

Comparison of Algorithms for Baseline Correction of LIBS Spectra for Quantifying Total Carbon in Brazilian Soils

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Abstract

LIBS is a promising and versatile technique for multi-element analysis that usually takes less than a minute and requires minimal sample preparation and no reagents. Despite the recent advances in elemental quantification, the LIBS still faces issues regarding the baseline produced by background radiation, which adds non-linear interference to the emission lines. In order to create a calibration model to quantify elements using LIBS spectra, the baseline has to be properly corrected. In this paper, we compared the performance of three filters to remove random noise and five methods to correct the baseline of LIBS spectra for the quantification of total carbon in soil samples. All combinations of filters and methods were tested, and their parameters were optimized to result in the best correlation between the corrected spectra and the carbon content in a training sample set. Then all combinations with the optimized parameters were compared with a separate test sample set. A combination of Savitzky-Golay filter and 4S Peak Filling method resulted in the best correction: Pearson's correlation coefficient of 0.93 with root mean square error of 0.21. The result was better than using a linear regression model with the carbon emission line 193.04 nm (correlation of 0.91 with error of 0.26). The procedure proposed here opens a new possibility to correct the baseline of LIBS spectra and to create multivariate methods based on the a given spectral range.

Introduction

Laser-induced breakdown spectroscopy (LIBS) is a multi-element analytical technique widely employed in the last years [3, 8, 13, 28, 31, 35] and has great potential to be applied in field [4, 9, 14]. A LIBS measurement usually takes less than a minute and can be remotely applied in hazardous areas or of difficult access, for example, Mars, deep sea water, and radioactive or toxic places [2, 15, 30, 37]. The LIBS also satisfies the precept of "green chemistry", in which no toxic residue is generated during the analytical process, since the technique does not require chemical reagents [3, 34]. The LIBS is also considered a promising technique for many applications, specially for soil analysis ranging from the quantification of carbon [25], nutrients [17] to contaminants [27]. Nonetheless, the technique suffers from a low reproducibility and repeatability compared to other analytical techniques (e.g. inductively coupled plasma - ICP), mainly due to matrix effects [7, 23, 33]. Such effects comprise the radiation-matter interaction, composition and aggregation state of samples, homogeneity, laser pulse energy density, and optical

alignment. Each LIBS measurement, therefore, results in an unique plasma formation, whose line emissions and background radiation depends on. To overcome such difficulties, hundreds of LIBS measurements are generally performed and averaged for each sample, and the delay time between the laser shot and spectral acquisition is adjusted for the best signal to noise ratio and for attenuating the background radiation. Even with the adjustment of delay time, the background radiation is still present in the spectra, which corresponds to the spectral baseline as in Figure 1, and imposes difficulties for quantitative elemental analysis.

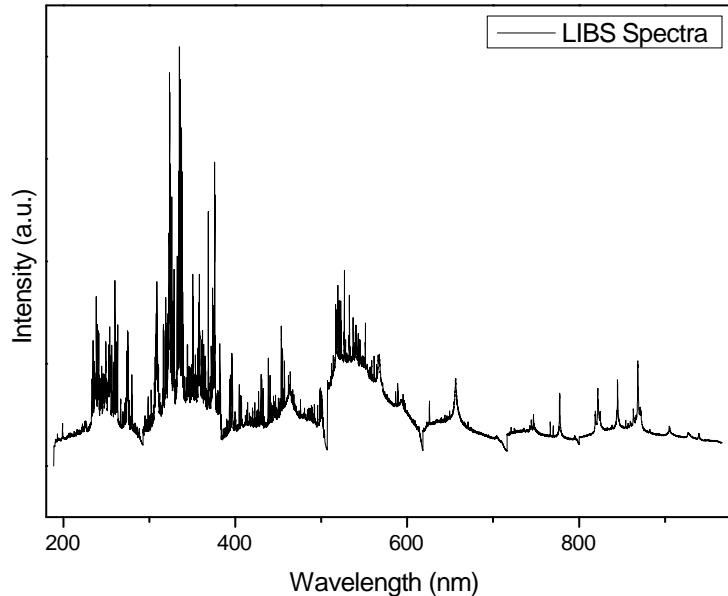


Figure 1. A example of LIBS spectrum without correction depicting a pronounced irregular baseline. Seven distinct regions can be identified in this spectrum, each one corresponding to a spectrometer.

A common solution for the background radiation issues in LIBS is to correct the baseline by subtracting a straight line that connects the neighbourhood of the emission line of interest [6]. Such solution is, however, limited to non-interfered emission lines with a neighbourhood clearly belonging to the baseline (without other emission lines). Furthermore, a proper automated method for a broad spectral range has not been developed exclusively for LIBS.

Thus, the purpose of this work was to find a combination of random noise filters and baseline correction methods that minimized the influence of the background radiation over calibration models for quantifying soil carbon. We compared the performance three filters: Low Pass [1], Median [16], and Savitzky-Golay [32] to remove random noise; and five methods to correct the baseline: Statistics-Sensitive Non-Linear Iterative Peak-Clipping (SNIP) [24,29], Top Hat (TH) [12,36], Median [12], Rolling Balls (RB) [18], and 4S Peak Filling (PF) [20], which were developed for other photonic techniques such as X ray, Raman, infrared and atomic mass spectroscopy. All combinations of filters and baseline correction methods were optimized with a training soil sample set to get the best correlation with the reference technique. Then all optimized combinations were tested with a separated validation set. After the filtering and the baseline correction,

the corrected spectra were used as input variables in the partial least square regression method, and the models built were tested with 10-fold cross-validation. The results were given in the Pearson's correlation coefficient ρ and the root mean square error (RMSE) for each combination. The combinations were then ranked according to ρ .

1 Materials and methods

1.1 Samples and reference measures

All the soil samples used in this experiment were extracted from Canchim Farm, São Carlos, Brazil. These soil samples were prepared to be used by drying the samples, homogenizing them and transforming them in pellets by applying a pressure of $8 \times 10^8 \text{ Nm}^{-2}$ for approximately 30 seconds. These samples were utilized by LIBS measures. For reference measures of carbon in the soil samples, that were made in a Perkin-Elmer 2400 CHNS/O analyser, the samples were milled into smaller particles which 0.15 mm, then they were weighed inside a tin capsule and after placed at the analyzer.

1.2 LIBS spectroscopy

The LIBS measures were made with a LIBS2500+ spectrometer of the Ocean Optics, Dunedin, USA, equipped with a pulsed Nd:YAG Q-switched 1064 nm produced by Quantel (Big Sky Laser Ultra 50) and that works with 50mW of maximum energy and 10Hz what is sufficient for plasma formation. The laser beam was focused at the surface of the samples that were located inside an ablation chamber and the plasma emission was collected by a collection of optical fibers connected at seven spectrometers.

All the measures were taken in a presence of atmospheric air and the spectra acquisition was made between 189 – 966 nm with optical resolution of 0.1 nm. O The spectrum generated by the emission of excited species was analyzed in the regions UV-VIS-IP, but it's important to notice that the X-ray are also possible, depending of the incident laser energy on the sample. To improve the precision of the results 60 spectra were captured for each soil sample, where each spectra corresponds to a different place on the sample. The experimental setup of the LIBS used to make the measures is shown at the Figure 2.

1.3 Spectral processing

1.3.1 Tradicional baseline correction

The method of traditional correction by three points [6], also known as a heuristic method, consists of correct the baseline by subtracting the spectral region around the peak of interest by the straight line which connects the side of the peak . Thus, it is possible to obtain values for the height or the peak area, from which are generated models of single or multivariable linear regression. The height is the maximum intensity of the peak corrected, while the area is the integral of the peak or the area of a fitted distribution (e.g., Gaussian, Lorentzian or Voigt).

1.3.2 Noise suppression

Three signal smoothing filters were previously applied to the spectra, later to be made automatic baseline correction. They are: Savitzky-Golay Filter (SGF), Low Pass Filter (LPF) and Median Filter. The SGF smoothes the data, increasing the signal to noise ratio without significantly distort the signal. This is possible from a convolution of successive subsets of adjacent data points with a polynomial using the method of linear least

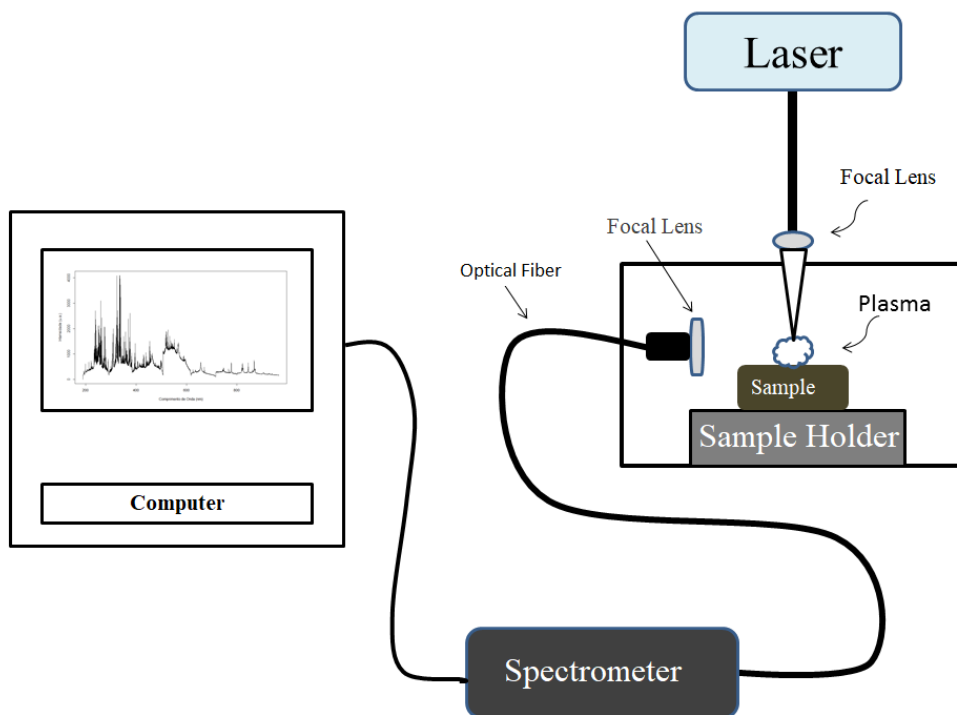


Figure 2. Aparato experimental do sistema LIBS composto por laser, conjunto óptico, câmara de ablação, conjunto de espectrômetros com sete fibras ópticas e computador.

squares [32]. The LPF has been improved by the group through a Voigt profile [26], which attenuates noises greater than those related to a cutoff frequency. In this way some parameters are adjusted, which are constituents of the convolution function. Finally, there is the Median, that replaces each input element (noise) by the median of the inputs of the neighbors, where the standard of neighbors is called *window* and moves by the full spectrum [16].

1.3.3 Automatic methods for baseline correction

The methods for baseline correction selected by visual inspection were SNIP, TH, Median, RB and FP [10, 11, 20, 21, 24, 29, 36]. The method SNIP (Statistics-Sensitive Non-Linear Iterative Peak-Clipping) is an algorithm developed to be applied in atomic mass spectroscopy, that was constructed in three stages for obtaining the baseline, independently of the data acquisition system. This is possible due to application of digital filter called *Low Statistics*, smoothes the spectrum in accordance with a small amount of pixels per window. TP is a structured method from a Fourier transform of the spectrum intensity, which extracts small elements and details of the spectrum data that are more relevant than those of their proximity (noise) through a sliding window, whose size is indicated by user.

The Median method is based on local averages calculations, where each spectral point is replaced by the average of the neighbors. These averages are made, for example, between the surrounding places of peaks or between noise regions, all built in local windows, that is, given a series of numbers and a fixed size subset, the first element of the moving average is obtained by taking the average subset initially set by the user. Then, the subset is modified through a window offset, creating new subset of numbers

whose average is calculated again. This process is repeated iterate times throughout the data set. RB is a method developed originally for processing data of X-ray spectroscopy that was built thinking in a sphere with fixed radius that is rolling under the spectrum. Its trajectory creates a smoothed line that is used to extract the baseline of the spectrum. And the last used method is called 4S Peak Filling, PF, that is an iterative method based on suppression of baseline by averaging local windows. For this purpose, the method requires as input the second derivative for primary smoothing, which indicates that the baseline should be monotonically decreasing, the average size of the data window, the number of used windows and the number of iterations made in loop suppression of baseline. In an established local window, the minimum of averages and iterations is selected as the new baseline.

1.3.4 Calibration model

The method of multivariate regression by Partial Least Squares (PLS) was used to construct a calibration model of the LIBS spectra for prediction of total carbon in the samples. This method was used because it reduces the dimension of the input variables and maximizing the correlation with the response variable [5, 22]. With the established prediction model, was made the validation of the results obtained with those of the reference method, which gives the Pearson coefficients that measure the degree of correlation between two variables. They are represented by ρ and assumes values between -1 and 1 , where $\rho \geq 0.7$ indicates strong correlation, $0.3 < \rho < 0.7$ indicates moderate correlation and $\rho \leq 0.3$ corresponds to a weak correlation between the results [19]. The most used value to quantify differences between estimated values by the model and the reference measures is the root mean square uncertainty (RMSE) of the correlation, which can be estimated by the equation::

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2}, \quad (1)$$

where \hat{y}_i is the value estimated by the model for the i -th sample and n is the number of samples.

1.3.5 Analysis proceedings

The approach to the problem of determining the best baseline correction method was as follows: the set of corrected spectra were obtained and divided into two parts, $\frac{2}{3}$ of the total spectrum to build the PLS model and optimization signal filter parameters and line correction method, and the rest for test of the model. For the optimization was constructed a regression model with the corrected spectra and the carbon content measured by the reference method *CHNS*. The model validation occurred through cross-validation, obtaining a value of ρ and ϵ , where ρ corresponds to the Pearson coefficient, and ϵ represents the uncertainty of the model given in mass percentage of total carbon. This process was repeated iterated times, and the values of ρ were saved, so that the end of the iterative process, $\bar{\rho}$ was calculated the the associated uncertainty. The greatest value of $\bar{\rho}$ with the lowest ϵ was used as a condition for determining the set of parameters. Thus, this set was applied to the second set of spectra for building a regression model that was validated by cross validation.

2 Results and discussions

The study was focused in the spectral range of $190 - 289nm$, corresponding to the first equipment spectrometer. In this range there are two peaks of interest for the study of total

carbon in soil, which are located in $193,04 \text{ nm}$ and $247,86 \text{ nm}$, respectively. However, that range has a high degree of complexity as the determination of their corresponding baseline because of the large amount of chemical species emitting radiation simultaneously and strong presence of radiation at all wavelengths (white radiation) caused mainly by thermal effect of the plasma. The Figure 3 represents the average of a LIBS spectrum of a sample without any treatment and a hypothetical baseline that could correct the spectral range. In Figure it is remarkable how much the continuum background radiation interferes on the spectrum shape, making the baseline quite pronounced, particularly in regions between 230 and 265 nm . It is important to notice that this spectral range has many emissions due to different degrees of ionization of many chemical species such as Fe, C, Al and Si.

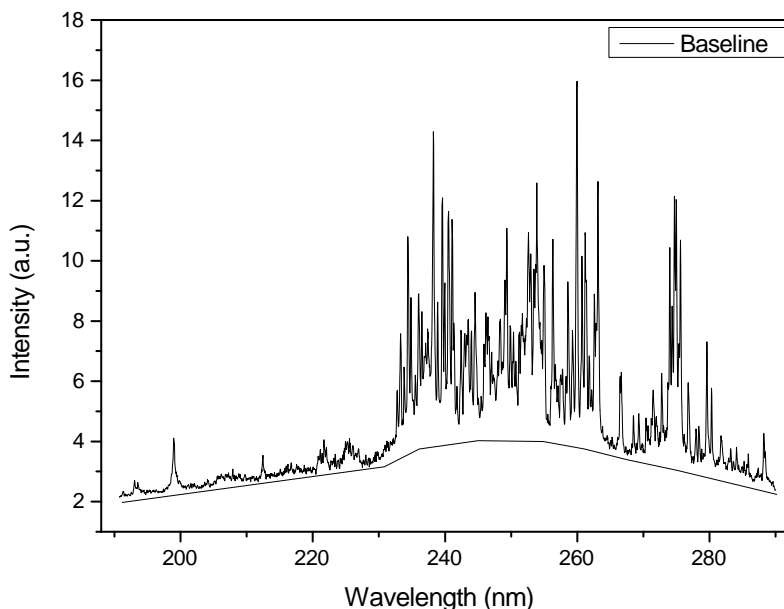


Figure 3. Average spectrum from a soil sample without baseline correction and its supposed baseline.

The traditional method for baseline corrections allows to correct only the spectral range that contains the peak of interest of C in 193.04 nm and fails when it is applied to other peak located at 247 nm , since this peak is surrounded by several other emission lines and it is not possible to find a lateral region to the peak that is sufficient to correct their baseline. Thus, it was built a linear model with the peak area 193.04 nm and carbon concentrations, which returned $\bar{\rho}_{training} = 0.92$ with $\epsilon_{training} = 0.24$ for the training set, and $\bar{\rho}_{test} = 0.91$ with $\epsilon_{test} = 0.26$ for the test set, where ϵ is the uncertainty for the content total carbon.

The baseline correction methods PF, RB, TH, Median and SNIP were combined with the smoothing filters Median, LPF and SGF and they were applied independently for the training and test sets. The optimized parameters of these combinations are shown in Table 1 and Pearson coefficients for the cross-validation of reference measurements and prediction model with its respective uncertainty for percentage of total carbon are shown in Table 2.

The SNIP method was able to correct the spectra, without significantly deform

Table 1. Set of optimized parameters through training set, applied to the test set, with respect to baseline correction methods and noise smoothing filters.

Method	Filter	Filter Par.	λ	β	I	α
SNIP	SGF	[O.P.,P.J.] = [8, 13]	-	-	100	-
	<i>LPF</i>	$\sigma = 0.44, \gamma = 10.25$	-	-	103	-
	Median	N= 1	-	-	14	-
TH	SGF	[O.P.,P.J.] = [8, 15]	-	274	-	-
	<i>LPF</i>	$\sigma = 0.20, \gamma = 4.6$	-	276	-	-
	Median	N= 2	-	14	-	-
Median	SGF	[O.P.,P.J.] = [1, 13]	-	260	-	-
	<i>LPF</i>	$\sigma = 1.22, \gamma = 16.22$	-	277	-	-
	Median	N= 1	-	14	-	-
RB	SGF	[O.P.,P.J.] = [6, 13]	-	[wn,ws] = [340, 30]	-	-
	<i>LPF</i>	$\sigma = 0.43, \gamma = 11$	-	[wn,ws] = [374,47]	-	-
	Median	N= 3	-	[wn,ws] = [340,30]	-	-
PF	SGF	[O.P.,P.J.] = [8, 13]	3	10	9	70
	<i>LPF</i>	$\sigma = 0.20, \gamma = 4.6$	3	10	9	70
	Median	N= 2	3	10	9	70

O.P. = polynomial order

P.J. = Window points for smoothing

I = Number of iterations

N = Number of points for moving window Median filter

σ, γ = Setting parameters of Voigh profile curve of the *LPF*

λ = penalty parameter to the second derivative to primary smoothing, according to [20]

α = Number of areas where spectrum is divided

β = window number of points

wn = local window points to minimize / maximize

ws = local window points for smoothing

peaks of interest and returned appreciable results for $\bar{\rho}$ when it was applied together to SGF. Complicated ranges such as those between 230 to 265 *nm* showed a smooth baseline, as it were expected. However, this did not happen when SNIP was applied with Median and *LPF*. In those cases, the baseline was overestimated and many peaks were deformed, as well as the whole spectrum shape. So, it is impossible to analyse carbon or other chemical species with these data treatments. The best result obtained for the combination method-filter SNIP-SGF. resulted in $\bar{\rho}_{training} = 0.96$ with $\epsilon_{training} = 0.17$ for the training set, and $\bar{\rho}_{test} = 0.92$ with $\epsilon_{test} = 0.21$ for the test set.

The spectra corrected by combinations of those three smoothing filters with the TH method had issues with determining an useful baseline, because it used some spectrum points that were not expected belonging to the baseline. With this, all calculated baselines were overestimated, even if there is high correlation between calibration and reference model. The same issue was observed when the procedure previously discussed was applied to the Median method. All method-filter combinations result in spectra with many peaks whose baseline was overestimated, what returned spectra with peaks with negative values for relative intensity. This therefore shows that combinations of the method Median with those three types of smoothing filter is also inadequate for the treatment of LIBS spectra.

When RB was combined with those smoothing filters good results was obtained for the baseline when the peaks are not belonging to spectral ranges in which there are a lot of emissions (230 to 265 *nm*). However, the method fails to estimate a baseline for

Table 2. Pearson Coefficient ($\bar{\rho}$) and RMSE(ϵ) to validate the model *PLS* with relation to the various noise filter combinations and baseline correction method for training and test sets.

Method	Filter	$\bar{\rho}_{training}$	$\epsilon_{training}$	$\bar{\rho}_{test}$	ϵ_{test}
SNIP	SGF	0,96	0.17	0.92	0.21
	<i>LPF</i>	0.95	0.17	0.91	0.23
	Median	0.95	0.19	0.93	0.21
TH	SGF	0.96	0.17	0.93	0.20
	<i>LPF</i>	0.96	0.18	0.92	0.21
	Median	0.96	0.19	0.88	0.26
Median	SGF	0.97	0.16	0.92	0.21
	<i>LPF</i>	0.96	0.18	0.92	0.22
	Median	0.94	0.22	0.90	0.24
RB	SGF	0.95	0.19	0,93	0,20
	<i>LPF</i>	0.95	0.19	0.92	0.21
	Median	0.95	0.19	0.92	0.21
PF	SGF	0.96	0.17	0.93	0.21
	<i>LPF</i>	0.95	0.19	0.91	0.22
	Median	0.95	0.20	0.91	0.23
Traditional		0.92	0.24	0.91	0.26

transition regions between points with few emissions and those with many emissions. Even so, the method returned appreciable results for correlation, with $\bar{\rho}_{training} = 0.95$ and $\epsilon_{training} = 0.19$ for training set and $\bar{\rho}_{test} = 0,93$ com $\epsilon_{test} = 0,20$ for test set for the combination RB - SGF.

The PF method presented the best results for correction of LIBS spectra, especially with high Pearson coefficients for all smoothing filter combinations. The combination that stood out the most was the one that used SGF. In this case, the peaks were fairly defined and all spectral regions were corrected satisfactorily. This can means that the corrections did not compromise spectral information that could lead to errors in predicting carbon. The model constructed with the training set obtained the following results: $\bar{\rho}_{training} = 0.96$ with $\epsilon_{training} = 0.17$, and for the test set: $\bar{\rho}_{test} = 0.93$ with $\epsilon_{test} = 0.21$. The combination of *4S Peak Filling* with Median filter also returned relevant results and its PLS model obtained a good prediction for the total carbon concentration, which was not achieved through *LPF*, since the spectra were distorted by degree of smoothing. Figure 4 shows the corrected spectra of a sample for each PF/smoothing filter combination.

The baseline correction through the traditional method achieves a good result when the peak in question is relatively isolated from other peaks, with free lateral regions, so that a straight line connecting them can be constructed. In the case of the peak of carbon 193.04 nm, this one is interfered with by aluminum, even so, the method was able to satisfactorily solve these peaks by bilorentzian deconvolution, calculate the area of the peak of the carbon and construct multivariate model with this value . However, such a method is only useful in relatively unpopulated regions of emission lines, which is not so common to be found in LIBS spectra. And this completely restricts application of the traditional method.

The use of the smoothing filters was of fundamental importance in the definition of the peak shapes of the different chemical species and in the noise removal, which generates greater precision in the quantification of total carbon of the samples. In particular, the SGF was able to satisfactorily model the spectra for all methods. The

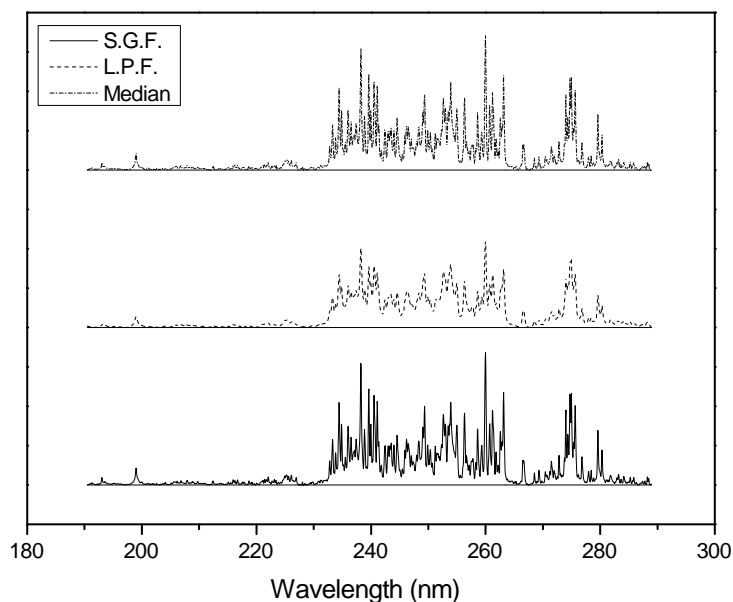


Figure 4. Spectra corrected by the 4S Peak Filling method for three different smoothing filters.

principle of this filter is to find a polynomial function of degree n that fits the spectrum and its different spectral regions, be they the most complex as found between 230 and 265 nm. The black spectrum of Figure 4 represents the combination of PF-SGF, in which the power of correction of this technique can be verified. In the problematic region cited, the baseline found was fairly smooth, as can be seen in Figure 5.

3 Conclusions

This study aimed to compare different baseline correction methods with the purpose of application to correct LIBS spectra, since the literature is very poor in alternatives to those who seek an effective correction for this type of spectroscopy. The SNIP, Top Hat, Median, 4S Peak Filling and Rolling Balls methods were evaluated in combination with the LPF, SGF and Median noise filters, and compared to the traditional baseline correction method to find the best path for data processing for the LIBS spectra that maximized carbon quantification.

For each method combined with the filters and also for the traditional method PLS models were constructed with cross validation and their results for the training and test sets were compared. Each method was optimized to improve the correlation between LIBS spectra and carbon concentration in the samples. Some filters combined with baseline correction methods distorted the spectrum, thus compromising the definition of peaks and, consequently, making it impossible to quantify chemical elements. Others of them have significantly improved the spectrum format, emphasizing spectral regions that were not well understood before. Smoothing filters have been able to define important peaks for quantification of different chemical species, especially carbon.

It should be noted that the Peak Filling 4S method, which combined with the Savitzky-Golay polynomial noise filter, returned the Pearson coefficient $\rho_{test}^- = 0.93$ and

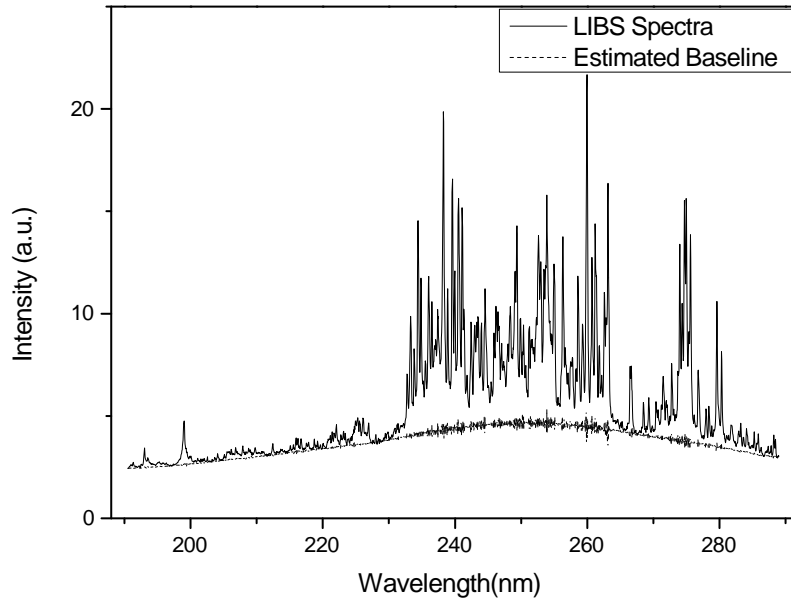


Figure 5. Baseline estimated by the 4S Peak Filling method for the spectral region between 193.04 nm and 247.86 nm.

RMSE $\epsilon_{test} = 0.21$ for the test set. This result was significantly better than that of the traditional baseline correction method, whose result obtained with the 193.04 nm peak was $\rho_{test} = 0.91$ with RMSE $\epsilon_{test} = 0.26$. This shows that the baselines of the LIBS spectra can be corrected satisfactorily by the 4S Peak Filling baseline correction method added to the Savitzky-Golay noise filter. Thus, the processing of the LIBS spectral data is significantly more robust when using the method proposed in this work, compared to the traditional method. In addition, the LIBS technique proved promising for the determination of total carbon in soils and possibly for quantification of other elements in matrices as complex as the soil. This work can also be extended to predict nutrients in plants, whose objective is the detection of plant diseases in the asymptomatic phase.

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References

1. A. Antoniou. *Digital signal processing*. McGraw-Hill Toronto, Canada, 2006.
2. S. G. Buckley, H. A. Johnsen, K. R. Hencken, and D. W. Hahn. Implementation of laser-induced breakdown spectroscopy as a continuous emissions monitor for toxic metals. *Waste Management*, 20(5):455–462, 2000.
3. D. A. Cremers, F.-Y. Yueh, J. P. Singh, and H. Zhang. *Laser-Induced Breakdown Spectroscopy, Elemental Analysis*. Wiley Online Library, 2006.

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4. J. Cunat, S. Palanco, F. Carrasco, M. Simon, and J. Laserna. Portable instrument and analytical method using laser-induced breakdown spectrometry for in situ characterization of speleothems in karstic caves. *Journal of Analytical Atomic Spectrometry*, 20(4):295–300, 2005.
 5. J. V. A. CUNHA and A. C. COELHO. Regressão linear múltipla. *CORRAR, L.J; PAULO E.; DIAS FILHO, JM (coordenadores). Análise multivariada: para cursos de administração, ciências contábeis e economia. São Paulo: Atlas, 2007.*
 6. J. Dawson, R. Snook, and W. Price. Background and background correction in analytical atomic spectrometry. part 1. emission spectrometry. a tutorial review. *J. Anal. At. Spectrom.*, 8(4):517–537, 1993.
 7. A. S. Eppler, D. A. Cremers, D. D. Hickmott, M. J. Ferris, and A. C. Koskelo. Matrix effects in the detection of pb and ba in soils using laser-induced breakdown spectroscopy. *Applied Spectroscopy*, 50(9):1175–1181, 1996.
 8. E. C. Ferreira, E. J. Ferreira, P. R. Villas-Boas, G. S. Senesi, C. M. Carvalho, R. A. Romano, L. Martin-Neto, and D. M. B. P. Milori. Novel estimation of the humification degree of soil organic matter by laser-induced breakdown spectroscopy. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 99:76–81, 2014.
 9. M. Ferretti, G. Cristoforetti, S. Legnaioli, V. Palleschi, A. Salvetti, E. Tognoni, E. Console, and P. Palaia. In situ study of the porticello bronzes by portable x-ray fluorescence and laser-induced breakdown spectroscopy. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 62(12):1512–1518, 2007.
 10. S. Gibb and K. Strimmer. Maldiquant: a versatile r package for the analysis of mass spectrometry data. *Bioinformatics*, 28(17):2270–2271, 2012.
 11. J. Gil and M. Werman. Computing 2-dimensional min, median and max filters. In *Artificial Intelligence and Computer Vision: Proceedings of the Seventh Israeli Conference, 26-27 December, 1990, Ramat Gan, Israel*, page 395. North Holland, 1991.
 12. J. Gil and M. Werman. Computing 2-dimensional min, median and max filters. 1996.
 13. D. W. Hahn and N. Omenetto. Laser-induced breakdown spectroscopy (libs), part ii: review of instrumental and methodological approaches to material analysis and applications to different fields. *Applied spectroscopy*, 66(4):347–419, 2012.
 14. R. S. Harmon, F. C. De Lucia, A. W. Miziolek, K. L. McNesby, R. A. Walters, and P. D. French. Laser-induced breakdown spectroscopy (libs)—an emerging field-portable sensor technology for real-time, in-situ geochemical and environmental analysis. *Geochemistry: Exploration, Environment, Analysis*, 5(1):21–28, 2005.
 15. F. E. Hoge and R. N. Swift. Airborne detection of oceanic turbidity cell structure using depth-resolved laser-induced water raman backscatter. *Applied optics*, 22(23):3778–3786, 1983.
 16. T. Huang, G. Yang, and G. Tang. A fast two-dimensional median filtering algorithm. *Acoustics, Speech and Signal Processing, IEEE Transactions on*, 27(1):13–18, 1979.
 17. T. Hussain, M. Gondal, Z. Yamani, and M. Baig. Measurement of nutrients in green house soil with laser induced breakdown spectroscopy. *Environmental monitoring and assessment*, 124(1-3):131–139, 2007.

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18. M. Kneen and H. Annegarn. Algorithm for fitting xrf, sem and pixe x-ray spectra backgrounds. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 109:209–213, 1996.
 19. I. Lawrence and K. Lin. A concordance correlation coefficient to evaluate reproducibility. *Biometrics*, pages 255–268, 1989.
 20. K. H. Liland. 4s peak filling–baseline estimation by iterative mean suppression. *MethodsX*, 2:135–140, 2015.
 21. K. H. Liland, T. Almøy, and B.-H. Mevik. Optimal choice of baseline correction for multivariate calibration of spectra. *Applied spectroscopy*, 64(9):1007–1016, 2010.
 22. G. d. A. MARTINS and J. S. d. FONSECA. Curso de estatística. *Atlas*, 6^a Edição, 1996.
 23. W. T. Y. Mohamed. Study of the matrix effect on the plasma characterization of six elements in aluminum alloys using libs with a portable echelle spectrometer. *Progress in Physics*, page 42, 2007.
 24. M. Morháč. An algorithm for determination of peak regions and baseline elimination in spectroscopic data. *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, 600(2):478–487, 2009.
 25. G. Nicolodelli, B. S. Marangoni, J. S. Cabral, P. R. Villas-Boas, G. S. Senesi, C. H. dos Santos, R. A. Romano, A. Segnini, Y. Lucas, C. R. Montes, et al. Quantification of total carbon in soil using laser-induced breakdown spectroscopy: a method to correct interference lines. *Applied optics*, 53(10):2170–2176, 2014.
 26. J. Olivero and R. Longbothum. Empirical fits to the voigt line width: a brief review. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 17(2):233–236, 1977.
 27. S. Pandhija, N. Rai, A. K. Rai, and S. N. Thakur. Contaminant concentration in environmental samples using libs and cf-libs. *Applied Physics B*, 98(1):231–241, 2010.
 28. D. Rusak, B. Castle, B. Smith, and J. Winefordner. Fundamentals and applications of laser-induced breakdown spectroscopy. *Critical Reviews in Analytical Chemistry*, 27(4):257–290, 1997.
 29. C. Ryan, E. Clayton, W. Griffin, S. Sie, and D. Cousens. Snip, a statistics-sensitive background treatment for the quantitative analysis of pixe spectra in geoscience applications. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 34(3):396–402, 1988.
 30. B. Sallé, J.-L. Lacour, E. Vors, P. Fichet, S. Maurice, D. A. Cremers, and R. C. Wiens. Laser-induced breakdown spectroscopy for mars surface analysis: capabilities at stand-off distances and detection of chlorine and sulfur elements. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 59(9):1413–1422, 2004.
 31. C. H. d. Santos, R. A. Romano, G. Nicolodelli, C. M. Carvalho, P. R. Villas-Boas, L. Martin-Neto, C. R. Montes, A. J. Melfi, and D. M. Milori. Performance evaluation of a portable laser-induced fluorescence spectroscopy system for the assessment of the humification degree of the soil organic matter. *Journal of the Brazilian Chemical Society*, 26(4):775–783, 2015.

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32. A. Savitzky and M. J. Golay. Smoothing and differentiation of data by simplified least squares procedures. *Analytical chemistry*, 36(8):1627–1639, 1964.
 33. A. Segnini, A. A. P. Xavier, P. L. Otaviani-Junior, E. C. Ferreira, A. M. Watanabe, M. A. Sperança, G. Nicolodelli, P. R. Villas-Boas, P. P. A. Oliveira, and D. M. B. P. Milori. Physical and chemical matrix effects in soil carbon quantification using laser-induced breakdown spectroscopy. *American Journal of Analytical Chemistry*, 2014, 2014.
 34. G. S. Senesi. Laser-induced breakdown spectroscopy (libs) applied to terrestrial and extraterrestrial analogue geomaterials with emphasis to minerals and rocks. *Earth-Science Reviews*, 139:231–267, 2014.
 35. B. Stuart, M. Feit, S. Herman, A. Rubenchik, B. Shore, and M. Perry. Nanosecond-to-femtosecond laser-induced breakdown in dielectrics. *Physical Review B*, 53(4):1749, 1996.
 36. M. Van. A fast algorithm for local minimum and maximum filters on rectangular and octagonal kernels. *Pattern Recognition Letters*, 13(7):517–521, 1992.
 37. J.-I. Yun, R. Klenze, and J.-I. Kim. Laser-induced breakdown spectroscopy for the on-line multielement analysis of highly radioactive glass melt simulants. part ii: analyses of molten glass samples. *Applied spectroscopy*, 56(7):852–858, 2002.