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Review

Laser-induced breakdown spectroscopy for analysis of plant materials: A review

Dário Santos Jr. [a], Lidiane Cristina Nunes [b], Gabriel Gustinelli Arantes de Carvalho [b], Marcos da Silva Gomes [b,c], Paulino Florêncio de Souza [b,d], Flavio de Oliveira Leme [b], Luis Gustavo Cofani dos Santos [b], Francisco José Krug [b,*]

[a] Centro de Ciências Exatas e da Terra — Universidade Federal de São Paulo, 09972-270 Diadema-SP, Brazil
[b] Centro de Energia Nuclear na Agricultura — Universidade de São Paulo, 13416-000 Piracicaba-SP, Brazil
[c] Departamento de Química, Universidade Federal de São Carlos, 13565-905 São Carlos-SP, Brazil
[d] Centro de Tecnologia Canavieira, PO Box 162, 13400-970 Piracicaba-SP, Brazil

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ABSTRACT

Developments and contributions of laser-induced breakdown spectroscopy (LIBS) for the determination of elements in plant materials are reviewed. Several applications where the solid samples are interrogated by simply focusing the laser pulses directly onto a fresh or dried surface of leaves, roots, fruits, vegetables, wood and pollen are presented. For quantitative purposes aiming at plant nutrition diagnosis, the test sample presentation in the form of pressed pellets, prepared from clean, dried and properly ground/homogenized leaves, and the use of univariate or multivariate calibration strategies are revisited.

Contents

1. Introduction

In the last 10 years, the ability of laser-induced breakdown spectroscopy (LIBS) to interrogate solid samples has been demonstrated for the direct analysis of plant materials (*e.g.* leaves, roots, and fruits) in the widespread scenario of agricultural and environmental sciences. In general, test sample presentation varies from fresh or dried materials (*e.g.* whole leaf, leaf section, whole grain, and vegetables) to pellets prepared from ground and/or comminuted materials. The ablation chambers are designed to accommodate the test samples and the interrogation is carried out in air or argon atmospheres, generally by nanosecond pulses from Q-switched Nd:YAG laser, and seldom by femtosecond pulses. The emission from the excited species in the laser-induced plasma (atoms, ions and molecules) formed in the sample surface is collected

* Corresponding author. Tel.: +55 19 3429 4648; fax: +55 19 3429 4774.
E-mail address: fjkrug@cena.usp.br (F.J. Krug).

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Table 1
A survey of works dealing with LIBS analysis of plant materials. t_{delay}: delay time; t_{int}: integration time gate; CRMs: certified reference materials; PCA: principal component analysis; SIMCA: soft independent modeling of class analogy; PLS: partial least squares; PLS-DA: partial least squares — discriminant analysis; MW2D: moving window 2D; BRANN: Bayesian regularized artificial neural networks; GA: genetic algorithm; RSM-PCS: random subspace method in principal components space; RBM: rotation based method.

Test sample	Analytes	Laser (s)	Operational parameters					Remarks	Ref.
			mJ/pulse	J/cm^2	W/cm^2	t_{delay} (μs)	t_{int} (μs)		
Fresh leaves	Al, C, Ca, Mg, N, Si, Sr, Zn	Nd:YAG, 532 nm, 10 Hz, 4 ns	10	–	–	–	–	Qualitative	[9]
	Ag, Cu	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[10]
	Pb, Mn, K	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[11]
	Mg, Pb	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[12]
	Cu, Mg, Pb	Nd:YAG, 532 nm, 5 ns	10	–	–	–	–	Qualitative; mapping	[13]
	Mg, Pb	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[14]
	Ag, Cu	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[15]
	Ca, Cu, Fe, K, Mn, Na, Mo	Nd:YAG, 1064 nm, 100 Hz, 20 ns	0.3	–	–	–	–	Qualitative; mapping	[16]
	Fe, Zn, Ni, Mn, Cl, Na, C, H, O, Ca, N, K, Mg, S	Nd:YAG, 1064 nm, 10 Hz	50	–	–	48.5	–	Qualitative; PCA, SIMCA	[17]
	Fe	Ti:sapphire, 795 nm, 10 Hz, 160 fs	0.1	–	–	–	–	Qualitative; mapping	[18]
	Al, Ca, Cl, K, Li, Mg, Na, Si, Sr, Ti,	Nd:YAG, 1064 nm, 1–10 Hz, 8 ns	540	–	10^{10}	0.8	2000	Semi-quantitative	[19]
	Al, C, C_2, Ca, CN, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, O, Pb, Si, Ti, V, Zn	Nd:YAG, 1064 and 266 nm, 10 Hz, 10 ns	45	–	–	0.5	2000	Qualitative	[20]
	Al, Ca, Fe, Mn, Mg, Si, Ti	laser*, 1064 and 266 nm	10–80	–	–	–	–	Semi-quantitative	[21]
Dried leaves	Ca, Cu, Fe, Mg, Na	Ti:sapphire, 800 nm, 10 Hz, 150 fs	5.0	–	–	–	–	Qualitative	[22]
	K, Mn, Pb	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[23]
	Pb, Mn, K	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[11]
	Cd, Pb	Ti:sapphire, 795 nm, 10 Hz, 160 fs	0.1	–	–	–	–	Qualitative; mapping	[24]
	N, P, K, Ca, Fe, Ti, Mn, Na	laser*, 800 nm, 10 Hz, 100 fs	–	–	–	–	–	Calibration free	[25]
	Ca, Cu, Fe, K, Mn, Na, Mo	Nd:YAG, 1064 nm, 100 Hz, 20 ns	0.3	–	–	–	–	Qualitative; mapping	[16]
	Fe	Ti:sapphire, 795 nm, 10 Hz, 160 fs	0.1	–	–	–	–	Qualitative; mapping	[18]
	Ca, Cl, Cu, Fe, Mg, Mn, P, N, S, Zn,	Nd:YAG, 1064 nm, 10 Hz, 10 ns	200	–	–	1.28	–	Qualitative	[26]
Powder leaves	Mg	Nd:YAG, 1064 nm, 1 Hz	–	–	2.5×10^7	–	–	Normalization	[27]
	Cr, Pb	TEA CO_2, 10.6 μm, 200 ns	1500	–	1.8×10^8	–	–	Quantitative	[28]
	Al, B, C, Ca, Cu, Cr, Fe	TEA CO_2, 10.6 μm, 10 Hz, 200 ns	1500	–	–	10	100	Semi-Quantitative	[29]
	Ca, CH, Cr, Mg, Zn	TEA CO_2, 10.6 μm, 200 ns	1500	–	1.8×10^8	10	100	Quantitative; mapping	[30]
	Ca, CH	Nd:YAG, 355 nm, 10 Hz, 5 ns Nd:YAG, 1064 nm, 10 Hz, 5 ns	5.0 110	–	–	1.0	50	Semi-quantitative; Double pulse	[31]
	Al, Ca, Cu, Fe, Mg, Mn, P, Zn	Nd:YAG, 1064 nm, 1 Hz, 5 ns	100			1.0	10	Quantitative: calibration with CRMs	[32]
Pellets from leaves	Pb	Nd:YAG, 1064 nm, 10 Hz	–	–	–	–	–	Quantitative	[33]
	B, Cu, Fe, Mn, Zn	Nd:YAG, 532 nm, 10 Hz, 12 ns	70	35	2.0	1.1	9.0	Quantitative; PLS	[34]
	Al, B, Ca, Cd, Cu, Fe, K, Mg, Mn, P, Pb, Zn	Nd:YAG, 1064 nm, 10 Hz, 5 ns	–	10–80	–	2.0	5.0	Calibration with CRMs	[35]
	P, K, Ca, Mg, B, Fe, Cu, Mn, Zn	Nd:YAG, 1064 nm, 10 Hz, 5 ns	110	25	–	2.0	4.5	Qualitative	[36]
	Al, Ca, K, Mn, Pb, Sr	Nd:YAG, 1064 nm, 8 ns	80		7×10^{10}	5.0	15	Qualitative	[37]
	Pb	–	–	–	–	–	–	Qualitative	[38]
	Ca, Mg, Fe, Mn, Cd, Cu, Ni, Zn	Nd:YAG, 532 nm, 10 Hz	23	–	–	0.5	10	Semi-quantitative	[39]
	Al, B, Ca, Cu, Fe, Mg, Mn, P, Si, Zn	Nd:YAG, 1064 nm, 10 Hz, 12 ns	70	35	–	1–5	3–10	Doehlert, BRANN, GA optimization	[40]
	B, Ca, Cu, Fe, K, Mg, Mn, P, Zn	Nd:YAG, 1064 nm, 10 Hz, 5 ns	110	25	–	2.0	4.5	Quantitative; PLS	[41]
	Ca, K, Mg, P	Nd:YAG, 1064 nm, 20 Hz, 12 ns	65 or 78	–	–	7.0	1.0	Quantitative	[42]
	Al, Ba, Ca, Cr, Fe, K, Mg, Na, Sr	Nd:YAG, 1064 nm, 5 ns	450	–	–	–	–	Qualitative	[43]
	Ca, K, Mg, P	Nd:YAG, 1064 nm, 10 Hz, 5 ns	200	23	4.6×10^9	2.0	5.0	Quantitative: calibration with CRMs	[7]
	B, Cu, Fe, Mn, Zn	Nd:YAG, 1064 nm, 10 Hz, 5 ns	200	23	4.6×10^9	2.0	5.0	Quantitative: calibration with CRMs	[8]
Fresh roots	Ag, Cu	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[10]
	Mg, Pb	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[12]
	Cu, Mg, Pb	Nd:YAG, 532 nm, 5 ns	10	–	–	–	–	Qualitative; mapping	[13]
	Ag, Cu	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[15]
Dried roots	Cd, Pb	laser*, 795 nm, 10 Hz, 160 fs	0.1	–	–	–	–	Qualitative; mapping	[24]
Fresh stem	Cu, Mg, Pb	Nd:YAG, 532 nm, 5 ns	10	–	–	–	–	Qualitative; mapping	[13]
	Ag, Cu	Nd:YAG, 532 nm, 5 ns	10	–	–	1.0	10	Qualitative; mapping	[15]
Cell wall	Ca	Nd:YAG, 355 nm, 20 Hz, 6 ns Ti:sapphire, 790 nm, 1 kHz, 30 fs	– –	120–2130 55–120	– –	0.025–0.075 0.04–0.16	0.015 0.015	Qualitative	[44]