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Semi - Quantitative Calibration of PORTALIBS 2000 for Magnesium

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Abstract: Using Laser Induced Breakdown Spectroscopy (LIBS) as a qualitative and quantitative elemental composition determination method, a complete sample examination can be done quickly. The purpose of the paper is to present a methodology and to realise a semi-quantitative calibration of a PORTALIBS 2000 spectrometer. The (semi)quantitative calibration consists in identification of the wavelengths most sensitive at magnesium. A set of seven experiments was conducted, using seven different concentrations of MgO. There were identified six wavelengths sensitive at magnesium and the corresponding measured signals were analysed.

Keywords: spectral analysis; (semi)quantitative determination; wavelengths analysis

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a form of atomic emission spectroscopy, capable of real-time determination of the elemental composition of any substance [1,2]. In principle any gas, liquid or solid samples can be analyzed using this method. The PORTALIBS 2000 spectrometer, used in the present study, is dedicated to the analysis of solid samples.

The LIBS method is based on plasma cloud analysis resulted from the laser ablation of a small quantity of sample material [1,2,3]. The analyses performed using LIBS method is using a small amount of material from sample to be studied in the range of "pg" (picograms) or less.

Laser ablation represents the technique that converts a small part from sample into vaporized state via plasma, following the impact between a laser

beam and the sample surface [2,3]. The plasma cloud occurs due to high power of laser beam reaching to samples surface.

The amount of vaporized material and the resulting plasma from the laser ablation are correlated with the operational parameters (e.g. the distance between the focusing lens and the sample, the laser beam power density emitted from laser source, the environmental conditions from the analysis chamber such as pressure, composition, etc.). By changing these parameters the analytic signals will be modified and their intensity also. Due to the influence of these parameters, the analysis results on the elemental composition of materials can be compromised [4,5,6].

The intensity of the laser beam from the same source may vary with maximum 5%, but this variation does not explain the usual dramatic fluctuation of the results from one experiment to another. Those variations may be determined by a lot of causes [4,7].

The qualitative and quantitative analysis of elemental composition of studied samples requires a study on the electromagnetic radiation reflected from sample, which is detected (using an optical system) and converted into electrical signals using Charge Coupled Devices (CCD) sensors [8, 9].

The purpose of the paper is to identify the measuring wavelengths corresponding to magnesium and to analyze the signal intensities determined on these wavelengths, in order to develop a (semi)quantitative calibration.

2. Material

The chemical material of study was represented by 7 different amounts of MgO mixed with 50 ml of distilled water resulting 7 different solutions to be analyzed, characterized in table 1.

Table 1: Amounts of MgO added in 50 ml distilled water.

Solution id	MgO quantity [g]	MgO quantity [mol/dm^3]
#1	1.0030	0.497712
#2	2.0096	0.997211
#3	3.0015	1.489416
#4	4.0096	1.989659
#5	5.0175	2.489803
#6	6.0006	2.97764
#7	7.0028	3.474956

The experiments were developed using as support, samples of filter paper with a thickness of 0.28 mm, provided by Carl Schleicher & Schüll. The samples dimensions used in experiments were 33x33 mm. The samples were immersed in homogeneous solution and allowed to dry before the analysis.

Two samples of paper filters were prepared for each solution. Thus were obtained 14 samples for analysis. Each of these samples was measured in different 4 points (where the laser beam reached the sample) marked with circles on *Fig.* 1.a. The home made mounting device, of the samples into the analysis chamber is presenting in *Fig.* 1.b. The assembly of the filter paper on the mounting device is shown in *Fig.* 1.c.

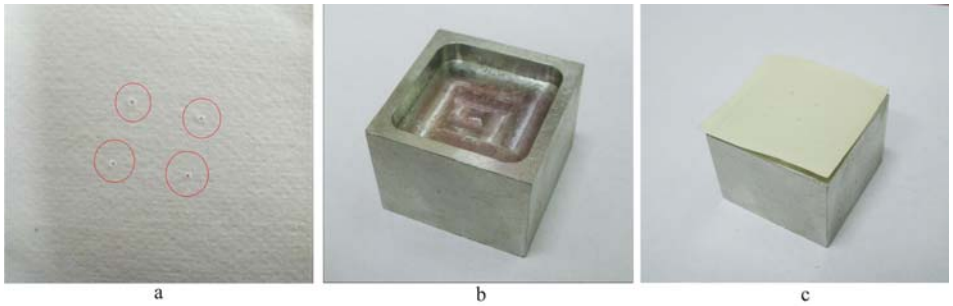

Figure 1: a) Filter paper sample; b) Mounting device;
c) Assembly of filter paper on mounting device

3. Method

The samples spectra were obtained using a portable LIBS system, model PORTA-LIBS-2000, provided by StellarNet. A detailed description can be found in [9].

This method of analysis was tested before with success, in other qualitative and quantitative determinations made on different samples (soil, metals, and nonmetals) [9, 10,11,12].

A schematic diagram of the experimental setup is shown in *Fig.* 2. Experimental device is equipped with a Nd:YAG laser source of 25 mJ with pulse duration of 4 ns, repetition rate of 1 Hz. The obtained radiation is transformed into electrical signal by a CCD detector with 2048 pixels as part of detection and conversion unit (DCU). In all the experiments were used three DCU and the total spectrometric covered range is 186 - 856 nm. The optical resolution of DCU is 0.2 nm according to [10].

All experiments were conducted with a delay time for the spectrum acquisition after the formation of the plasma, set on 32 μs. The integration time, representing the necessary time for the integration of signal, was set on 30 ms (time elapsed since CCD reached the signal and digitizer - DIG send it to local PC).

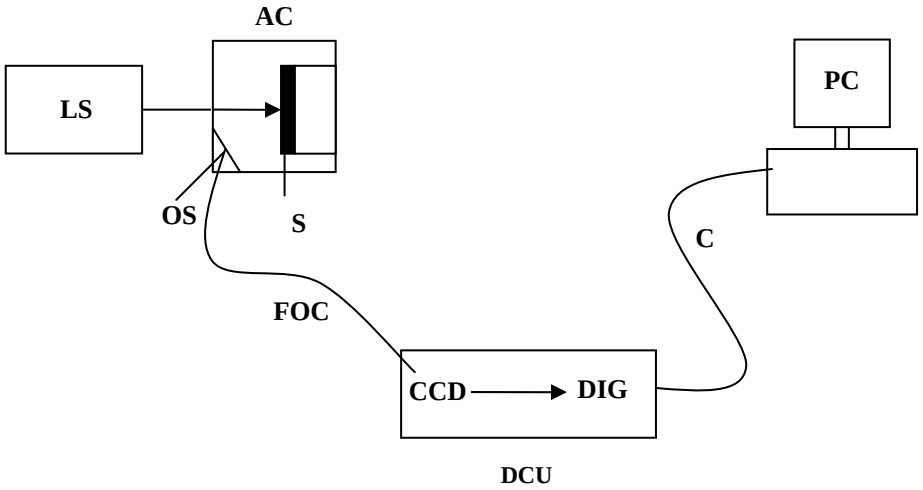

Figure 2: Experimental setup schematic diagram of PORTALIBS 2000
AC - analysis chamber; LS - laser source; S - sample; OS - optical sensors; FOC - fiber optic cable; CCD - Charged Coupled Device; DIG - digitizer; DCU - detection and conversion unit; C - USB cable; PC - computer.

4. Results

For each concentration of MgO were obtained eight spectra (2 samples x 4 measurements) and averaged spectra were calculated and presented in *Fig.* 3 - 9 for each sample.

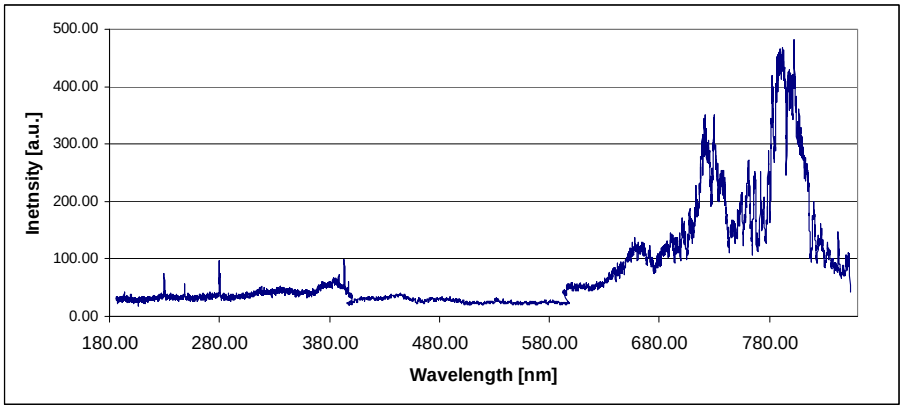

Figure 3: Spectrum for MgO sample #1.

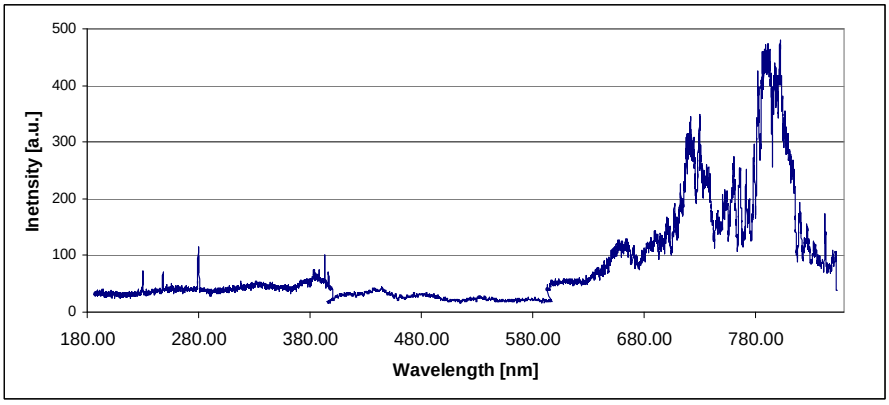

Figure 4: Spectrum for MgO sample #2.

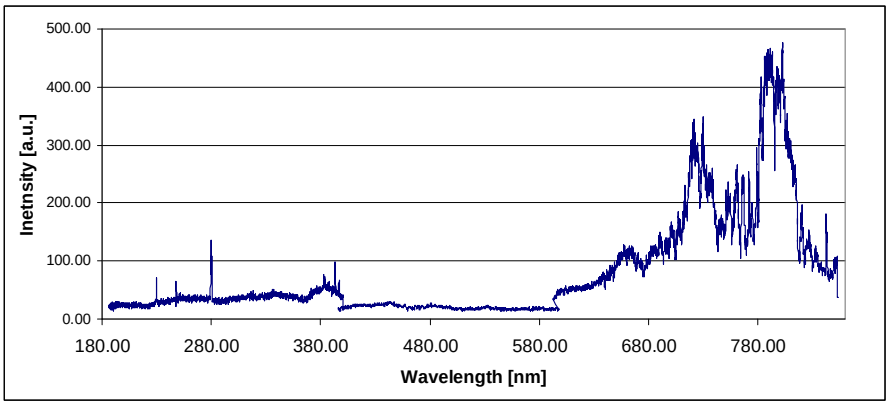

Figure 5: Spectrum for MgO sample #3.

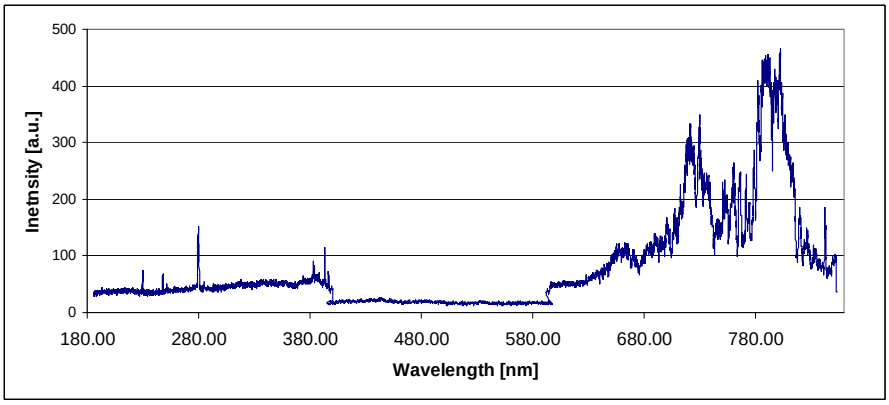

Figure 6: Spectrum for MgO sample #4.

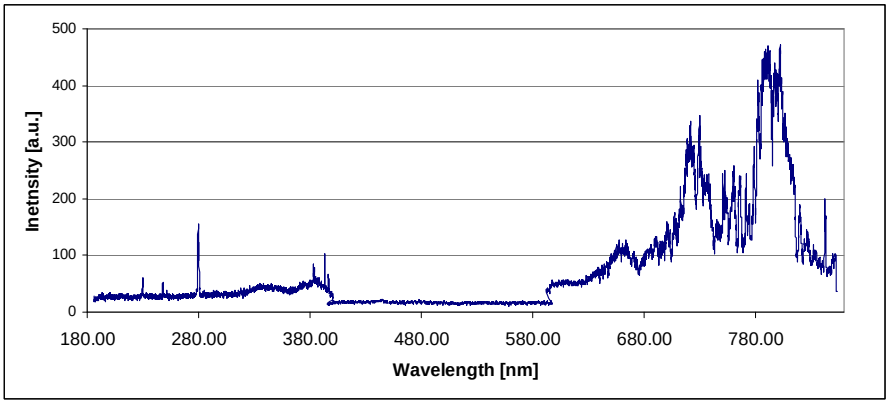

Figure 7: Spectrum for MgO sample #5.

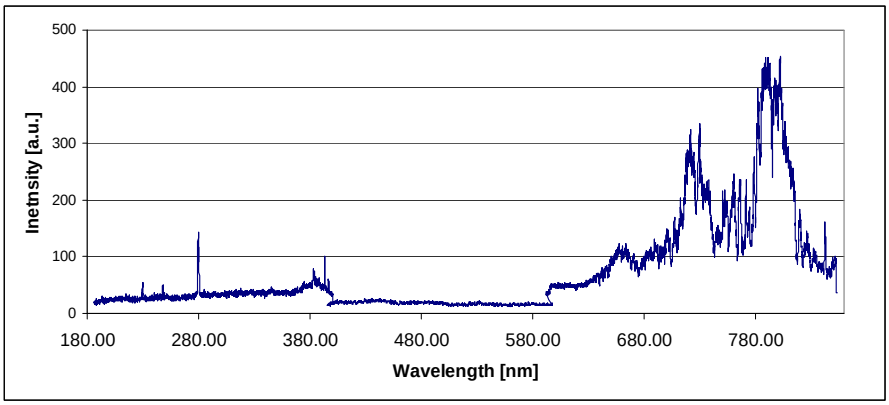

Figure 8: Spectrum for MgO sample #6.

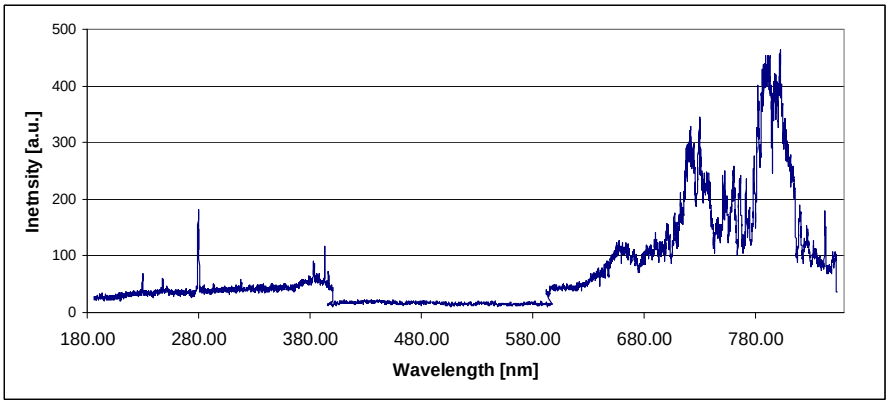

Figure 9: Spectrum for MgO sample #7.

In order to identify the wavelengths of Mg on which the device is measuring, was interrogated the National Institute of Standards and Technology (NIST) database [13]. It was found that PORTALIBS 2000 is measuring a number of 43 wavelengths in perfect match with NIST wavelengths for Mg. In *Fig.* 10 are shown the wavelengths and corresponding intensities for all the performed experiments. Only intensities measured on these wavelengths were considered in the analysis. The values corresponding to the smallest concentration of MgO were represented with light blue and the greatest concentrations were represented with dark blue.

There were selected three wavelengths with tendency of signal increasing with the increasing concentration of MgO from solution: 279.48 nm, 279.79 nm and 280.42 nm.

There were also selected three wavelengths with tendency of signal decreasing with the increasing concentration of MgO from solution: 502.37 nm, 506.96 nm and 571.11 nm.

On *Fig.* 10 were marked with green all the wavelengths with tendency of signal increasing and with red all the wavelengths with tendency of signal decreasing.

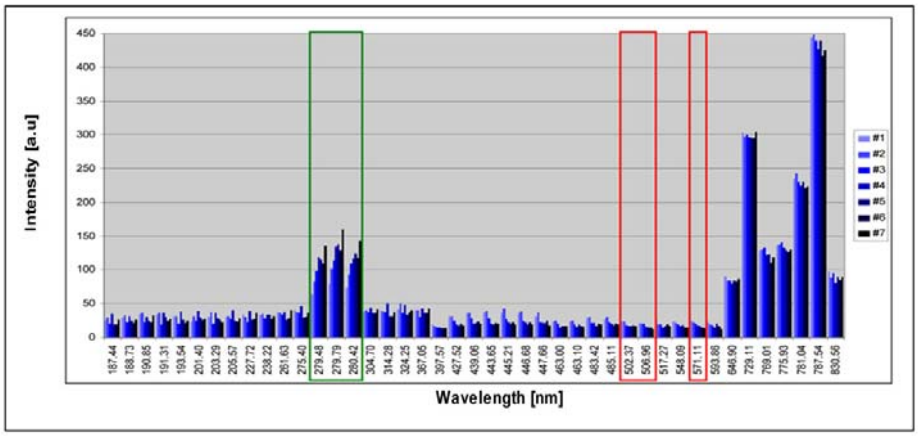

Figure 10: Specific Mg wavelength measured by experimental device.

In *Fig.* 11 were represented the averaged values of signal intensities corresponding to the 3 wavelengths with tendency of signal increasing with increasing of concentration.

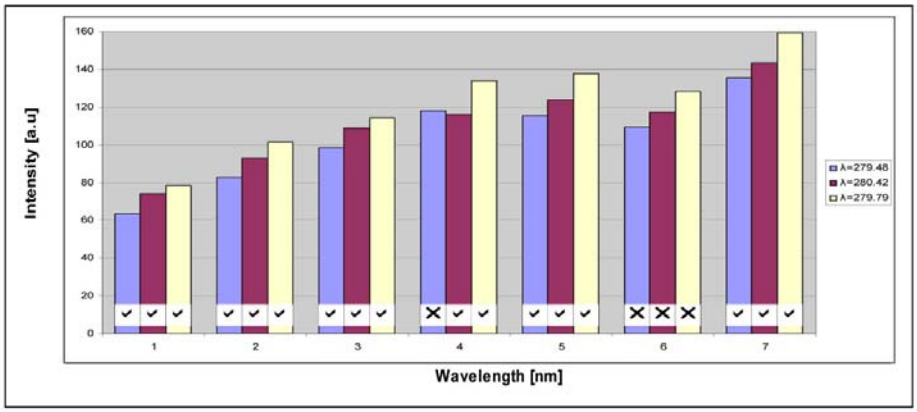

Figure 11: Averaged values of signal intensities for Mg wavelengths with increasing tendency with increasing concentration of MgO

✔ - Values respecting the trend; ✘ - Values don't respecting the trend

In *Fig.* 12 were represented the averaged values of signal intensities corresponding to the 3 wavelengths with tendency of signal decreasing with increasing of concentration.

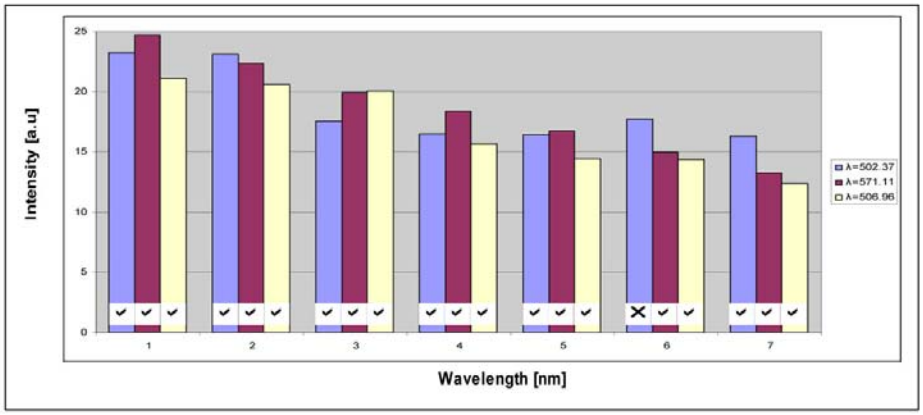

Figure 12: Averaged values of signal intensities for Mg wavelengths with decreasing tendency with increasing concentration of MgO.

✔ - Values respecting the trend; ✘ - Values don't respecting the trend

In order to determine the degree of association between the concentration of MgO and the signal intensity for chosen wavelengths, 7 correlation coefficients were calculated according to [14]and presented in table 2.

Table 2: Correlation coefficients between concentration of MgO and signal intensity of chosen wavelength

Correlation coefficients	Wavelengths (λ, [nm])					
Correlation Model	571.11	506.96	280.42	279.79	279.48	502.37
Gamma	1	1	0.905	0.810	0.714	0.714
K-Tau-a	1	1	0.905	0.810	0.714	0.714
K-Tau-b	1	1	0.905	0.810	0.714	0.714
K-Tau-c	0.857	0.857	0.776	0.694	0.612	0.612
Pearson	0.997	0.961	0.941	0.931	0.920	0.810
Spearman	1	1	0.964	0.893	0.857	0.786
s-Quant	0.998	0.981	0.952	0.912	0.888	0.798
Σ	6.852	6.799	6.347	5.858	5.420	5.148

In table 3 are presented the differences between maximum possible sum of correlation coefficients, which is 7, and the real sum of correlation coefficients, calculated for each of six selected wavelength (last row in table 2). These differences reveal the degree of association and/or disassociation between the signal intensities and the concentration of samples. High values of mentioned differences are indicating height degree of dissociation and low degree of association. Low values of mentioned differences are indicating low degree of dissociation and height degree of association. Furthermore, height degree of association suggests height correlation between measured signal intensity on a certain wavelength and the sample concentration. Height degree of disassociation suggests low correlation between measured signal intensity on a certain wavelength and the sample concentration.

Table 3: Differences between maximum sum (7) of correlation coefficients and the sum calculated for each of six selected wavelength

Wavelength (λ, [nm])	Differences values	Interpretation
571.11	0.148	Low
506.96	0.201	↑
280.42	0.653	Degree of
279.79	1.142	disassociation
279.48	1.580	↓
502.37	1.852	Height

5. Discussion

The spectra shown in figures 3 – 9 are containing the averaged signal corresponding to the 6153 lines from the three signal detectors.

Analyzing the figures 3 - 9 can be observed that between 200 nm and 400 nm there is a number of wavelengths that can be associated with the sample concentration.

By simple analysis of spectra of each concentration, other sensitive wavelengths can not be remarked. Analyzing the numerical data set, obtained from each experiment, it can be found if there are any other wavelengths sensitive to the concentration of the sample.

Six of the Mg specific wavelengths, were selected for the current research.

Three chosen wavelengths are presenting a tendency of signal increasing with increasing of concentration (*Fig.* 11). It can be observed that all the values of signal intensities obtained for solution #6 and the value of signal intensity corresponding to 279.48 nm from sample #4 doesn't fit to the general trend.

Three chosen wavelengths are presenting a tendency of signal decreasing with increasing of concentration (*Fig.* 12). It can be observed that at 502.37 nm the signal intensity corresponding to sample #6 doesn't fit to the general trend.

The correlation coefficients (table 2), is highlighting a strong correlation between the signal intensity and concentration of MgO from samples on all the six selected wavelengths.

The maximum sum of correlation coefficients is 7 (ideal case). The maximum sum of calculated correlation coefficients is 6.852 (table 2).

The difference between the sum of correlation coefficients corresponding to wavelengths 571.11 nm and 506.96 nm is 0.053. This value represents the minimal difference from the set of differences between the sums of correlation coefficients corresponding to wavelengths. For complete calibration of PORTALIBS 2000 needed in quantitative analysis, the two wavelengths must be taken into consideration, because both have same and height degree of association between signal intensity and concentration quantitative analysis.

Table 3 presents the order of wavelengths based on the degree of disassociation between signal intensity and concentration quantitative analysis. This order was established by differences made between maximum sum of correlation coefficients, and the sum calculated for each of six selected wavelength

6. Conclusions

In order to achieve the purpose of the research (the semi-quantitative calibration of PORTALIBS 2000 for Mg), were identified six wavelengths with

observed strong correlations between the corresponding signal intensity and concentration of MgO from samples.

It was highlighted that wavelengths of 571.11 nm and 506.96 nm must be taken into consideration when complete quantitative calibration has to be performed because both have height degree of association between signal intensity and concentration.

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References

[1] Harmon, R.S., Remus, J., McMillan, N.J., McManus, C., Collins, L., Gottfried Jr., J. L., DeLucia, Frank C., and Miziolek, A. W., "LIBS analysis of geomaterials: Geochemical fingerprinting for the rapid analysis and discrimination of minerals", Applied Geochemistry 24, 2009, pp. 1125–1141

[2] Hassan, M., Sighicelli, M., Lai, A., Colao, F., Hanafy Ahmed, A.H., Fantoni, R., and Harith, M.A., "Studying the enhanced phytoremediation of lead contaminated soils via laser induced breakdown spectroscopy", Spectrochimica Acta Part B 63, 2008, pp. 1225–1229

[3] Ferreira, E.C., Milori, D.M.B.P., Ferreira, E. J., Da Silva, R. M., Martin-Neto, L., "Artificial neural network for Cu quantitative determination in soil using a portable Laser Induced Breakdown Spectroscopy system", Spectrochimica Acta Part B 63, 2008, pp. 1216–1220

[4] Michel, A.P.M., and Chave, A.D., "Analysis of laser-induced breakdown spectroscopy spectra: The case for extreme value statistics", Spectrochimica Acta Part B 62, 2007, pp. 1370–1378

[5] Cremers, D. A., and Chinni, R. C., "Laser-Induced Breakdown Spectroscopy – Capabilities and Limitations", Applied Spectroscopy Reviews 44: 6, 2009, pp. 457–506

[6] Senesi, G.S., Dell'Agli, M., Gaudiuso, R., De Giacomo, A., Zaccone, C., De Pascale, O., Miano, T. M., and Capitelli, M., „Heavy metal concentrations in soils as determined by laser-induced breakdown spectroscopy (LIBS), with special emphasis on chromium", Environmental Research 109, 2009, pp. 413–420

[7] Nunes, L.C., Da Silva, G.A., Trevizan, L.C., Júnior, D.S., Poppi, R.J., Krug, F.J., "Simultaneous optimization by neuro-genetic approach for analysis of plant materials by laser induced breakdown spectroscopy", Spectrochimica Acta Part B 64, 2009, pp. 565–572

[8] McMillan, N.J., Harmon, R.S., De Lucia, F.C., Miziolek, A.M., "Laser-induced breakdown spectroscopy analysis of minerals: Carbonates and silicates", Spectrochimica Acta Part B 62, 2007, pp. 1528–1536

[9] Pierce, W., Christian, S. M., Myers, M. J., and Myers, J. D., Field-testing for environmental pollutants using briefcase sized portable LIBS system, 3rd International Conference on Laser Induced Plasma Spectroscopy and Applications, 2004, pp. 1-14
[10] Da Silva, R.M., Milori, D.M.B.P., Ferreira, E.C., Ferreira, E.J., Krug, F. J., Martin-Neto, L., "Total carbon measurement in whole tropical soil sample", Spectrochimica Acta Part B 63 (2008) 1221–1224
[11] Burakov, V. S., Raikov, S. N., Tarasenko, N. V., Tarasenko, N. V., Belkov, M. V. and Kiris, V. V., "Development Of A Laser-Induced Breakdown Spectroscopy Method For Soil And Ecological Analysis (Review)", Journal of Applied Spectroscopy, Vol. 77, No. 5, 2010, pp. 595 - 608
[12] Bredice, F., Borges, F.O., Sobral, H., Villagran-Muniz, M., Di Rocco, H.O., Cristoforetti, G., Legnaioli, S., Palleschi, V., Pardini, L., Salvetti, A., Tognoni E., "Evaluation of self-absorption of manganese emission lines in Laser Induced Breakdown Spectroscopy measurements", Spectrochimica Acta Part B 61 (2006) 1294–1303
[13] http://physics.nist.gov/PhysRefData/ASD/lines_form.html
[14] Sorana BOLBOACĂ, Lorentz JÄNTSCHI, Pearson Versus Spearman, Kendall's Tau Correlation Analysis on Structure-Activity Relationships of Biologic Active Compounds, Leonardo Journal of Sciences, AcademicDirect, ISSN 1583-0233, www, Internet, 5(9), p. 179-200, CAS-AN 2007:1026159, 2006.