

LASER INDUCED – BREAKDOWN SPECTROSCOPY FOR QUANTITATIVE Sn AND Nb ANALYSIS IN Zr BASED ALLOYS

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Abstract

Laser induced breakdown spectroscopy (LIBS) calibration curves for SnZr and NbZr alloys were obtained. Relationships between the atomic emission lines present in the spectra and the Sn and Nb concentrations of the samples showed a linear behavior. Also Zy-2 standards were measured to contrast the behavior of the technique in different kind of alloys. The choice of proper Sn, Nb and Zr lines and the equipment's parameters, such as "integration start delay" and the spectrometer height, were fundamental to enhance the measurements. The samples were analyzed by X-ray fluorescence for a precise determination of their Sn and Nb concentrations.

Keywords: LIBS; ZrSn and ZrNb alloys; Calibration curves; Nuclear.

CURVAS DE CALIBRAÇÃO DE Sn E Nb EM Zr E LIGAS DE Zr POR ESPECTROSCOPIA - INDUZIDA POR LASER.

Resumo

Foram obtidos por espectroscopia a laser (LIBS avaria) curvas de calibração para as ligas de SnZr e NbZr. As relações entre linhas de emissão atômica presentes mostraram um comportamento linear. Zy-2 também foram medidos para comparar as regras de comportamento da arte em diferentes tipos de ligas. A escolha de linhas apropriadas de Sn, Nb e Zr e parâmetros de equipamentos, tais como a "integração de atraso da partida" e a altura do espectrômetro, foram fundamentais para melhorar as medições. Todas as amostras foram analisadas por fluorescência de raios para uma determinação exata das concentrações de Sn e Nb.

Palavras-chave: LIBS; ZrNb ZrSn e ligas; Curvas de calibração; Nuclear.

I INTRODUCTION

It is known in the field of nuclear materials science that zirconium meets essential requirements as the lower section of neutron capture, high corrosion resistance and good mechanical properties at high temperatures [1-3]. Based on these characteristics, Zr based alloys are widely used in the nuclear industry: Zircaloy (base Zr, Sn as the main alloying element and Fe as an impurity) and Zr-Nb alloys. Currently, prototypes of new reactors operating at higher temperatures require the development of new alloys that meet good mechanical properties and corrosion resistance as those presently used. The most studied are those containing

Zr as a base element and Sn as the main alloying element (eg Zirlo (USA), E635 (Russia), Excel (Canada)), or those with Zr as a base and Nb as the main alloying (M5 (France), EI 10 (Russia)). A better understanding of thermodynamic and diffusive aspects of these elements in the alloys will optimize existing technologies in critical elements fabrication methods and new alloys designs. The Sn has a fundamental role in many of the alloys mentioned, so it is immediately its study. Zircalloy (Zr based and Sn as main alloying element) is used in Atucha I and II nuclear power plants. Niobium is used as alloying to stabilize Zr beta phase, a typical concentration in

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cladding nuclear fuel is 1% niobium, forming intermetallic particles of cubic and hexagonal structures; in contrast to other alloying elements as tin, which is more soluble in zirconium hcp [4]. The interest in ZrNb alloys resides in its use in the pressure pipes of CANDU reactor (Central Nuclear Embalse, CNE, Argentina), these tubes are made of Zr - 2.5wt% Nb alloy.

The LIBS technique (laser induced breakdown spectroscopy) is a technique that allows semi-quantitative and quantitative qualitative analysis (under certain conditions) of solid samples, liquid or gaseous. The amount of material required is minimal and very simple or no preparation. In the measurement process, a laser pulse is focused by a lens on the sample, so that a small volume is transformed to a plasma transient state, releasing energy as radiation. Collects and analyzes a spectrometer radiation, allowing signals from features, identification of components present in the sample. This technique allows mainly performed qualitative analysis; quantification requires careful calibration patterns from that must be associated with the selected spectral data [5,6]. In Figure 1 a schematic of the LIBS technique is presented. Compared to other methods such as atomic emission spectroscopy (AES, atomic emission spectroscopy) LIBS has significant advantages: ability to analyze all the elements present simultaneously; applicable to solids, liquids and gases; requires a very small amount of sample, little preparation and fast data acquisition [7,8]. LIBS promising results were obtained in qualitative analysis, while quantitative analysis has not yet established a methodology that can generate results systematically [9]. A careful evaluation of optical, electronic and spectral variables has to be accomplished so as to obtain optimum conditions for the particular work system [10,11].

A calibration curve is a reference curve constructed from samples of known composition. Reproducible measurement conditions for all samples must be ensured to generate directly comparable results.

The LIBS technique associated with a calibration curve offers the possibility of developing direct quantitative analysis of alloying concentrations (particularly Sn and Nb in this work) on Zr based alloys. Indirectly, evaluation of alloying elements will contribute to understand mechanical and chemical properties, the establishment of appropriate thermomechanical treatments, etc. [4,12].

2 EXPERIMENTAL

LIBS measurements were performed on nine samples of Zr-Sn with concentrations between 0.5 and 3.35 wt% Sn from a previous work [13] and on as cast samples of ZrNb and ZrNbSn with concentrations of Nb in the range of 0.05 to 2.5 wt%. Measurements were performed using a commercial equipment LIBS Ocean Optics® 2500+ provider, having a Nd-YAG laser (1064 nm, 50 mJ, 200-500 nm).

The sample preparation consisted of mechanical abrasion with 600 grit sandpaper

A thorough analysis of the spectra was performed to select the most appropriate lines of Zr (matrix), Sn and Nb (alloying elements). Figures 2, 3 and 4 present a comparison between ZrSn and ZrNb samples spectra with Zr, Sn and Nb

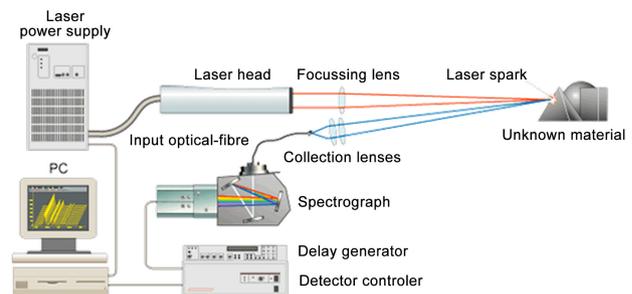


Figure 1. LIBS Schematic.

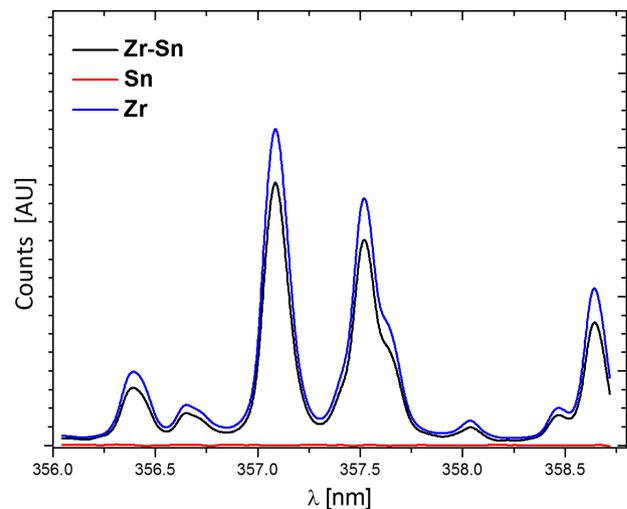


Figure 2. Comparison of spectral peaks of Zr at 357 nm.

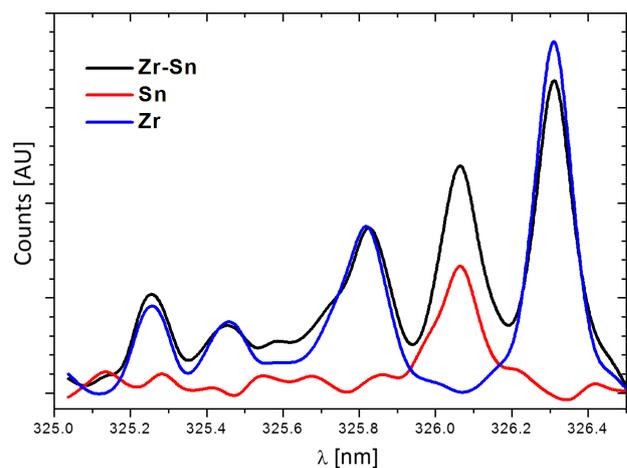


Figure 3. Comparison of spectral peaks of Sn at 326 nm.

pure samples spectra. As seen in Figure 2 no Sn emission lines are present in that wavelength range while a Zr line is present at 357 nm. However, the range between 325-326nm presents a characteristic Sn line at 326.16 nm, shown in Figure 3. In addition, as seen in Figure 4, characteristic Nb and Zr lines are present at 322 and 327 nm respectively. Thus, a pair of spectral lines were selected for ZrSn system while a different pair was selected for ZrNb and ZrNbSn systems. Selection was conducted as to minimize overlapping lines of other constituent elements of the system. This means that selected lines should be free of interference with other lines of the system and must also have a well defined shape. Information provided by NIST [14] on spectral atomic lines was used for elements study.

Measurements procedure implied a modification of device parameters as to optimize the spectra obtained [15]. Laser shot control is managed by the variable Q-Switch, being system synchronization control between the process of laser shooting and ablation.

The time between laser firing and the beginning of plasma formation is called "Q-Switch Zero". Time interval between the "Q-Switch Zero" and the start of data acquisition is referred to as "Integration Start Delay" (ISD). For ZrSn alloys, the best signal to noise ratio for Zr and Sn selected peaks was obtained with an $ISD = -0,42\mu s$ while for ZrNb and ZrNbSn alloys an $ISD = -1.25\mu s$ was selected. Proximity of lines in the spectrum, so to be measured with the same spectrometer, reduces errors by optical effects.

Spectrometer height was varied between 5 and 10 mm from the ablation point, in order to obtain the greatest number of counts. An optimal height of 7 mm was selected for all samples. Also, the number of shots averaged was varied considering the Sn/Zr and Nb/Zr ratios for each spectrum. The mean value was selected as representative, corresponding to an average of 50 shots.

Laser energy increase improves resolution when analyzing trace elements. Equipment energy was adjusted to 4.53 J and

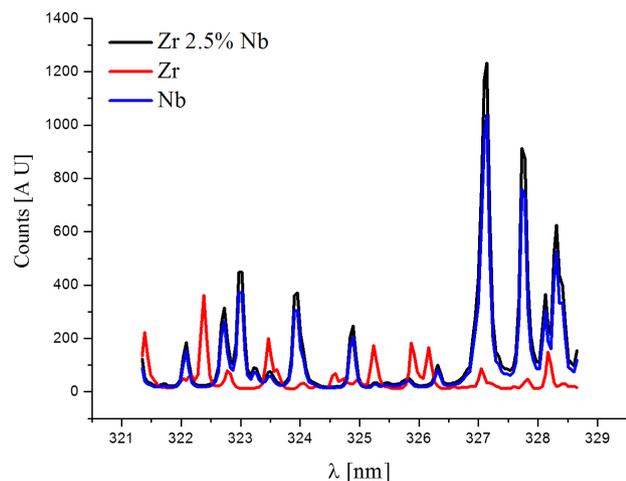


Figure 4. Comparison of spectral peaks of Nb at 322 nm and Zr at 327 nm.

then to 4.60 J to be compared. Although measured samples did not contain Sn or Nb as trace elements, amplitude differences were observed in the spectra, remaining their relative amplitudes unchanged. Table 1 presents selected LIBS parameters for ZrSn, ZrNb and ZrNbSn systems.

3 RESULTS AND DISCUSSION

Upon validating new quantitative analysis techniques is beneficial to rely on standardized methods. X-ray fluorescence (XRF) is a fully developed and robust technology. Samples were measured by XRF for quantifying their Sn and Nb concentration. Also, some ZrNb and ZrNbSn samples were measure by microprobe. Table 2 presents Sn and Nb concentration measured for each sample.

ZrSn samples along with Zy-2 (Zircalloy-2) NIST certified standards were measured with LIBS equipment. Obtained values were used to perform the calibration curve.

Relationships between peak areas were established, resulting in a linear relationship between different Sn and Nb concentrations. It was necessary to check peaks width to improve relationships resolution; it remained constant for all measurements. Peaks areas of ZrSn alloys were calculated considering five and eleven samples for Sn326 and Zr357 respectively. Five samples for Nb322 and six for Zr327 were used in ZrNb alloys.

Figure 5 presents two calibration curves: one for ZrSn system and one for Zy-2 patterns. Considering their

Table 1. Parameters LIBS selected for the ZrSn system

LIBS parameter	Value	Unit
Spectrometer Height	7	mm
Q-Switch Zero	150	μs
ISD	$-0.42(Sn) / -1.25(Nb)$	μs
Averaged Shots	50	-
Laser Energy	4.53 - 4.60	J

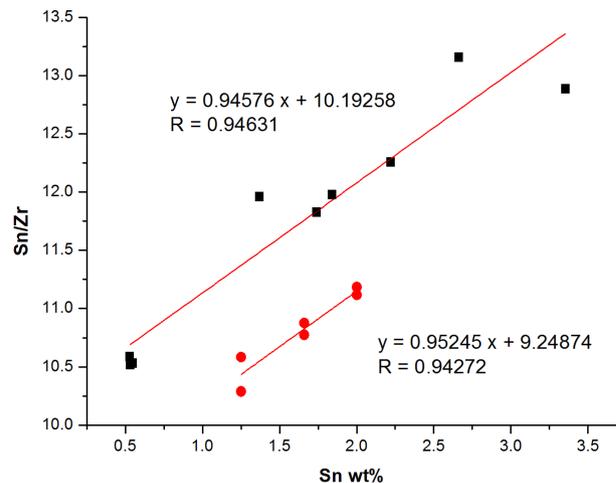


Figure 5. Calibration curves for Sn in the ZrSn system (■) and patterns of Zy-2 (●).

equations, it can be appreciated that slopes are similar. In fact is possible to calculate a correction factor and depend on a single curve. It is suggested that this correction factor presents the influence of Zy-2 minority elements, non-existing in the binary ZrSn alloy. This correction factor emerges from adjusting y-axis interception value of Zy-2 curve to ZrSn curve overlapping them; for this case it was obtained a $R = 0.9443$. Therefore, a single calibration curve was obtained for both systems, presented in Figure 6. In addition, for ZrNb and ZrNbSn systems results fitted a unique linear regression.

Thus, promising results for quantitative analysis of multi-alloy Zr based systems was obtained. The calibration curve follows a linear equation with $R = 0.995$. Figure 7 presents the calibration curve obtained for LIBS quantification of Nb in Zr based alloys.

Measurement errors involved were mainly dependent of data analysis methodology implemented, samples inherent characteristics and imposed experimental parameters. Previous studies [16, 17] agree an error between 10% and 15% for values higher concentrations to 1% w / w and about 20% to concentration between 0.1-1% w / w.

Table 2. Samples characteristics

Sample	Nb wt%	Sn wt%	Analysis method	Origin
JC1	-	3.355	FRX	As Cast
JC2	-	1.841	FRX	As Cast
JC3	-	0.547	FRX	As Cast
JE1	-	2.22	FRX	As Cast
JE2	-	1.74	FRX	As Cast
JE3	-	0.53	FRX	As Cast
JETT1	-	2.663	FRX	As Cast HT
JETT2	-	1.371	FRX	As Cast HT
JETT3	-	0.534	FRX	As Cast HT
Zy-2 867	0.0102	2	Certified	Patrón-NIST
Zy-2 868	0.0570	1.25	Certified	Patrón-NIST
Zy-2 869	0.0276	1.66	Certified	Patrón-NIST
Eutectic	20	-	FRX	Comercial
High 1	10	-	Microprobe	As Cast
High 2	7.5	-	Microprobe	As Cast
Ternary A	0.98	1.964	Microprobe	As Cast
Ternary B	2.4	4.02	Microprobe	As Cast
CAC I	0.5	-	FRX	As Cast
Zr 2.5	2.5	-	FRX	Comercial
CNE Pressure Tube	2.5	-	Certified	Comercial ATI Wah Chang

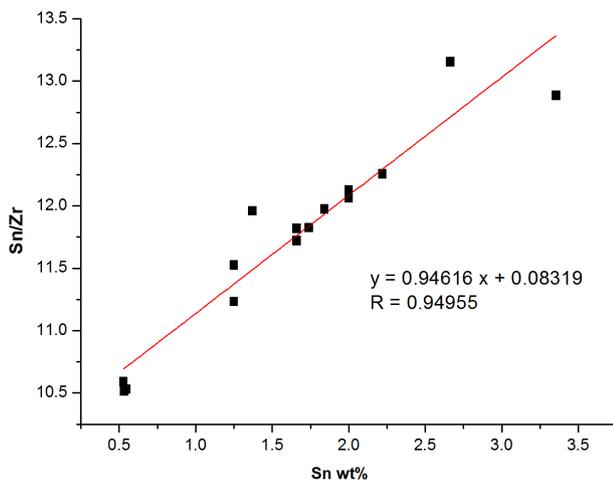


Figure 6. Calibration curve for both ZrSn and Zy-2, With correction factor.

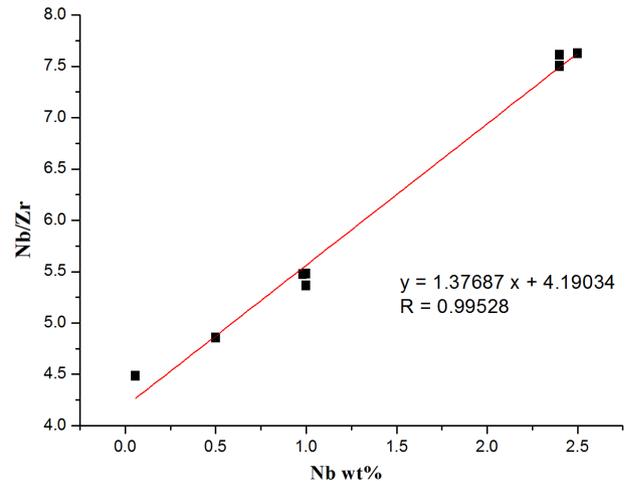


Figure 7. Calibration curve for Nb in the ZrNb and ZrNbSn systems.

4 CONCLUSIONS

The following factors are critical to perform a LIBS calibration curve allowing quantitative analysis:

- Selecting the peak of work for each element based on their shape and no presence of interference signals from other elements.
- Selecting a suitable ISD looking to improve the signal to noise ratio.
- Adjust the height of the spectrometer in order to increase the number of counts across the spectrum.
- The number of shots averaged to minimize the standard deviation.

- The peak area selected to increase resolution.

Once the optimal parameters for ZrSn, ZrNb and ZrNbSn systems were defined, respective calibration curves were obtained. ZrSn system presented a linear regression with a slope of 0.946 and $R = 0.949$. For Zr-2, a correction factor allowed the adjustment to the binary ZrSn calibration.

In addition, ZrNb calibration curve obtained is valid for both ZrNb and ZrNbSn systems in the concentration range evaluated. A linear regression with a slope of 1.377 and $R = 0.995$ was obtained. Emission lines belonging to a non-ionized state were overlapped for ZrNb and ZrNbSn samples evaluated.

Future work involves the evaluation of other alloying elements normally present in Zr based alloys for nuclear applications.

REFERENCES

- 1 Gruzin PL, Emelyanov VS, Ryabova GG, Federov GB. Study of the diffusion and distribution of the elements in zirconium and titanium base alloys by the radioactive isotope method. In: Proceedings of the the 2nd Conference on the peaceful uses of atomic energy. 1958.
- 2 Moan GD, Rudling P. Zirconium in the nuclear industry: thirteenth international symposium. New Jersey: ATSM International; 2002.
- 3 Suman S, Khan MK, Pathak M, Singh RN, Chakravarty JK. Hydrogen in Zircaloy: mechanism and its impacts. International Journal of Hydrogen Energy. 2015;40(17):5976-5994. <http://dx.doi.org/10.1016/j.ijhydene.2015.03.049>.
- 4 Glasstone S, Sesonske A. Nuclear reactor engineering. Barcelona: Reverte; 1990.
- 5 Burakov VS, Kiris VV, Naumenkov PA, Raikov SN. Calibration free laser spectral analysis of glasses and copper alloys. Journal of Applied Spectroscopy. 2004;71(5):740-746. <http://dx.doi.org/10.1023/B:JAPS.0000049638.55151.80>.
- 6 Galbács G, Gornushkin IB, Smith BW, Winefordner JD. Semi-quantitative analysis of binary alloys using laser-induced breakdown spectroscopy and a new calibration approach based on linear correlation. Spectrochimica Acta. Part B, Atomic Spectroscopy. 2001;56(7):1159-1173. [http://dx.doi.org/10.1016/S0584-8547\(01\)00205-1](http://dx.doi.org/10.1016/S0584-8547(01)00205-1).
- 7 Barbieri Gonzaga F, Pasquini C. A compact and low cost laser induced breakdown spectroscopic system: Application for simultaneous determination of chromium and nickel in steel using multivariate calibration. Spectrochimica Acta. Part B, Atomic Spectroscopy. 2012;69:20-24. <http://dx.doi.org/10.1016/j.sab.2012.02.007>.
- 8 Labutin TA, Popov AM, Raikov SN, Zaytsev SM, Labutina NA, Zorov NB. Determination of chlorine in concrete by laser - induced breakdown spectroscopy in air. Journal of Applied Spectroscopy. 2013;80(3):315-318. <http://dx.doi.org/10.1007/s10812-013-9766-8>.
- 9 Chaleard C, Mauchien P, Andre N, Uebbing J, Lacour JL, Geertsen C. Correction of matrix effects in quantitative elemental analysis with laser ablation optical emission Spectrometry. Journal of Analytical Atomic Spectrometry. 1997;12:183-188. <http://dx.doi.org/10.1039/a604456e>.
- 10 Rinaldi CA, Ferrero JC. Analysis of Ca in BaCl₂ matrix using laser-induced breakdown spectroscopy. Spectrochimica Acta. Part B, Atomic Spectroscopy. 2001;56(8):1419-1429. [http://dx.doi.org/10.1016/S0584-8547\(01\)00256-7](http://dx.doi.org/10.1016/S0584-8547(01)00256-7).
- 11 Castle BC, Talabardon K, Smith BW, Winefordner JD. Variables Influencing the Precision of Laser-Induced Breakdown Spectroscopy Measurements. Journal of Applied Spectroscopy. 1998;52(5):649-657. <http://dx.doi.org/10.1366/0003702981944300>.
- 12 Smith W. Materials science and engineering. 4th ed. New York: Mac Graw Hill; 2004.
- 13 Carricondo JI, Iofrida MJ, Corvalán C, Ararat-Ibarguen C, Iribarren M. Primeras mediciones LIBS para determinar curva de calibración en el sistema Zr-Sn de uso nuclear. In: 98° Reunión Nacional de Física. 2013.

- 14 National Institute of Standards and Technology. Gaithersburg: NIST Electronic Database. 2013 [cited 2013 Sept 13]. Available at: <http://www.nist.gov/pml/data/handbook/index.cfm>.
- 15 Bassiotis I, Diamantopoulou A, Giannoudakos A, Roubani-Kalantzopoulou F, Kompitsas M. Effects of experimental parameters in quantitative analysis of steel alloy by laser-induced breakdown spectroscopy. *Spectrochimica Acta. Part B, Atomic Spectroscopy*. 2001;56(6):671-683. [http://dx.doi.org/10.1016/S0584-8547\(01\)00225-7](http://dx.doi.org/10.1016/S0584-8547(01)00225-7).
- 16 Dell'Aglio M, De Giacomo A, Gaudioso R, De Pascale O, Senesi GS, Longo S. Laser Induced Breakdown Spectroscopy applications to meteorites: Chemical analysis and composition profiles. *Geochimica et Cosmochimica Acta*. 2010;74(24):7329-7339. <http://dx.doi.org/10.1016/j.gca.2010.09.018>.
- 17 Tognoni E, Cristoforetti G, Legnaioli S, Palleschi V, Salvetti A, Mueller M, et al. A numerical study of expected accuracy and precision in Calibration-Free Laser-Induced Breakdown Spectroscopy in the assumption of ideal analytical plasma. *Spectrochimica Acta B*. 2007;62(12):1287-1302. <http://dx.doi.org/10.1016/j.sab.2007.10.005>.

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