



Discrimination of wood species using laser-induced breakdown spectroscopy and near-infrared reflectance spectroscopy

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Abstract

A new method is proposed for the discrimination of wood species by combining near-infrared reflectance spectroscopy (NIRS) and laser-induced breakdown spectroscopy (LIBS) and using chemometrics for data analysis. The method was applied to the analysis of 42 samples from six different species: *Amburana cearensis*, *Copaifera lucens*, *Phyllocarpus riedelii*, *Cariniana legalis*, *Bowdichia virgilioides*, and *Aspidosperma pyricollum*. The spectra from both techniques were merged on a single data matrix and pretreated by standard normal variate (SNV) and Savitzky–Golay first derivative with smoothing. Principal component analysis was applied to the exploratory data analysis and showed a clear formation of sample groups according to the wood species only when the data from both analytical techniques and the data pretreatment were used. Sample discrimination using partial least squares discriminant analysis was proved possible, but with an average misclassification of about 10%. Sample grouping and discrimination were shown to be probably related to different concentrations of iron, copper, zinc, and/or sodium (affecting the LIBS spectra) and lignin, water, cellulose, and/or hemicellulose (affecting the NIRS spectra).

Introduction

Wood is a complex biological material composed mainly of cellulose microfibrils within a hemicellulose–lignin matrix. Different wood species can have different physical and chemical properties, which affect their cost, application, and

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production. In addition, many tree species are on the official list of endangered plants, making it necessary to improve control over wood exploitation. Moreover, regardless of the species, woods can have different geographical origins or be submitted to different physical or chemical treatments. However, the visual identification of different woods is a very costly and difficult task, requiring highly qualified personnel. Therefore, the development of instrumental methods for the discrimination of woods is very important for wood trading and for environmental conservation (Carballo-Meilan et al. 2014; Francisco-Fernández et al. 2015; Nisgoski et al. 2017; Cui et al. 2019).

For the discrimination of wood species, several analytical techniques have been employed that use chemometrics for multivariate data analysis, such as mass spectrometry (Zhang et al. 2019), chemiresistor gas sensor array (Kalaw and Sevilla III 2018), laser-induced breakdown spectroscopy (LIBS) (Cui et al. 2019), thermogravimetric analysis (Francisco-Fernández et al. 2012, 2015), molecular fluorescence (Piuri and Scotti 2010; Oliveira et al. 2015), mid-infrared spectroscopy (Carballo-Meilan et al. 2014), and mainly near-infrared spectroscopy (Shou et al. 2014; Park et al. 2017; Kurata 2017; Nisgoski et al. 2017; Ramalho et al. 2018). Other works have also reported wood discrimination based on properties other than the species: based on the wood type and using near-infrared spectroscopy (Hayashi et al. 2003), Raman spectroscopy (Lavine et al. 2001), or thermogravimetric analysis (Francisco-Fernández et al. 2017); based on the geographical origin and using mass spectrometry (Horacek et al. 2009); based on the thermal treatment and using near-infrared spectroscopy (Bächle et al. 2012); and based on the wood preservative and using near-infrared spectroscopy (Bouslamti et al. 2013) or LIBS and X-ray fluorescence spectroscopy (Solo-Gabriele et al. 2004).

Near-infrared reflectance spectroscopy (NIRS) has been widely used for wood discrimination because it is a fast, noninvasive, and nondestructive instrumental technique and requires very few or no sample preparation. For the same reasons, the application of LIBS to wood discrimination has increased in recent years, although very few works have been published yet. Both instrumental techniques typically provide the different but complementary chemical information. While in NIRS, the sample is illuminated by an appropriate polychromatic light source, and the diffusely reflected light is collected and analyzed, containing information on molecular absorbance due to vibrational energy transitions, in LIBS, the sample is hit by a high-power pulsed and focused laser beam, and the resulting plasma radiation is collected and analyzed, containing information on atomic emissions due to electronic energy transitions (Gonzaga et al. 2017; Zhu et al. 2019). Recently, a work has reported on a successful combination of LIBS and NIRS data in the analysis of forage plants (Oliveira et al. 2019).

This work presents a new method for the discrimination of wood species by combining LIBS and NIRS and using chemometrics for data analysis. The method was evaluated for the discrimination of woods from *Amburana cearensis*, *Copaifera lucens*, *Phyllocarpus riedelii*, *Cariniana legalis*, *Bowdichia virgilioides*, and *Aspidosperma pyricollum*. The generated spectroscopic data were analyzed by principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA).

Materials and methods

Instrumentation

For the acquisition of the LIBS spectra, a home-made, compact, and low-cost instrument was employed. It has, among other optical components, a Standa STA-01-8 microchip laser (1053 nm wavelength, 600 μJ pulse energy, 470-ps pulse duration, and 100 Hz pulse repetition rate), a sample holder coupled to a Standa 8MT30-50 translation stage, and a B&W Tek Exemplar LS mini-spectrometer with a classical Czerny–Turner polychromator and a 2048 pixel non-gated, non-intensified, and non-cooled CCD sensor array (200–850 nm spectral range, 1.2 nm resolution). More details about the instrument were given in a previous work (Gonzaga et al. 2015).

For the acquisition of the NIRS spectra, a PerkinElmer Spectrum GX Fourier transform instrument was used, coupled to a Pike FlexIR module for operation in diffuse reflectance mode.

Samples

Forty-two wood samples (different pieces of wood) from six different species were analyzed using both instruments. The samples were randomly taken from different transversal regions of wood trunks, from the core up to near to the shell. A description of the samples is given in Table 1.

Experimental procedures

Prior to the analysis on each instrument, the samples were pretreated by polishing to remove any possible surface contaminations.

For the LIBS analysis, one spectrum was obtained for each sample, using a 200–750 nm spectral range, about 0.38 nm nominal resolution, 100 Hz laser pulse repetition rate, an average of four scans (each scan from a different micro-region of the sample surface, covering a circular region with about 1 cm diameter), and 4 s of integration time per scan (continuous integration of the radiation emitted by 400 plasmas). The translation stage was continuously displaced at 1.0 mm s^{-1} during the spectra acquisition to avoid plasma extinction (Lopez-Moreno et al. 2005).

Table 1 Description of the wood samples analyzed

Species name	Acronym	Number of samples
<i>Amburana cearensis</i>	AC	5
<i>Copaifera lucens</i>	CL	5
<i>Phyllocarpus riedelii</i>	PR	8
<i>Cariniana legalis</i>	CE	9
<i>Bowdichia virgilioides</i>	BV	6
<i>Aspidosperma pyricollum</i>	AP	9

For the NIRS analysis, one spectrum was obtained for each sample, using a 1100–2500 nm spectral range, about 1.30 nm nominal resolution, and an average of 16 scans (all scans from the same circular region, with about 1 cm diameter, of the sample surface).

Data pretreatment and chemometrics

First, the data from LIBS (42 samples and 1466 variables) and NIRS (42 samples and 1273 variables) were merged, by placing each NIRS spectrum right after the end of the respective LIBS spectrum for each sample, resulting in a data matrix with 42 rows (samples) and 2739 variables (wavelengths). Thereafter, the data were pretreated by standard normal variate (SNV) and Savitzky–Golay first derivative with smoothing (11 points data window and polynomial order 2) using CAMO The Unscrambler 9.7 software (Savitzky and Golay 1964). Although the pretreatment was carried out after merging the NIRS and LIBS data, the pretreatment procedures were applied to the NIRS and LIBS data separately. Additionally, the resulting NIRS data were also multiplied by 4.3. Then, an exploratory data analysis was carried out by PCA using CAMO The Unscrambler 9.7 software, and wood discrimination was evaluated by PLS-DA using Chemoface 1.61 software. In both cases, the data were additionally pretreated by mean centering. In PLS-DA, nine samples were randomly selected for the external validation, whereas the remaining 33 samples were used for calibration with full cross-validation.

Results and discussion

LIBS and NIRS spectra

Figure 1 shows the raw LIBS and NIRS spectra acquired for all wood samples. As can be seen, the LIBS spectra have thin peaks, which are typical for atomic spectroscopy, whereas the NIRS spectra have wide bands, which are typical for vibrational spectroscopy. As can also be observed, the spectra contain some noise (mainly LIBS), baseline variations, and effects from light scattering (common in the analysis of solid samples). Therefore, several pretreatment methods were tried to correct/minimize these problems in the spectra. The best results (best sample grouping and separation according to the wood species) were obtained using SNV (correction of effects from light scattering) and Savitzky–Golay first derivative with smoothing (correction of baseline variation and minimization of noise) for all spectra and additional multiplication of NIRS data by 4.3 (so that LIBS and NIRS data had similar final maximum intensities). Figure 2 shows all the spectra after the cited pretreatment. Zooming in the spectral regions of 240–300 nm (LIBS spectra) and 1900–2100 nm (NIRS spectra) is shown in Fig. 2b, which presents large intensity variations. Although it was possible to see the grouping of some spectra according to the wood species in Fig. 2b, clearly there was also the overlapping of some spectra from different species, making necessary the use of multivariate data analysis for

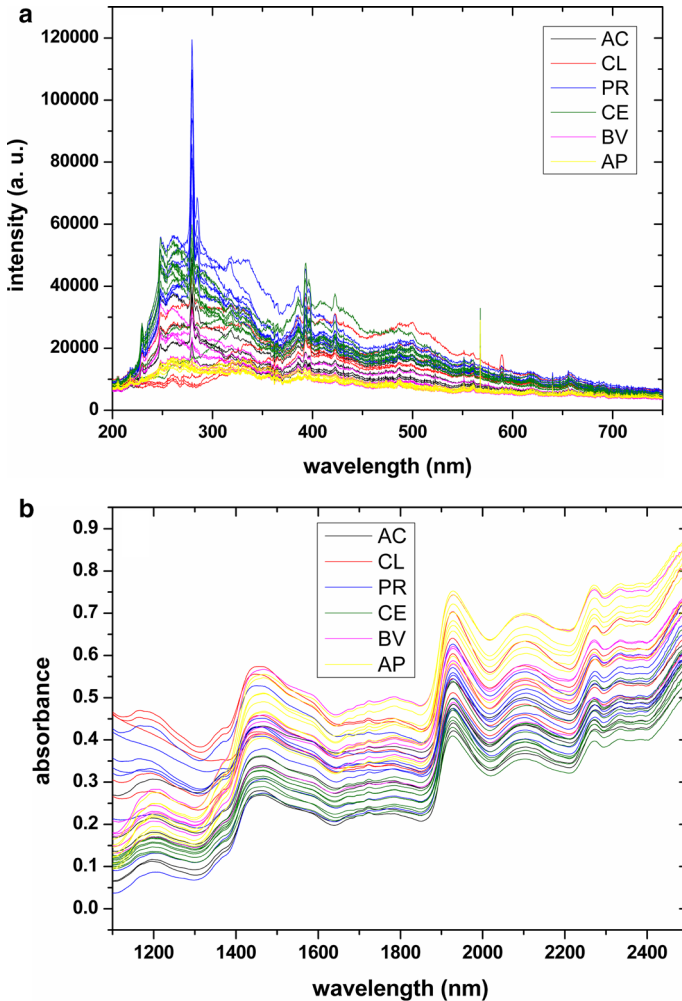


Fig. 1 Raw LIBS (a) and NIRS (b) spectra for all wood samples

improving the sample discrimination. The spectra were also additionally pretreated by mean centering, right before the PCA or PLS-DA, which also improved sample grouping and separation.

Exploratory data analysis

As cited before, the data from LIBS and NIRS were placed together in a single 42×2739 matrix, even before the data pretreatment. PCA was applied to the data before and after the cited pretreatment to check for some sample grouping/separation according to the wood species and to evaluate the improvement in data quality resulting from the data pretreatment. In this case, for the PCA with the raw data, the

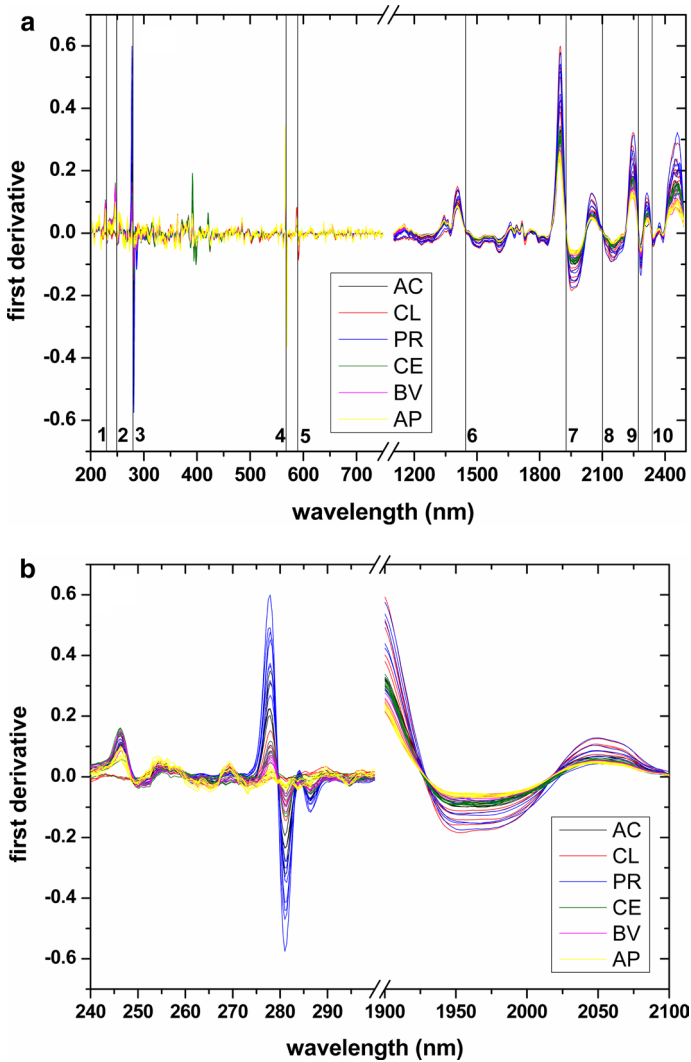


Fig. 2 Pretreated LIBS (left) and NIRS (right) spectra for all wood samples: **a** all spectral range (numbers inside the plotting area according to Table 2), **b** zooming in 240–300 nm (LIBS) and 1900–2100 (NIRS)

NIRS data were previously multiplied by 136,294, so that LIBS and NIRS data had similar final maximum intensities. Therefore, Fig. 3 shows the PCA score plots in the first two principal components. Some sample groupings related to the wood species can be observed in the score plot resulting from the raw data (Fig. 3a), with no sample groups from a single species fully separated from the other samples. However, the score plot resulting from the pretreated data (Fig. 3b) shows a clear formation of sample groups according to the wood species, separated from each other, although with some minor group overlapping between some group boundaries (for

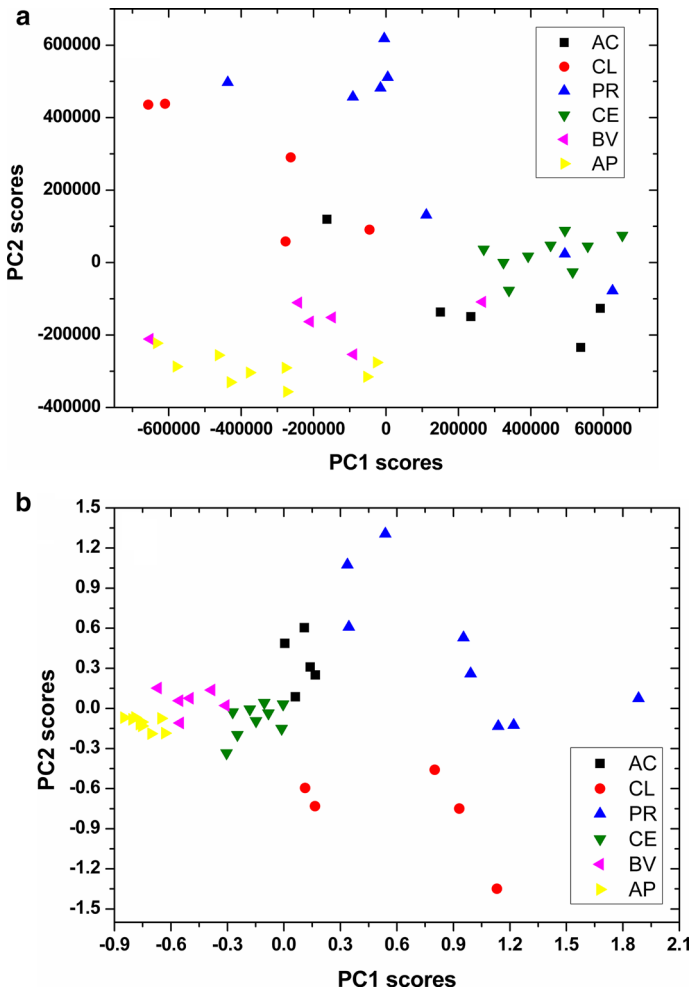


Fig. 3 PCA score plots from all raw (a) and pretreated (b) data (explained variances of 89% and 85%, respectively)

CE-BV, CE-AC, and BV-AP species) and with a wide sample dispersion within some groups (for CL and PR species).

For comparison purposes, PCA was also separately applied to the pretreated data from LIBS and NIRS to determine which analytical technique is responsible for the grouping and separation of which wood species. Thus, the PCA score plots in the first two principal components are shown in Fig. 4. As can be seen, the score plot from the LIBS data (Fig. 4a) shows a better sample grouping and separation, according to the wood species (compared to the score plot from the NIRS data in Fig. 4b), but with some group overlapping (mainly for CL-BV and CL-CE). The score plot from the NIRS data, although it has no sample group from a single species fully separated from the other samples, shows a full separation exactly between the sample

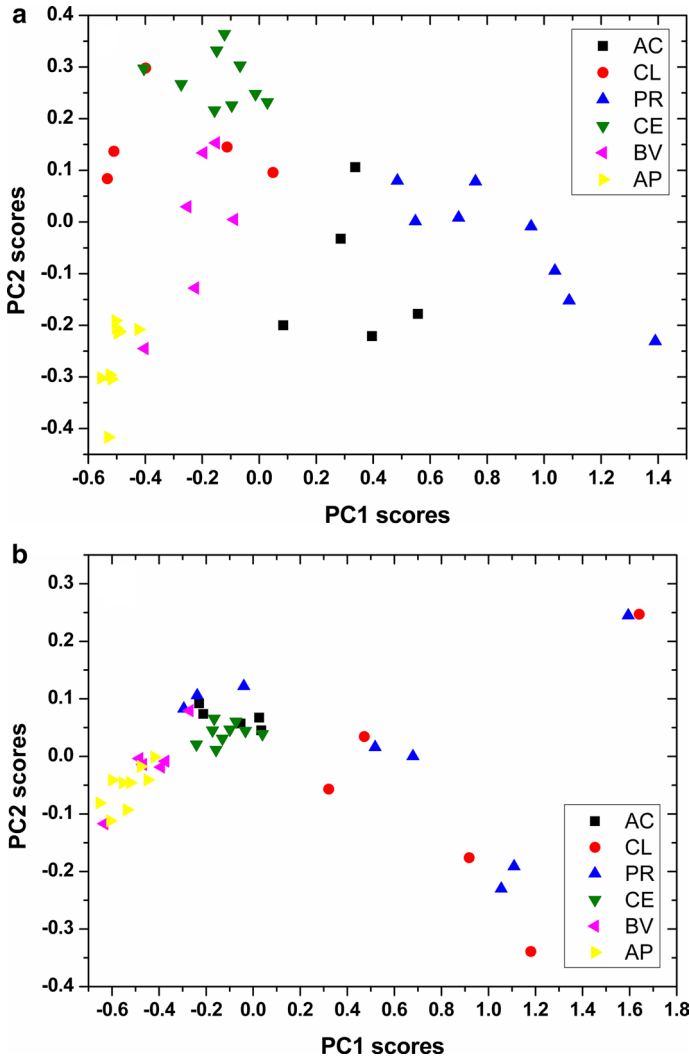


Fig. 4 PCA score plots from LIBS (**a**) and NIRS (**b**) pretreated data (explained variances of 84% and 96%, respectively)

groups where some group overlapping was observed at the score plot from the LIBS data. In other words, Fig. 4 shows that only a combination between the data from LIBS and NIRS can promote the best sample grouping and separation, according to the wood species, as shown in Fig. 3b.

The PCA loading plots from all the pretreated data are given in Fig. 5 for the first and second components. From the highest intensities observed in these plots, the more important variables could be selected related to the best sample grouping and separation shown in Fig. 3b. Therefore, ten variables were selected, related to five LIBS emission peaks and five NIRS absorption bands; the wavelengths were

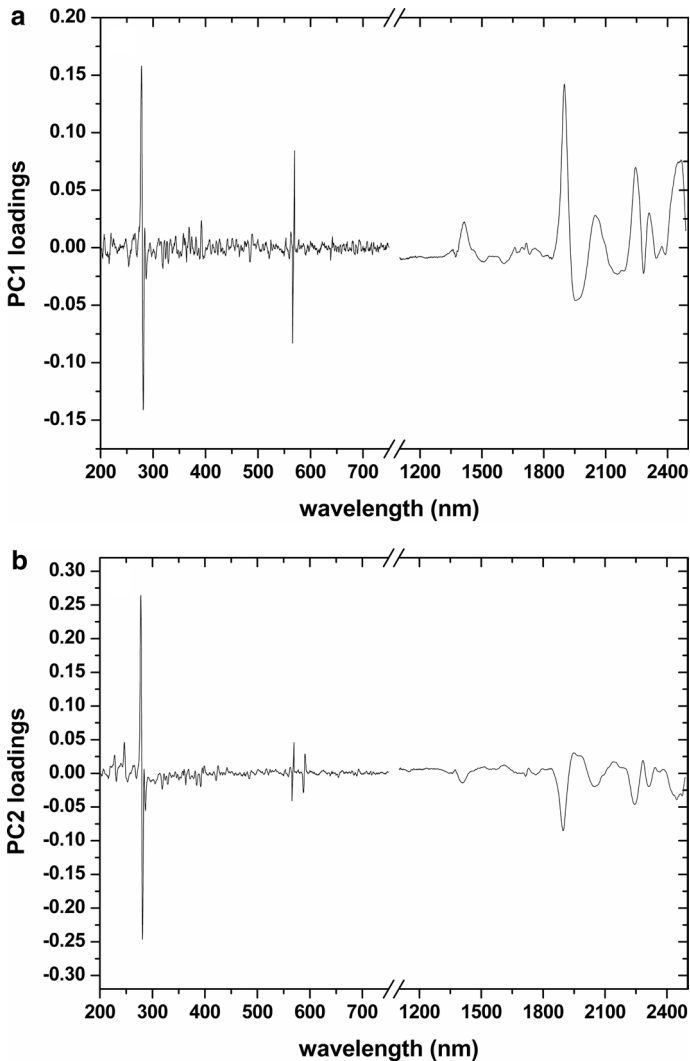


Fig. 5 PCA loading plots from all pretreated data for the first (a) and second (b) components

determined and are given in Table 2. Table 2 also shows an attempt for chemical assignment of these peaks/bands according to the literature. Mainly for the LIBS emission peaks, it was difficult to determine exactly which chemical element was related to each emission peak because of the relatively low spectral resolution of the LIBS instrument used in this work for atomic spectroscopy. However, in general, we can tell that different concentrations of mainly iron, copper, zinc, and/or sodium, and lignin, water, cellulose and/or hemicellulose among the samples were responsible for the sample grouping and separation according to the wood species.

Table 2 Assignments of the spectral peaks (LIBS) and bands (NIRS) related to the species separation at PCA

Number ^a	Observed wave-length (nm)	Chemical assignment ^b	Literature wavelength (nm) ^b
1	229.8	Cu	229.437, 229.949
		Fe	229.822, 230.117
2	248.9	Cu	248.579, 248.965
		Fe	248.983, 249.326
3	279.6	Cu	279.179, 279.953
		Fe	279.389, 279.663
		Zn	280.086
4	567.7	Cu	567.600
		Fe	567.525, 567.902
5	589.3	Cu	589.797
		Na	588.995, 589.592
6	1445.6	Lignin (–OH)	1447, 1448
7	1926.2	Water (–OH)	1916–1942
8	2100.8	Cellulose (–CH, –OH)	2092, 2110
9	2272.8	Cellulose (–CH ₂ , –COC–, –OH)	2270, 2271
		Hemicellulose (–CH, –CH ₂)	2271, 2272
10	2337.9	Cellulose (–CH, –CH ₂)	2335, 2338
		Hemicellulose (–CH)	2335
		Lignin (–CH, –CH ₂)	2336

^aAccording to Fig. 2

^bSchwanninger et al. (2011) and Kramida et al. (2018)

Wood discrimination

After the exploratory data analysis by PCA, the pretreated data from LIBS and NIRS were employed to evaluate the possibility of sample discrimination according to the wood species using PLS-DA. Only nine samples (about 21%) were selected for the external validation because of the relatively low number of samples so that a representative number of samples was available in the calibration step for a good modeling of all wood species. Figure 6 shows the variation in the successful predictions of the wood species as a function of the number of latent variables (LV) employed in the calibration with full cross-validation. From this figure, and taking into account the compromise between the highest successful prediction and the lowest LV number, the authors decided to use 8 LV in the PLS-DA. Therefore, Table 3 shows the results of the PLS-DA for wood discrimination, obtained from the calibration with full cross-validation and from the external validation. As can be observed, three out of 33 samples were misclassified in the calibration (about 9%), whereas one out of nine samples was misclassified in the external validation (about 11%). All the misclassifications involved exactly

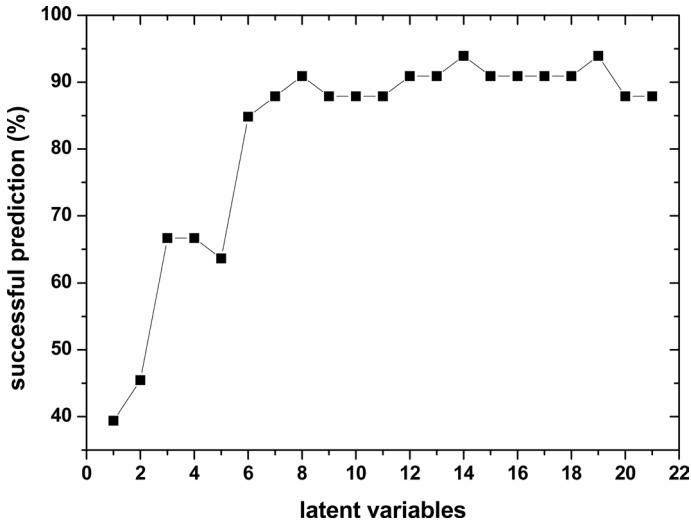


Fig. 6 Effect of the number of latent variables employed in the calibration on the successful prediction of the wood species using full cross-validation

Table 3 Results of the calibration with full cross-validation and external validation using PLS-DA for the discrimination of wood species (eight latent variables)

Full cross-validation		Predicted (33 samples)					
		AC	CL	PR	CE	BV	AP
Reference	AC	4	0	0	1	0	0
	CL	0	5	0	0	0	0
	PR	0	1	7	0	0	0
	CE	0	0	0	9	0	0
	BV	0	0	0	0	5	1
	AP	0	0	0	0	0	9
External validation		Predicted (9 samples)					
		AC	CL	PR	CE	BV	AP
Reference	AC	1	0	0	0	0	0
	CL	0	1	0	0	0	0
	PR	0	1	1	0	0	0
	CE	0	0	0	2	0	0
	BV	0	0	0	0	1	0
	AP	0	0	0	0	0	2

the sample groups with some minor group overlapping between their boundaries (CE-AC and BV-AP) or the sample groups with a wide sample dispersion (PR and CL).

Conclusion

A new method was proposed for the discrimination of wood species by using a home-made, compact, and low-cost LIBS instrument and a commercial Fourier transform NIRS instrument together with chemometrics. The method was evaluated in the analysis of 42 samples from six different wood species. The spectra from LIBS and NIRS were combined in a single matrix and pretreated to remove signal noise, baseline variations, and effects from light scattering and to equalize the maximum intensities between the spectra from both analytical techniques. The exploratory data analysis by PCA showed a clear formation of sample groups according to the wood species only when the data from both analytical techniques and the data pretreatment were used. The sample grouping was probably related to different concentrations of iron, copper, zinc, and/or sodium, in the case of LIBS data, and lignin, water, cellulose, and/or hemicellulose, in the case of NIRS data. The sample discrimination according to the wood species was proved possible by using PLS-DA, but with some minor misclassifications. The misclassifications were related to some minor group overlapping or to sample groups with a wide sample dispersion, as previously observed by PCA.

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Conflict of interest The authors declare that they have no conflict of interest.

References

- Bächle H, Zimmer B, Wegener G (2012) Classification of thermally modified wood by FT-NIR spectroscopy and SIMCA. *Wood Sci Technol* 46:1181–1192. <https://doi.org/10.1007/s00226-012-0481-z>
- Bouslamti MA, Irle MA, Belloncle C et al (2013) Classification of treated wood using Fourier transform near infrared spectroscopy and multivariate data analysis. *Int Wood Prod J* 4:116–121. <https://doi.org/10.1179/2042645312Y.0000000026>
- Carballo-Meilan A, Goodman AM, Baron MG, Gonzalez-Rodriguez J (2014) A specific case in the classification of woods by FTIR and chemometric: discrimination of Fagales from Malpighiales. *Cellulose* 21:261–273. <https://doi.org/10.1007/s10570-013-0093-2>
- Cui X, Wang Q, Zhao Y et al (2019) Laser-induced breakdown spectroscopy (LIBS) for classification of wood species integrated with artificial neural network (ANN). *Appl Phys B* 125:56. <https://doi.org/10.1007/s00340-019-7166-3>
- Francisco-Fernández M, Tarrío-Saavedra J, Mallik A, Naya S (2012) A comprehensive classification of wood from thermogravimetric curves. *Chemom Intell Lab Syst* 118:159–172. <https://doi.org/10.1016/j.chemolab.2012.07.003>
- Francisco-Fernández M, Tarrío-Saavedra J, Naya S et al (2015) Classification of wood using differential thermogravimetric analysis. *J Therm Anal Calorim* 120:541–551. <https://doi.org/10.1007/s10973-014-4260-y>
- Francisco-Fernández M, Tarrío-Saavedra J, Naya S et al (2017) Statistical classification of early and late wood through the growth rings using thermogravimetric analysis. *J Therm Anal Calorim* 127:499–506. <https://doi.org/10.1007/s10973-016-5917-5>
- Gonzaga FB, Rocha WFC, Correa DN (2015) Discrimination between authentic and false tax stamps from liquor bottles using laser-induced breakdown spectroscopy and chemometrics. *Spectrochim Acta Part B At Spectrosc* 109:24–30. <https://doi.org/10.1016/j.sab.2015.04.011>
- Gonzaga FB, Braga LR, Sampaio AP et al (2017) A simple method for forward variable selection and calibration: evaluation for compact and low-cost laser-induced breakdown spectroscopy system. *Anal Bioanal Chem* 409:3017–3024. <https://doi.org/10.1007/s00216-017-0247-4>

- Hayashi K, Tsuchikawa S, Inoue K, Noma J (2003) Application of near-infrared spectroscopy to wood discrimination. *J Wood Sci* 49:29–35. <https://doi.org/10.1007/s100860300005>
- Horacek M, Jakusch M, Krehan H (2009) Control of origin of larch wood: discrimination between European (Austrian) and Siberian origin by stable isotope analysis. *Rapid Commun Mass Spectrom* 23:3688–3692. <https://doi.org/10.1002/rcm.4309>
- Kalaw JM, Sevilla FB III (2018) Discrimination of wood species based on a carbon nanotube/polymer composite chemiresistor array. *Holzforschung* 72:215–223. <https://doi.org/10.1515/hf-2017-0097>
- Kramida A, Ralchenko Y, Reader J, NIST ASD Team (2018) NIST: atomic spectra database (version 5.6.1). <https://physics.nist.gov/asd>. Accessed 2 Apr 2019
- Kurata Y (2017) Nondestructive classification analysis of wood soaked in seawater by using near-infrared spectroscopy. *For Prod J* 67:63–68. <https://doi.org/10.13073/FPJ-D-15-00049>
- Lavine BK, Davidson CE, Moores AJ, Griffiths PR (2001) Raman spectroscopy and genetic algorithms for the classification of wood types. *Appl Spectrosc* 55:960–966. <https://doi.org/10.1366/0003702011953108>
- Lopez-Moreno C, Amponsah-Manager K, Smith BW et al (2005) Quantitative analysis of low-alloy steel by microchip laser induced breakdown spectroscopy. *J Anal At Spectrom* 20:552. <https://doi.org/10.1039/b419173k>
- Nisgoski S, de Oliveira AA, de Muñiz GIB (2017) Artificial neural network and SIMCA classification in some wood discrimination based on near-infrared spectra. *Wood Sci Technol* 51:929–942. <https://doi.org/10.1007/s00226-017-0915-8>
- Oliveira EM, Braga JWB, da Costa AF (2015) Discrimination between similar woods by molecular fluorescence and partial least squares. *Quim Nova* 5:5. <https://doi.org/10.5935/0100-4042.20150127>
- Oliveira DM, Fontes LM, Pasquini C (2019) Comparing laser induced breakdown spectroscopy, near infrared spectroscopy, and their integration for simultaneous multi-elemental determination of micro- and macronutrients in vegetable samples. *Anal Chim Acta* 1062:28–36. <https://doi.org/10.1016/j.aca.2019.02.043>
- Park S-Y, Kim J-C, Kim J-H et al (2017) Possibility of wood classification in Korean softwood species using near-infrared spectroscopy based on their chemical compositions. *J Korean Wood Sci Technol* 45:202–212. <https://doi.org/10.5658/WOOD.2017.45.2.202>
- Piuri V, Scotti F (2010) Design of an automatic wood types classification system by using fluorescence spectra. *IEEE Trans Syst Man Cybern Part C (Appl Rev)* 40:358–366. <https://doi.org/10.1109/tsmcc.2009.2039479>
- Ramalho FMG, Andrade JM, Hein PRG (2018) Rapid discrimination of wood species from native forest and plantations using near infrared spectroscopy. *For Syst* 27:e008. <https://doi.org/10.5424/fs/2018272-12075>
- Savitzky A, Golay MJE (1964) Smoothing and differentiation of data by simplified least squares procedures. *Anal Chem* 36:1627–1639. <https://doi.org/10.1021/ac60214a047>
- Schwanninger M, Rodrigues JC, Fackler K (2011) A review of band assignments in near infrared spectra of wood and wood components. *J Near Infrared Spectrosc* 19:287–308. <https://doi.org/10.1255/jnirs.955>
- Shou G, Zhang W, Gu Y, Zhao D (2014) Application of near infrared spectroscopy for discrimination of similar rare woods in the Chinese market. *J Near Infrared Spectrosc* 22:423–432. <https://doi.org/10.1255/jnirs.1136>
- Solo-Gabriele HM, Townsend TG, Hahn DW et al (2004) Evaluation of XRF and LIBS technologies for on-line sorting of CCA-treated wood waste. *Waste Manag* 24:413–424. <https://doi.org/10.1016/j.wasman.2003.09.006>
- Zhang M, Zhao GJ, Liu B et al (2019) Wood discrimination analyses of *Pterocarpus tinctorius* and endangered *Pterocarpus santalinus* using DART-FTICR-MS coupled with multivariate statistics. *IAWA J* 40:58–74. <https://doi.org/10.1163/22941932-40190224>
- Zhu M-Z, Wen B, Wu H et al (2019) The quality control of tea by near-infrared reflectance (NIR) spectroscopy and chemometrics. *J Spectrosc* 2019:1–11. <https://doi.org/10.1155/2019/8129648>