, iron, silicon, titanium, and aluminum. LIBS is used due to its high sensitivity. It is a very rapid and useful method for *in situ*, *in vivo*, and real time analysis [11]. Recently, this technique has been applied to study a variety of materials. LIBS has been used to study the mineral content of green leafy vegetables [12].

Material and Method. The samples were collected from Phaphamau near Allahabad, India. They were sorted and washed with fresh water. The washed leaf samples were used for *in situ* analysis. We also have made pellet samples. The temperature and pressure of the vacuum chamber were maintained around 50°C and 100 mm Hg, respectively. The vacuum-dried samples were powdered using a grinder, and then pellet samples were formed in a KBr die using a hydraulic press by applying a pressure of 10 tons for a few minutes.

The experimental setup is shown in Fig. 1. It consists of a broad band spectrometer (Ocean Optics LIBS 2000+, USA) equipped with a CCD and a Nd:YAG laser (Continuum Surelite III-10, USA). The maximum deliverable pulse energy of the laser at 532 nm is 425 mJ with a pulse width of 4 ns and a repetition rate of 10 Hz. The laser energy was measured with a calibrated energy meter (Genetec, SOLO PE UP19K 30H VMDO). To generate the laser induced plasma on the sample surfaces, a 15-cm convex lens was used. The emission from the plasma was collected by a lens (diameter 5 mm, *f*-number *f*/2) fixed at the tip of the fiber bundle and then brought to the entrance slit of a LIBS 2000+ spectrometer using a fiber cable. The spectrometer had three modules to provide high resolution (FWHM 0.1 nm) in the 200–500 nm wavelength range, and a fourth, low-resolution, module (FWHM 0.75 nm) in the 200–900 nm wavelength range. In this study, LIBS spectra were

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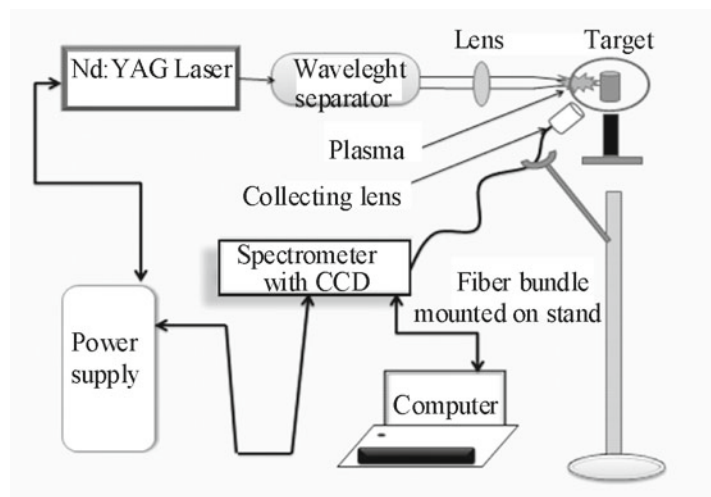


Fig. 1. Experimental setup.

recorded from the upper and lower surfaces of the leaves with an optimized laser energy of 10 mJ (irradiance $\sim 10^{12}$ W/cm²). The collecting optics was also adjusted to obtain maximum emission signals [11–13].

Result and Discussion. The LIBS spectra of the leaves of different green vegetables were recorded to detect minerals in them. Only one single laser shot was performed at a particular place to avoid the formation of craters on the surface. In the present study, five LIBS spectra of each leaf were chosen and analyzed to reproduce the data.

The LIBS spectra of the fresh leaves of chenopodium, spinach, fenugreek, chickpea, and mustard were recorded to study the mineral content in these samples. The persistent spectral lines of Si (288.1, 251.4 nm), Mg (285.1, 279.5, 279.8 nm), Ti (334.9, 336.1, 337.2 nm), Fe (344.1, 238.3, 240.4 nm), Ca (422.6, 393.3, 396.8, 443.5, 445.5 nm), C (247.8, 229.6 nm), and Al (308.2, 309.2 nm) were present in the LIBS spectra of all the samples, which confirms the presence of these (Si, Mg, Ti, Fe, Ca, C, and Al) minerals in them. A typical LIBS spectrum of the chenopodium leaf sample is shown in Fig. 2.

We have also recorded LIBS spectra of different green leafy vegetables by preparing pellets of their leaves. LIBS spectra were recorded in the range 200–500 nm. A typical LIBS spectrum is shown in Fig. 3a. This research confirms the presence of Mg, Si, C, and Ca in the samples. LIBS spectra in the spectral range 700–825 nm (see Fig. 3b) confirm the presence of Na, K, N, and O. The spectral signature of these minerals is also seen in *in situ* LIBS spectra of these vegetables. It is clear from Figs. 2 and 3 that the intensity of spectral lines of Mg, Ca, C, Fe, Ti, and Mn is larger in pellets in comparison with fresh leaves.

The spectral intensity of an element in the LIBS spectra of a sample is represented by the Boltzmann equation

$$I_{\lambda}^{ki} = FCA_{ki}g_k \frac{\exp(-E_k/k_B T)}{U(T)}, \quad (1)$$

where C is the concentration of the element in the sample, A_{ki} is the transition probability, g_k is the degeneracy factor, $U(T)$ is the partition function of the species at plasma temperature T (K), E_k is the upper energy level, k_B is the Boltzmann constant, λ is the wavelength of the transition, and F is a constant. Thus, we see that the intensity of the spectral line of an element is proportional to its concentration in the sample [14–24]. Spectral intensities of elements for different green leafy vegetables were measured and compared in Fig. 4. It is clear from Fig. 4a that mustard leaves are an excellent source of calcium, because the spectral intensity of Ca is higher in comparison to the other leaves. Spinach leaves is the second rich source of Ca, followed by chickpea, fenugreek, and chenopodium leaves. Regular consumption of mustard greens prevents arthritis, osteoporosis, and iron deficiency anemia, and protects against cardiovascular disease, asthma, and colon and prostate cancer [25, 26].

Spinach is an excellent source of iron, followed by chickpea, chenopodium, fenugreek, and mustard (Fig. 4b). Spinach contains iron absorption-inhibiting substances, including high levels of oxalate, which can bind to iron to form ferrous oxalate [27]. As shown in Fig. 4e, mustard leaves are rich in magnesium. The presence of Mg in mustard indicates that the consumption of it helps to maintain a normal blood vessel tone. They help to reduce blood pressure and subsequently the

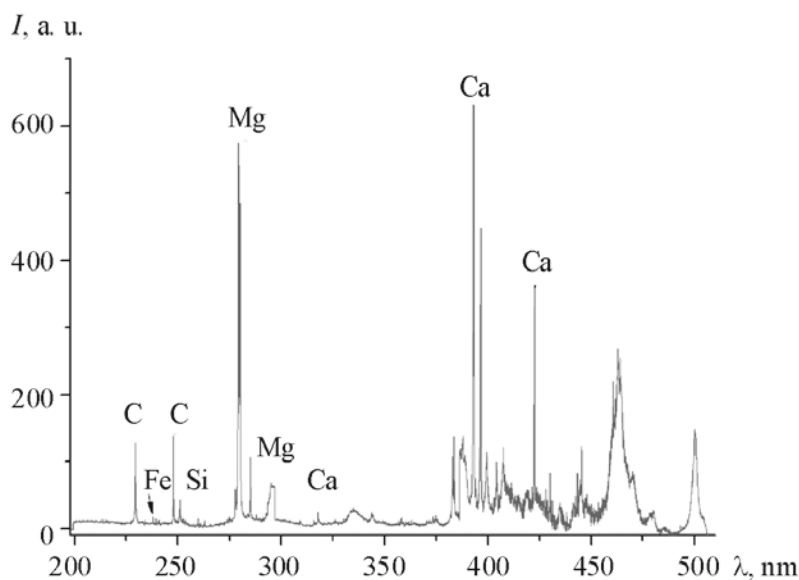


Fig. 2. *In situ* LIBS spectra of chenopodium samples.

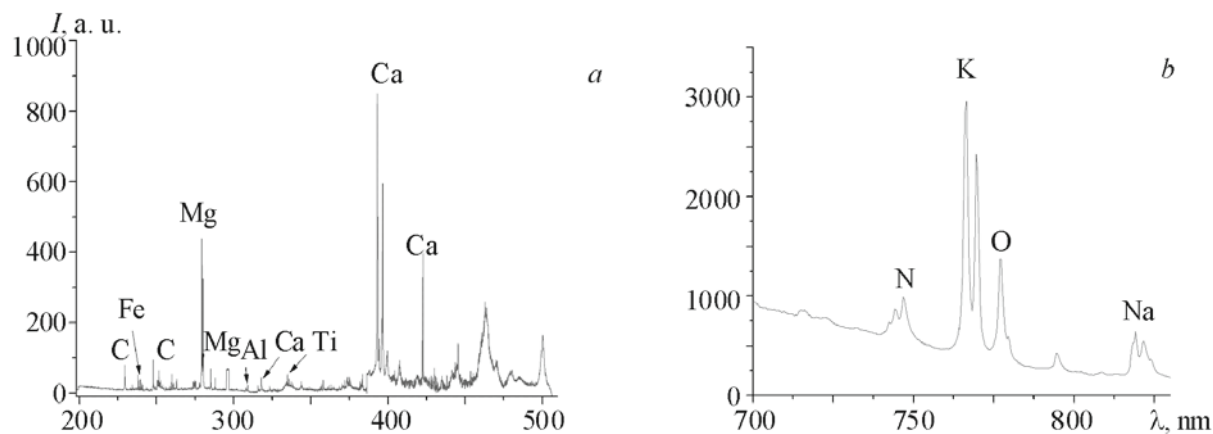


Fig. 3. LIBS spectra of chenopodium pellets in the spectral range 200–500 (a) and 700–825 nm (b).

risk of heart disease [28]. Fenugreek leaves have a large amount of silicon, as shown in Fig. 4d. Chickpea and chenopodium leaves also have large amounts of silicon, which is an inessential but beneficial plant nutrient. It is clear from Fig. 4e that mustard and fenugreek leaves have similar amounts of manganese, and chenopodium leaves are the second richest source of Mn.

The amount of Ti in all leaf samples is nearly equal (Fig. 4f). There is no clear data about the biological role of titanium. It has been estimated that we take about 0.8 mg of it a day, but it is not absorbed by the body. It is noteworthy that titanium is not a poisonous metal. Figure 4g shows that chickpea leaves have the largest amount of aluminum compared with the other four leaf samples. The biological role of aluminum is not clear. It is not required for any biological processes in either plants or animals. It shows low toxicity and is easily processed by kidneys. However, there are concerns that aluminum can have an adverse effect on people with poor kidney function. The consumption of high amounts of Al can result in nerve damage. According to Fig. 4h, carbon is equally present in all the samples. Fenugreek leaves have a large amount of Na. Chenopodium, chickpea, and spinach have the same amounts of Na (Fig. 4i). Potassium is a vital component of cell and body fluids, helping to control the heart rate and blood pressure [29, 30]. Chenopodium is the richest source of potassium among the five green leafy vegetables according to Fig. 4j.

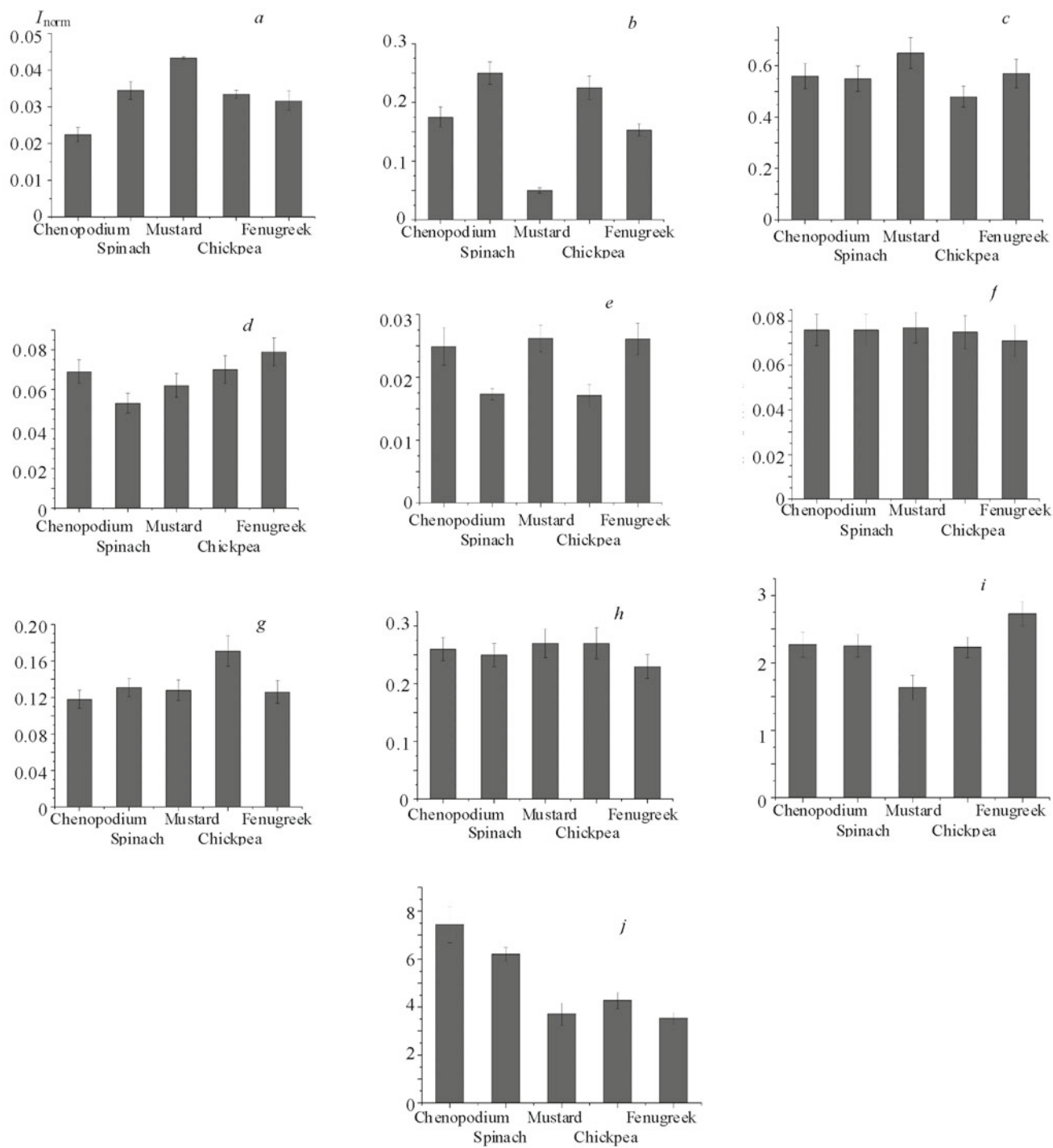


Fig. 4. Variations of Ca (a), Fe (b), Mg (c), Si (d), Mn (e), Ti (f), Al (g), C (h), Na (i), and K (j) in different leafy vegetables.

After the analysis of minerals, we considered the nutrition values of these vegetables. They were calculated after drying the leaves. The results are shown in Table 1. It is clear that chenopodium leaves have a larger amount of moisture than the other vegetables. The moisture content in other samples is almost similar. It is also clear that chenopodium has the highest level of ash. Spinach is an excellent source of fiber.

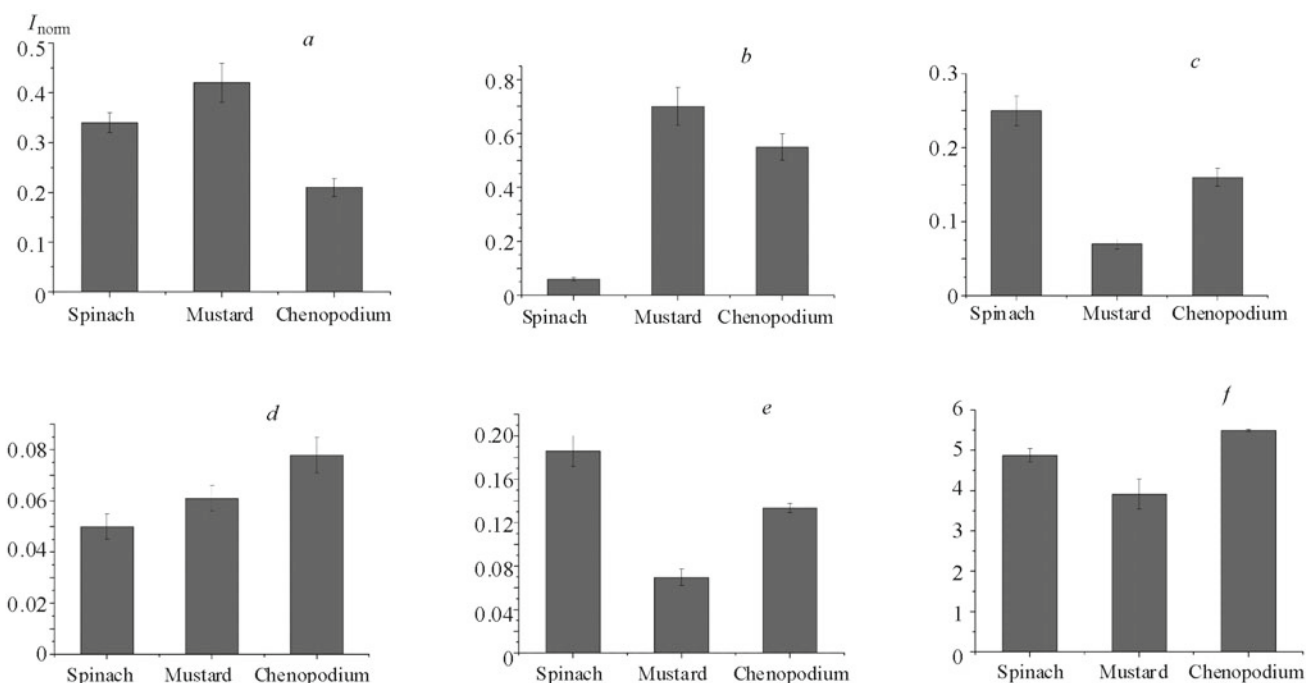


Fig. 5. Variations of Ca (a), Mg (b), Fe (c), Si (d), Na (e), and K (f) in the ash of leafy vegetables.

TABLE 1. Nutrition Values of the Vegetables

Sample	Moisture, %	Protein, %	Fiber, %	Fat, %	Ash, %
Chenopodium	12.5 ± 0.4	22.4 ± 0.3	5.1 ± 0.1	1.2 ± 0.1	14.2 ± 0.4
Spinach	12.1 ± 0.2	12.6 ± 0.2	6.1 ± 0.2	1.8 ± 0.1	10.1 ± 0.3
Chickpea	11.4 ± 0.3	20.1 ± 0.5	5.6 ± 0.3	1.2 ± 0.1	9.6 ± 0.1
Mustard	11.9 ± 0.2	24.6 ± 0.4	6.7 ± 0.3	1.8 ± 0.1	9.3 ± 0.2
Fenugreek	12.0 ± 0.4	27.1 ± 0.6	6.3 ± 0.1	1.6 ± 0.1	9.2 ± 0.2

Then we studied the degradation of minerals in the remaining residue (ash) of the vegetables. We prepared pellets and examined their LIBS spectra. The spectral signature, present in the corresponding vegetables, was also present. Variations of the amount of minerals are shown in Fig. 5. It is clear that the amount of minerals present in ash is similar to the amount of minerals in pellets.

Conclusions. The results of the present study clearly demonstrate that these leafy vegetables are rich in minerals. This study also provides evidence that LIBS is a suitable tool for *in situ* studies of different food materials, including leaves. It may be also used to quickly detect metal contamination in foods without any sample preparation.

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