LIBSsa: an open source software for analyzing LIBS spectra

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Software

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Summary

Laser-Induced Breakdown Spectroscopy (LIBS) is a technique that uses a high-energy pulsed laser to detect and analyze elements present in a sample. The laser beam is directed through an optical system (commonly mirrors, lenses, prisms, or optical fibers) and focused onto the sample's surface. When the laser interacts with the sample, a part is ablated, vaporized, and generates a high-temperature plasma. The species in the plasma emit electromagnetic radiation characteristics of each element in the sample. This radiation is collected by lenses and conveyed through an optical fiber to a spectrometer, where diffraction occurs. The diffracted light is detected using a CCD (charge-coupled device) or ICCD (intensified charge-coupled device). Finally, a spectrum (Figure 1) is generated (Miziolek et al., 2006).

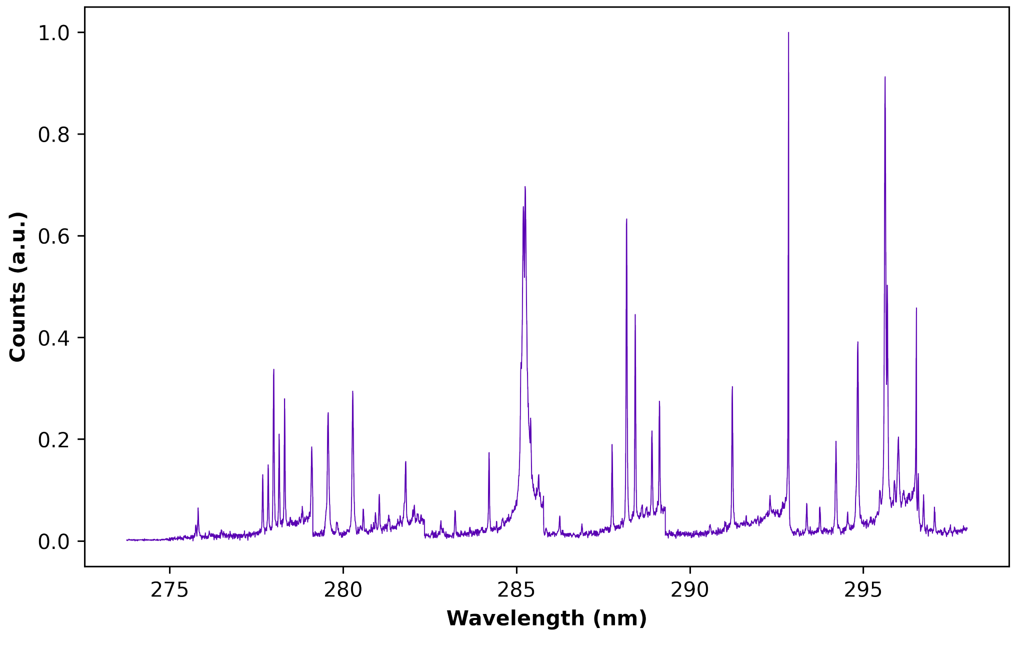

Figure 1: Characteristic LIBS spectrum. Source: self-authored.

Due to its advantages, the LIBS technique has been widely used for elemental characterization in several types of samples, including soils (Ferreira et al., 2011; Nicolodelli et al., 2014; Stenio, Xavier, et al., 2022; Villas-Boas et al., 2016), leaves (Ranulfi et al., 2018; Stenio, Costa, et al., 2022), fertilizers (Marangoni et al., 2016), river sediments (de Morais et al., 2021), food (Vinicius Câmara Costa et al., 2018), metallic alloys (Noll et al., 2018) and electronic waste

The Journal of Open Source Software

(Vinícius Câmara Costa et al., 2018), to name a few.

The Laser-Induced Breakdown Spectroscopy spectra analyzer (**LIBSsa**) is open-source software written in Python focused on analyzing LIBS spectra. It combines multiple tools used in LIBS analysis into one application, such as outliers removal, isolation of spectral lines, curve fitting, linear models (calibration curves), principal components analysis (PCA), and plasma temperature and electron density calculation.

Figure 2: Logo of LIBSsa. Source: LIBSsa repository.

Statement of need

LIBS measurement is much simpler than other standard elementary characterization techniques, such as Flame Absorption Atomic Spectrometry (FAAS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES), since it does not require acid digestion for sample preparation. Furthermore, the user can obtain a sample spectrum in seconds. Nonetheless, the analysis of the resulting signal may be highly complex.

Much of the complexity in analyzing LIBS spectra arises mainly due to matrix effects, which hinder the ability to obtain calibration blanks and generate universal calibration curves. As a result, analysts need to adopt various calibration and signal-processing strategies to achieve quantitative measurements.

In general, those working with LIBS commonly develop tools to process the measured signal and extract satisfactory results. However, this practice has the effect of generating highly specialized users of the technique, not only in terms of using instrumentation but also in scientific data analysis tools, such as R, MATLAB, OriginLab, Weka, among others. Although these platforms provide powerful tools for signal analysis, they are not dedicated tools for LIBS spectra analysis.

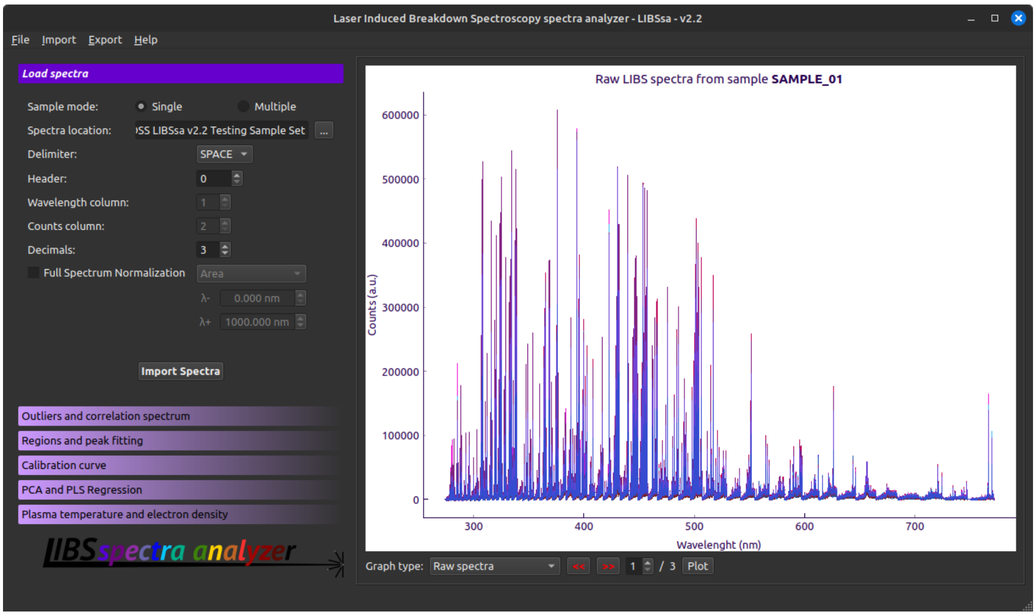

Figure 3: LIBSsa home screen tab with spectra loaded. Source: self-authored.

Knowing about these challenges and aiming to make the LIBS technique more widely used, the authors (Stenio, 2023) proposed a software creation that would automate the LIBS analysis, incorporating strategies used in several works in the literature (Castro & Pereira-Filho, 2016; de Morais et al., 2021; Marangoni et al., 2016; Nicolodelli et al., 2014; Stenio, Xavier, et al., 2022; Stenio, Costa, et al., 2022). In this way, the LIBSsa software was conceived (Figure 3).

The main purpose of LIBSsa is to help scientists in the LIBS/spectroscopy field gain speed and practicality when analyzing LIBS spectra, allowing fast assessment of which is the best calibration strategy for the sample set.

Brief software description

LIBSsa is straightforward: the user selects the input source (where LIBS spectra are located), loads them into the program, and performs a wide range of analyses, including: removal of outliers using SAM (Keshava, 2004) or MAD (Leys et al., 2013) algorithms, full spectrum normalization (FSN), correlation spectrum, peak isolation, peak fitting (Gaussian, Lorentzian, and Voigt), univariate linear models, multivariate partial least squares regression (PLSR), principal components analysis (PCA), and plasma temperature and electron density calculation using the Saha-Boltzmann equation (Stenio, 2023). Figure 4 shows some of the graphics generated by LIBSsa.

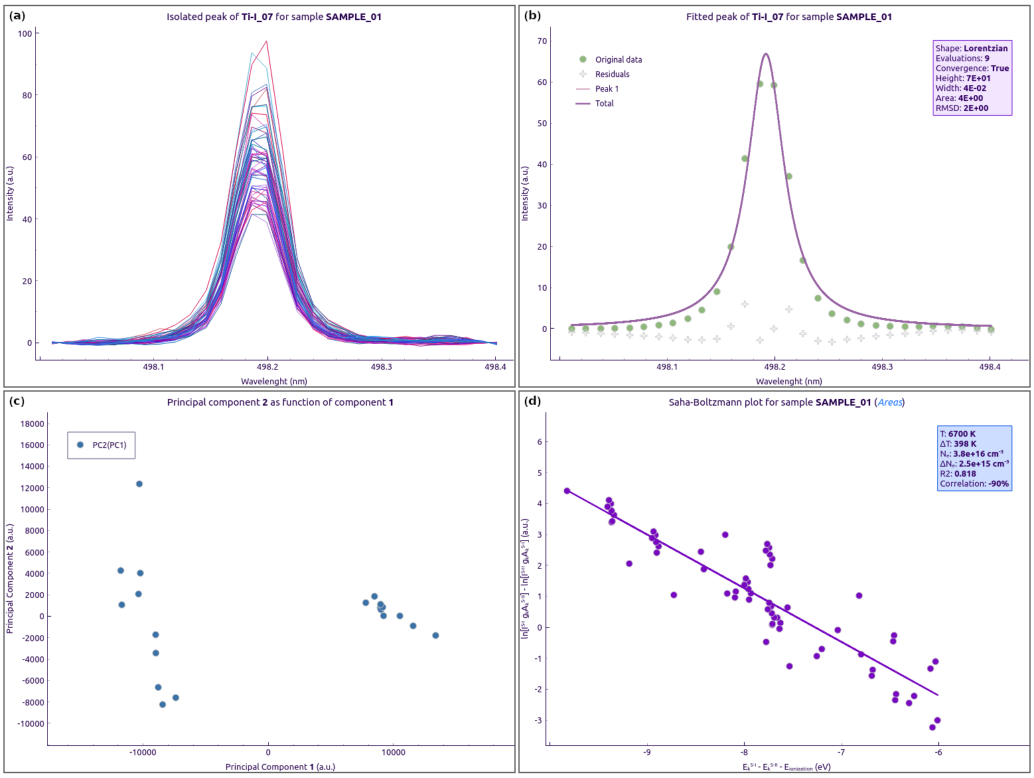

Figure 4: Some analyses available in LIBSsa: peak isolation (a), peak fitting (b), PCA (c), and Saha-Boltzmann plot (d). Source: self-authored.

In each step of the analysis, it is possible to save/export data into multiple file formats (txt, csv, and xlsx). Figure 5 shows a typical LIBSsa analysis workflow.

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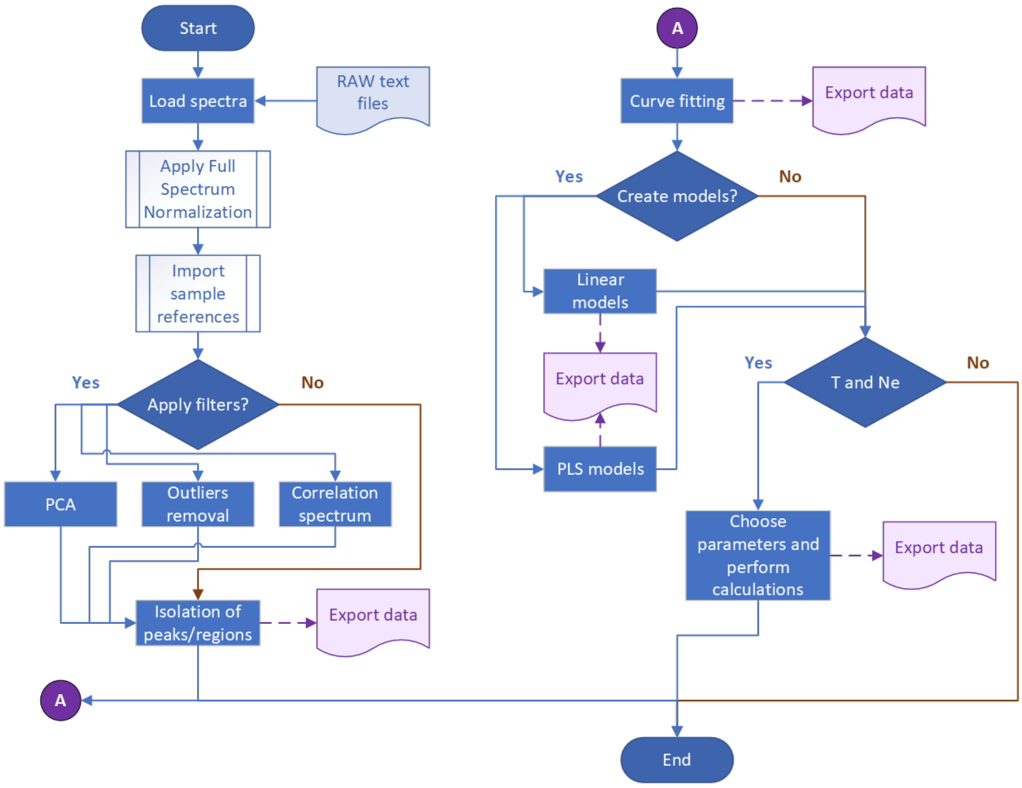

Figure 5: LIBSsa working flowchart. Source: self-authored.

In order to properly operate, the program uses the libraries **NumPy** (Harris et al., 2020) and **SciPy** (Virtanen et al., 2020) for most calculations, **pandas** (McKinney & others, 2010) and **openpyxl** (Team of developers of Openpyxl, 2023) to export spreadsheets, **scikit-learn** (Pedregosa et al., 2011) to fit linear, PLS and PCA models, **pyqtgraph** (Team of developers of PyQtGraph, 2023) to show in program graphics, and finally **PySide6** (The Qt Company, 2020) as the graphical user interface (GUI) framework.

Author contributions

Conceptualization: K. S., D. M. B. P. M.; data curation: K. S.; formal analysis: K. S.; funding acquisition: D. M. B. P. M.; investigation: K. S.; methodology: K. S.; project administration: K. S.; resources: D. M. B. P. M.; software: K. S.; supervision: D. M. B. P. M.; validation: K. S., D. M. B. P. M.; visualization: K. S.; writing – original draft: K. S.; writing – review & editing: K. S., D. M. B. P. M.

Conflicts of interest

There are no conflicts to declare.

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References

Castro, J. P., & Pereira-Filho, E. R. (2016). Twelve different types of data normalization for the proposition of classification, univariate and multivariate regression models for the direct analyses of alloys by laser-induced breakdown spectroscopy (LIBS). *Journal of Analytical Atomic Spectrometry*, *31*(10), 2005–2014. https://doi.org/10.1039/C6JA00224B

Costa, Vinícius Câmara, Castro, J. P., Andrade, D. F., Babos, D. V., Garcia, J. A., Sperança, M. A., Catelani, T. A., & Pereira-Filho, E. R. (2018). Laser-induced breakdown spectroscopy (LIBS) applications in the chemical analysis of waste electrical and electronic equipment (WEEE). *TrAC Trends in Analytical Chemistry*, *108*, 65–73. https://doi.org/10.1016/j.trac.2018.08.003

Costa, Vinicius Câmara, de Babos, D. V., de Aquino, F. W. B., Virgílio, A., Amorim, F. A. C., & Pereira-Filho, E. R. (2018). Direct determination of Ca, K and Mg in cassava flour samples by laser-induced breakdown spectroscopy (LIBS). *Food Analytical Methods*, *11*, 1886–1896. https://doi.org/10.1007/s12161-017-1086-9

de Morais, C. P., Nicolodelli, G., Mitsuyuki, M. C., da Silva, K. S. G., Mauad, F. F., Mounier, S., & Milori, D. M. B. P. (2021). Total phosphorus determination in eutrophic tropical river sediments by laser-induced breakdown spectroscopy techniques. *Analytical Methods*, *13*(1), 77–83. https://doi.org/10.1039/D0AY02008G

Ferreira, E. C., Milori, D. M. B. P., Ferreira, E. J., Dos Santos, L. M., Martin-Neto, L., & de Araújo Nogueira, A. R. (2011). Evaluation of laser induced breakdown spectroscopy for multielemental determination in soils under sewage sludge application. *Talanta*, *85*(1), 435–440. https://doi.org/10.1016/j.talanta.2011.04.001

Harris, C. R., Millman, K. J., Van Der Walt, S. J., Gommers, R., Virtanen, P., Cournapeau, D., Wieser, E., Taylor, J., Berg, S., Smith, N. J., & others. (2020). Array programming with NumPy. *Nature*, *585*(7825), 357–362. https://doi.org/10.1038/s41586-020-2649-2

Keshava, N. (2004). Distance metrics and band selection in hyperspectral processing with applications to material identification and spectral libraries. *IEEE Transactions on Geoscience and Remote Sensing*, *42*(7), 1552–1565. https://doi.org/10.1109/TGRS.2004.830549

Leys, C., Ley, C., Klein, O., Bernard, P., & Licata, L. (2013). Detecting outliers: Do not use standard deviation around the mean, use absolute deviation around the median. *Journal of Experimental Social Psychology*, *49*(4), 764–766. https://doi.org/10.1016/j.jesp.2013.03.013

Marangoni, B. S., Silva, K. S., Nicolodelli, G., Senesi, G. S., Cabral, J. S., Villas-Boas, P. R., Silva, C. S., Teixeira, P., Nogueira, A. R. A., Benites, V. M., & others. (2016). Phosphorus quantification in fertilizers using laser induced breakdown spectroscopy (LIBS): A methodology of analysis to correct physical matrix effects. *Analytical Methods*, *8*(1), 78–82. https://doi.org/10.1039/C5AY01615K

McKinney, W., & others. (2010). Data structures for statistical computing in python. *Proceedings of the 9th Python in Science Conference*, *445*, 51–56. https://doi.org/10.25080/Majora-92bf1922-00a

Miziolek, A. W., Palleschi, V., & Schechter, I. (2006). *Laser induced breakdown spectroscopy*. Cambridge University Press.

Nicolodelli, G., Marangoni, B. S., Cabral, J. S., Villas-Boas, P. R., Senesi, G. S., Dos Santos, C. H., Romano, R. A., Segnini, A., Lucas, Y., Montes, C. R., & others. (2014). Quantification of total carbon in soil using laser-induced breakdown spectroscopy: A method to correct interference lines. *Applied Optics*, *53*(10), 2170–2176. https://doi.org/10.1364/AO.53.002170

Noll, R., Fricke-Begemann, C., Connemann, S., Meinhardt, C., & Sturm, V. (2018). LIBS analyses for industrial applications–an overview of developments from 2014 to 2018. *Journal of Analytical Atomic Spectrometry*, *33*(6), 945–956. https://doi.org/10.1039/C8JA00076J

Pedregosa, F., Varoquaux, G., Gramfort, A., Michel, V., Thirion, B., Grisel, O., Blondel, M., Prettenhofer, P., Weiss, R., Dubourg, V., & others. (2011). Scikit-learn: Machine learning in python. *The Journal of Machine Learning Research*, *12*, 2825–2830. https://jmlr.csail.mit.edu/papers/v12/pedregosa11a.html

Ranulfi, A. C., Senesi, G. S., Caetano, J. B., Meyer, M. C., Magalhaes, A. B., Villas-Boas, P. R., & Milori, D. M. (2018). Nutritional characterization of healthy and Aphelenchoides besseyi infected soybean leaves by laser-induced breakdown spectroscopy (LIBS). *Microchemical Journal*, *141*, 118–126. https://doi.org/10.1016/j.microc.2018.05.008

Stenio, K. (2023). *Desenvolvimento de software e modelos para análise de nutrientes em material vegetal utilizando espectroscopia de emissão óptica com plasma induzido por laser (LIBS)* [PhD thesis, Universidade Federal de São Carlos - UFSCar]. https://repositorio.ufscar.br/handle/ufscar/18072

Stenio, K., Costa, V. C., De Morais, C. P., Magalhães, A. B., & Milori, D. M. B. P. (2022). Direct determination of nutrient elements in plant leaves by double pulse laser-induced breakdown spectroscopy: Evaluation of calibration strategies using direct and inverse models for matrix-matching. *Analytical Methods*, *14*(12), 1246–1253. https://doi.org/10.1039/D1AY02101J

Stenio, K., Xavier, A. A. P., De Morais, C. P., & Milori, D. M. B. P. (2022). Carbon quantification in soils with different textures using laser-induced breakdown spectroscopy: Spectral interference correction and use of a 3D plane model. *Analytical Methods*, *14*(42), 4219–4229. https://doi.org/10.1039/D2AY01424F

Team of developers of Openpyxl. (2023). *Openpyxl* (Version 3.1.2). https://foss.heptapod.net/openpyxl/openpyxl

Team of developers of PyQtGraph. (2023). *PyQtGraph* (Version 0.13.3). https://github.com/pyqtgraph/pyqtgraph

The Qt Company. (2020). *Qt for python* (Version 6.4.3). http://pyside.org/

Villas-Boas, P. R., Romano, R. A., de Menezes Franco, M. A., Ferreira, E. C., Ferreira, E. J., Crestana, S., & Milori, D. M. B. P. (2016). Laser-induced breakdown spectroscopy to determine soil texture: A fast analytical technique. *Geoderma*, *263*, 195–202. https://doi.org/10.1016/j.geoderma.2015.09.018

Virtanen, P., Gommers, R., Oliphant, T. E., Haberland, M., Reddy, T., Cournapeau, D., Burovski, E., Peterson, P., Weckesser, W., Bright, J., & others. (2020). SciPy 1.0: Fundamental algorithms for scientific computing in python. *Nature Methods*, *17*(3), 261–272. https://doi.org/10.1038/s41592-019-0686-2