

Analysis of Trace Elements in leaves using Laser-Induced Breakdown Spectroscopy

Xu Zhang ^{1,1},Mingyin Yao ^{1,2},Muhua Liu ¹,Zejian Lei ¹

¹Optics-Electronics Application of Biomaterials Lab, College of Engineering,
Jiangxi Agricultural University , Nanchang, Jiangxi 330045, China

Abstract: Laser-Induced Breakdown Spectroscopy (LIBS) is a new way to analyze the plant ecology. The experimental used a Q-switched Nd:YAG laser to be the laser source and equipped with an eight-channel model spectrometer which's wavelength range between 200 and 1100 nm. Studying the spectrum of the air-drying leaves and the nature leaves and detected the elements which contain Fe, Ca, Na, Mg, K, Cu, Al and Mn. Displaying the list which shows the all spectrum and elements. Refer to Fe as the benchmark, obtain the relative content of trace elements. At the same time, this technology can be employed for food safety and environment pollution evaluation. It will be the based for studying the portable LIBS instrument of detecting the pollution of heavy metal.

Key-words: LIBS, Trace element, Leaves, Air-drying, Relative content

1 Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is a new technology which can analyse the constitution and concentration of the matter. It is a laser-based omnipotent molecular and elemental analysis tool. This technology doesn't need to deal with the samples in complicated. And it can analyse several elements at the same time. LIBS is non-destructive, rapid detection, high sensitivity, on-site and online analysis. It is widely applied in the detection of trace elements in solid, liquid and gas, such as soil[1] alloy steel[2] solution[3] and even in biomedicine[4]. There are some reports about analysing the leaf by laser-induced breakdown spectroscopy. Lidiane[5] and other partners used LIBS to analyse the leaf by neuro-genetic approach. Miloslav[6] and his partners analysed the crop leaves and detected six certified reference materials of leaf tissues by LIBS.

Recently, in order to develop the level of LIBS, there are some experiments include nanosecond, femtosecond, monopulse, dipulse[7-8]. Although LIBS has been made a very great achievement in the analysis of material. But there are still many problems to be solved, such as how to decrease the matrix effect[9] in detecting several elements and how to increase the signal to noise ratio.

In our work, we analyzed trace elements in leaf by LIBS. This works about the analysis of leaf can help to study the information of tea leaf and tobacco in the

¹ Xu Zhang E-mail: zx8475396@126.com

² Corresponding author E-mail: mingyin800@126.com

future. In this paper, first of all, we introduce the information of sample and the experimental setup. We displayed the results of trace elements analysis and all spectral lines to the corresponding elements table in leaves by LIBS.

2 Experimental setup

In our experiments, we used a Q-switched Nd:YAG laser (BeamTech, Nimma-200, China) to be the laser source and the experimental setup includes an eight-channel model spectrometer, mirror, DG535, lens, optical fiber(1.5 m length, 400 um core diameter), fiber-optical probe, rotating stage, computer as shown in figure 1.

The fundamental wavelength of the laser is 1064 nm. And other parameters about laser are 8 ns pulse width, 10 Hz repetition rate. Laser beam was reflected to 45° by the mirror, and through the mirror with a hole focused on the sample which were put on the rotating stage by the lens which's focal length is 200 nm. The plasma was launched and focused on the fiber-optical probe through the lens which's focal length is 100 nm. The probe position is adjustable. We used an eight-channel model AVS-Rackmount-USB2 spectrometer(Avantes, France) which's wavelength range between 200 and 1100 nm to collect and analyse the plasma emission. The spectrometer has eight wavebands which is 200-317nm, 315-417nm, 415-499nm, 497-565nm, 563-673nm, 671-750nm, 748-931nm, 929-1100nm. The integration time and the delay time respectively were 2ms and 1.28 us by taking the signal-background ratio and signal-noise ratio into account.

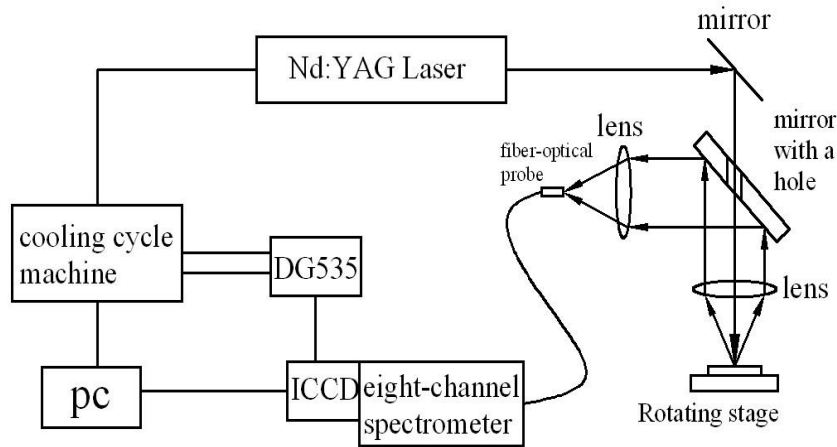


Fig. 1. LIBS experimental setup

3 Experimental results and analysis

The leaves came from the ecological orchard of Jiangxi Agricultural University. We picked the leaves in different orange trees. And then we washed the leaves by the

deionized water. The leaves were divided into two parts, a part of all was wiped dry using filter paper, the others was dry by air drying in the air. Because the laser would produce the points which the laser hit on samples into high temperature, we used a rotating stage in order to make the effects of the laser in different points.

The figure 2 shows that a part of the spectra of capsicum in leaves. Refer to the NIST atomic database[10] and the spectral data of the elements from the papers[11-13], we obtain the specific wavelength of trace elements and analysed all peak of waves showing table 1. From the table 1, we can find several elements such as Fe, Ca, Na, Mg, K, Cu, Al, Mn. The spectrum of Fe is most, reaching 61. At the same time, the elements C, H, O, N, Cl were detected by LIBS. But these elements which were detected maybe were in the air. In addition, we detected Mo which was the indispensable element in plants. Because Fe was the most element and spectrum. We choose Fe for the datum to compared with other elements.

As shown in table 2, the intensity of Na is strongest of all. According to the intensity of spectrum being proportional to the concentration, we can obtain the conclusion that content of Na is the highest in leaves. The intensity of the same elements in air-drying leaves is stronger than in nature leaves. It explains that water in leaves will affect the detection of elements. But the spectral intensity of Al and Na almost is the same between air-drying and nature. The water has a little effect to Al and Na in leaves.

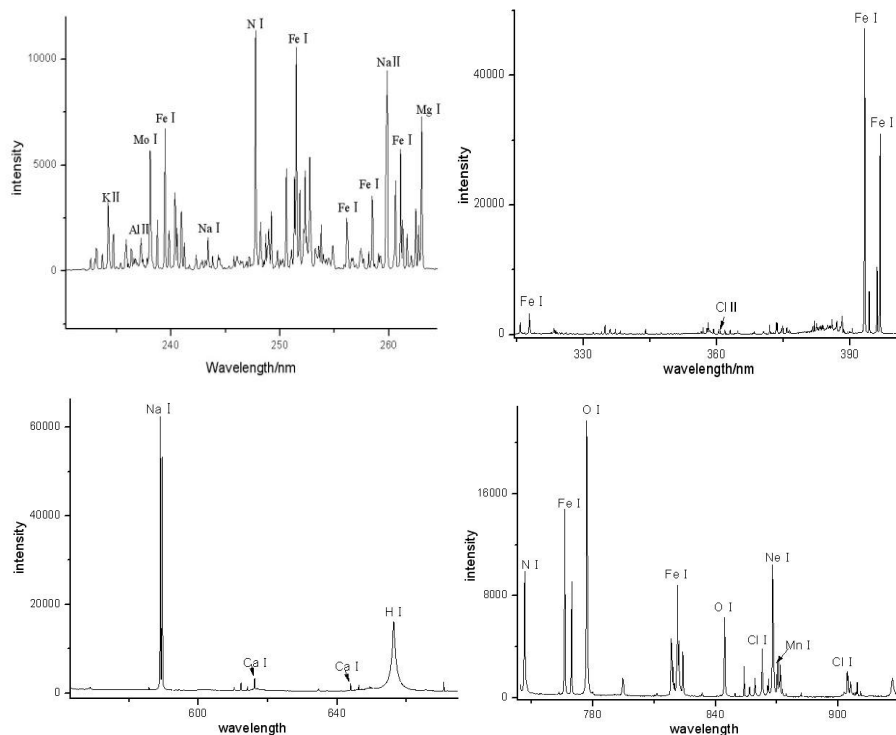


Fig. 2 A part of spectrum in leaves

Table 1. The spectrum of LIBS in leaves

Wavelength/nm	Elements	Wavelength /nm	Elements	Wavelength /nm	Elements	Wavelength /nm	Elements
232.606	O II	253.231	Mo II	381.977	He I	742.361	N I
233.120	Fe II	253.787	Mn II	388.193	Fe I	744.219	N I
233.698	Na II	254.834	C II	393.263	Fe I	746.814	N I
234.212	K II	256.125	Fe I	396.775	Fe I	766.340	Fe I
234.725	C II	257.412	Ne II	422.742	Fe I	769.678	Fe I
235.365	Fe II	258.452	Fe I	438.406	Na II	777.072	O I
235.877	K II	259.854	Na II	445.518	Na II	794.791	O I
236.325	Fe II	260.584	Fe II	498.216	Fe I	818.404	N I
237.218	Al I	261.070	Fe I	517.303	Fe I	821.545	Fe I
238.047	Mo I	262.463	Fe I	518.410	Fe I	824.163	N I
238.747	Mg II	262.705	Fe I	520.880	Fe I	844.481	O I
239.446	Fe I	263.008	Mg I	527.061	Fe I	849.626	Fe I
239.827	Ca I	267.634	Mn I	532.857	Fe I	854.050	Fe I
240.335	Cu II	273.859	Na II	537.208	Fe I	856.662	N II
240.969	Na II	274.564	Fe I	541.031	Fe I	859.256	Fe I
241.222	Fe I	275.502	Fe I	553.604	K II	862.839	Cl I
242.297	Fe II	279.463	Fe I	558.914	Ca I	866.025	N II
243.370	Na I	280.157	Al II	568.837	Na I	867.923	Ne I
244.315	Na II	285.095	Na II	585.729	Ca I	870.169	Mn I
245.760	Fe I	288.046	Fe I	588.977	Na I	871.063	N II
246.074	Na II	301.973	Fe II	589.571	Fe I	871.777	Mg I
247.201	Mo I	308.113	C II	610.303	Fe I	881.872	Fe I
247.764	N II	309.167	Fe I	612.246	Ca I	904.486	Cl I
248.201	Fe I	315.809	Fe I	614.173	Fe I	909.387	Fe I
248.700	Fe I	317.849	Fe I	616.203	Ca I	911.025	O II
248.949	Fe II	334.884	O II	643.895	Ca I	926.633	O I
249.199	Fe I	343.986	Fe I	646.244	Ca I	938.644	Fe I
249.759	Fe II	358.042	Fe I	656.229	H I	940.518	Fe I
250.565	Fe I	359.263	Fe I	670.770	Fe I	945.993	N I
251.064	Fe II	360.478	Cl II	693.816	K I	962.024	C I
251.498	Fe I	361.792	Fe I	714.761	Fe I	965.786	C I
251.808	Fe I	363.048	Ca I	715.673	O I	1011.511	N I
252.304	O II	364.713	Mn I	720.172	Ca I	1053.882	N I
252.737	Fe I	371.923	Mo I	732.544	Ca I		

Table 2. The trace elements' specific wavelengths, average spectral intensity and the ratio

Trace element	Specific wavelength (nm)	Average spectral intensity		The ratio of air-drying to nature	The ratio of element to Fe in Air-drying leaves
		Air-drying	Nature		
Fe	422.743	10147.72	7485.75	1.36	1.00
K	234.212	3225.88	2050.70	1.57	0.32
Al	237.218	1563.05	1525.63	1.02	0.15
Mg	263.008	7307.31	4734.69	1.54	0.72
Na	588.977	62501.57	64445.97	0.97	6.16
Ca	643.895	3152.75	1782.66	1.77	0.31
Mn	870.169	2755.64	1692.33	1.63	0.27

4 Conclusion

In this paper, we used the Laser-Induced Breakdown spectroscopy to detect the trace elements in leaves and obtained the spectrum of Fe, Ca, Na, Mg, K, Cu, Al, Mn, C, H, O, N, Cl. Concentration of Na is the highest. And we compared the air-drying leaves with nature leaves and got the conclusion that the water will affect the detection of elements in leaves. Experiment shows LIBS can quickly analyse the relative content of trace elements in leaves.

References

1. Edilene C.Ferreira, Debora M.B.P.Milori, Ednaldo J.Ferreira,Robson M.Da Silva, Ladislau Martin-Neto. Artificial neural network for Cu quantitative determination in soil using a portable laser induced breakdown spectroscopy system, *Spectrochimica Acta Part B*,63(2008)1216-1220.
2. SUN Lan-xiang,YU Hai-bin, XIN Yong, CONG Zhi-bo,Quantitative Analysis of Mn and Si of Alloy Steels by Laser-Induced Breakdown Spectroscopy, *Spectroscopy and Spectral Analysis*,Vol.30,No.12, pp3186-3190, December, 2010.
3. WU Jiang-lai,FU Yuan-xia,LiYing, Detection of Metal Ions in Water Solution by Laser Induced Breakdown Spectroscopy, *Spectroscopy and Spectral Analysis*,Vol.28, No.9,pp1979-1982,September,2008.
4. LIU Xian-yun,WANG Zhen -ya,HAO Li-qing, Application of laser induced breakdown spectroscopy technology in biom edicine field, *LASER TECHNOLOGY*.Vol.32,No.2, April, 2008.
5. Lidiane Cristina Nunes, Gilmore Antonia da Silva, Lilian Cristina Trevizan, Simultaneous optimization by neuro-genetic approach for analysis of plant materials by laser induced breakdown spectroscopy, *Spectrochimica Acta Part B*, 64(2009)565-572.
6. Miloslav Pouzar, Tomas Cernohorsky, Maria Prusova, Petra Prokopcakova and Anna Krejcova, LIBS analysis of crop plants, *Journal of Analytical Atomic Spectrometry*, 2009,24, 953-957.

7. O.Samek, J.Lambert, R.Hergenroder, M.Liska, J.Kaiser, K.novotny, and S.Kukhlevsky, Femtosecond laser spectrochemical analysis of plant samples, Laser Physics, Lett.3, No.1, 21-25(2006).
8. ZHANG Qian, XIONG Wei, CHEN Yu-qi, LI Run-hua, Rapid Measurement of Trace Mercury in Aqueous Solutions with Optical-Electrical Dual Pulse LIBS Technique, Spectroscopy and Spectral Analysis, Vol.31, No.2, pp521-524, February, 2011.
9. XIE Cheng-Li, LU Ji-Dong, LI Jie, Matrix effect on Laser-Induced Breakdown Spectroscopy of fine coal, JOURNAL OF ENGINEERING THERMOPHYSICS, Vol.29, No.2, Feb, 2008.
10. NIST, http://www.physics.nist.gov/PhysRefData/ASD/lines_form.html.
11. Zhang Da-Cheng, Ma Xin-Wen, Zhu Xiao-Long, Li Bin, Zu Kai-Ling, Application of laser-induced breakdown spectroscopy in analyzing micro elements in three kinds of fruit samples, ACTA PHYSICA SINICA, Vol.57, No.10, October, 2008
12. ZHANG Da-cheng, MA Xin-wen, ZHU Xiao-long, LI Bin, ZU Kai-ling, Microelements in Potato and Lily Samples Studied by Laser-Induced Breakdown spectroscopy Technology, Spectroscopy and Spectral Analysis, Vol.29, No.5, pp1189-1192, May, 2009.
13. Sun Dui-Xiong, Su Mao-Gen, Dong ChenZhong, Quantitative analysis of element concentration in Al alloy by using laser-induced breakdown spectroscopy, ACTA PHYSICA SINICA, Vol.59, No.7, July, 2010.