Determination of low alloying elements concentrations in cast iron by laser induced breakdown spectroscopy based on TEA CO$_2$ laser system

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Abstract: The analytical capability of laser-produced plasma for the analysis of low alloying elements in cast iron samples has been investigated. The plasma was induced by irradiation of a sample in air at atmospheric pressure using an infrared CO$_2$ laser. Emission spectra were recorded by time-integrated spatially-resolved measurement technique. A set of ten cast iron samples in a powder or particulate form were provided by BAM (Bundesanstalt für Material Forschung und Prüfung, Deutschland), seven of which were used for calibration, and three were treated as unknowns. Linear calibration curves were obtained for copper, chromium, and nickel, with correlation coefficients above 0.99. Precision and accuracy of the LIBS method was evaluated and compared to those obtained by the inductively coupled plasma (ICP) analysis of the same samples. Detection limits for Cu, Cr and Ni were close to those reported in the literature for other comparable iron-based alloys obtained using different LIBS systems. Analytical figures of merit of the studied LIBS system may be considered as satisfying, especially in the light of other advantages of the method, like cost effective and fast analysis with no sample preparation, and with a possibility for real-time on-site analysis.

Keywords: nanosecond transversely excited atmospheric carbon dioxide laser (TEA CO$_2$); laser-induced breakdown spectroscopy; quantitative analysis; cast iron.

INTRODUCTION

Cast iron is an iron–carbon–silicon alloy, containing from 2 to 4 % carbon and 0.3 to 3 % silicon, along with varying percentages of manganese, sulphur, and phosphorus. Other elements such as nickel, chromium, molybdenum, copper,

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vanadium, and titanium are commonly added to modify the structure and properties of the resulting alloy. Cast iron is an important engineering material, widely used in construction, automotive and heavy equipment industries. At the same time, huge amounts of ferrous scrap are generated from industrial and manufacturing sources. The accurate and sensitive elemental analysis of cast iron is of prime importance since desired metallurgical properties depend critically on the concentration of alloying elements. Beside manufacturing control and inspection testing, the chemical analysis of iron alloys is also important for recycling industries. Nowadays, iron-based alloys are the world's most recycled material.[1] The result of the recycling process is environmentally and cost-efficient raw material that is used for the production of new steel and cast iron material products.

Chemical composition of cast iron may be determined by wet chemical procedures involving gravimetric, spectrophotometric, atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS) techniques.[2,3] All of the aforementioned techniques have excellent analytical performance but also require complicated and time-demanding sample preparation procedures. The standard test methods for analysis of cast iron are also spark/arc atomic emission spectrometry and X-ray fluorescence spectrometry (XRF).[4,5] The main advantage of these techniques is little or no sample preparation and the possibility to perform fast on-site analysis.

In recent years another challenging technique, laser induced breakdown spectroscopy (LIBS), begins to gain increased importance as a tool for a rapid determination of alloy composition in numerous industrial process.[6] In addition to benefits like minimal sample preparation, multielemental analysis (including light elements), and speed of analysis, LIBS also offers the possibility to perform remote analysis (at distances up to several meters) and the applicability to samples regardless of its state (*e.g.*, molten or solid).

LIBS technique has already been used for qualitative and quantitative analysis of iron alloys, especially for steel.[7–12] Although different experimental configurations were used, most of the previous studies were done by using a nanosecond Nd:YAG laser. Related to a nanosecond Nd:YAG laser, pulsed TEA CO_2 laser has been much less exploited for LIBS. Nevertheless, for the analysis of a certain type of samples higher precision and sensitivity were obtained with CO_2 compared to Nd:YAG laser.[13–16]

In the present study, a laboratory LIBS setup was used, in which the infrared pulsed transversely excited atmospheric (TEA) CO_2 laser is applied as the excitation source and time-integrated space-resolved detection scheme is used for the acquisition of emission spectra. The main benefit of this non-gated LIBS system, compared to commonly practiced LIBS, is simplification of the instrumentation

and its cost. The applicability of TEA CO_2 laser based non-gated LIBS for spectrochemical analysis of various types of solid samples have already been investigated.[15–19]

The aim of the present study was to demonstrate the adequacy of a non-gated TEA CO_2 LIBS system for quantitative analysis of trace elements in a powder/ /particulate cast iron samples in air at atmospheric pressure. All cast iron samples (certified standards and unknown samples) were obtained by participation in the 2nd LIBS Inter-Laboratory comparison test "Powder/Particulate Cast Iron" in July–September 2016. To assess the analytical performance of the proposed LIBS system, the precision and accuracy of the method were evaluated, and compared to those obtained by ICP analysis of the same samples. Limits of detection (*LOD*) for Cu, Cr and Ni were calculated and compared to those reported in the literature.

EXPERIMENTAL

Laser induced plasma spectroscopy system

LIBS experimental setup used in this study was described in detail in prior publications,[15,17] and will be briefly summarized here.

The laser employed was a nanosecond pulsed TEA CO_2 laser system, developed at the Vinča Institute, Belgrade, which operates at 10.6 μm.[20] The laser pulse temporal profile is composed of a gain switched peak (100 ns) followed by a long-lasting tail (about 2 μs). About 35 % of the total irradiated laser energy is contained in the initial spike. The output pulse energy used in the experiments was 160 mJ, and a repetition rate was 1.3 Hz. The fluctuation of the laser energy was about 3 %. The laser plasma was generated by focusing a laser beam on the target using a ZnSe lens (f = 13 cm). The TEA CO_2 laser energy was measured in front of the ZnSe lens with Joulemeter ED-200 through a Tektronics TDS 1002 digital oscilloscope. The laser was run in a multimode regime. The angle of incidence of the laser beam with respect to the target surface was 90°.

The emission spectra were collected by a time-integrated space-resolved spectroscopy method.[21,22] The characteristics of TEA CO_2 laser (long infrared wavelength and characteristic pulse shape) are especially suitable for time-integrated measurements. The plasma is initiated during the initial peak while the remaining energy of the pulse is absorbed by the plasma plume causing additional heating and excitation.[15,17] All measurements were performed in air at atmospheric pressure. The targets were mounted on a rotating sample holder. Single shot craters, well separated in space, were achieved by the rotation of the sample, while repeated ablation of the same circular path was avoided by lateral movement of the sample. The optical emission from the plasma was viewed in the direction perpendicular to the the laser beam propagation axis, Fig. 1. By changing the position of the plasma along the *z*-axis (Fig. 1), while keeping a constant distance between the focusing lens and the target, different parts of the plasma were observed, *i.e.*, a spatial plasma resolution was achieved. The horizontal part of the plasma was projected by an achromatic lens at the entrance slit of the monochromator Carl-Zeiss PGS2 (entrance slit width 30 μm, height 1 mm, magnification 1:1). The monochromator was equipped with diffraction grating with 600 lines/mm (dispersion around 0.7 nm/mm, depending on the wavelength, and blaze at 330 nm in the first order). The spectra were monitored by CCD camera Apogee Alta F1007, consisting of 1024×122 pixels, 12 μm×12 μm

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each, and a total active area of 12.3 mm×1.46 mm. The laser was operated at 1.3 Hz, while the shutter of the non-gated CCD detector was opened for 30 s. This way, about 40 consecutive spectra were acquired without time resolution. Each recorded LIBS spectrum was an average spectrum, obtained by accumulation of consecutive spectra from 40 different locations on the sample. This procedure was as a rule repeated in triplicate, and the resulting spectra were averaged.
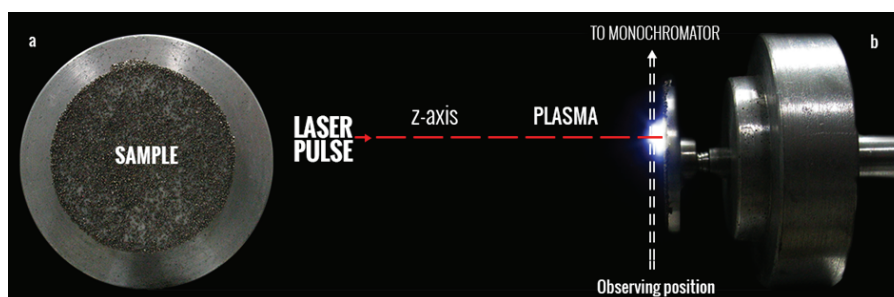

Fig. 1. a) Photography of the cast iron sample. The C3 sample glued to an aluminum subtarget with double sided sticky tape; b) photography of the plasma induced by focused TEA CO_2 laser beam on the cast iron sample with schematic representation showing sections of the plasma plume that were imaged onto the entrance slit of the monochromator.

Samples

The cast iron sample set consisted of 7 certified standards and 3 samples of unknown composition, provided in frame of LIBS 2016 proficiency test by BAM (Bundesanstalt für Material Forschung und Prüfung, Deutschland). The certified concentrations for Cu, Ni and Cr in BAM standards are listed in Table I. In all samples the iron concentration was higher than 95 % (calibration samples) or 92 % (unknown). The samples were in the form of particulate or powder. Samples with larger particles were first ground using an agate mortar and pestle. A thin layer of a sample material (approximately 1–2 mm as shown in Fig. 1) was placed on the double sticky tape and fixed to an aluminium subtarget.

TABLE I. Concentration (wt.%) of trace elements in reference cast iron samples

Element	Sample						
	C1	C2	C3	C4	C5	C6	C7
Cu	6.29	0.10	0.0256	0.548	0.0303	0.2445	1.231
	±0.02	±0.01	±0.0004	±0.013	±0.0006	±0.0025	±0.008
Ni	14.01	0.068	0.1247	0.057	0.0742	0.0549	2.234
	±0.04	±0.003	±0.0009	±0.004	±0.0010	±0.0014	±0.009
Cr	1.097	0.053	0.303	0.104	0.0845	0.0648	0.675
	±0.010	±0.003	±0.004	±0.006	±0.0019	±0.0012	±0.006

Reference method

To test the accuracy and precision of the LIBS measurements unknown samples were analysed by ICP OES. The samples were prepared by adding 15 ml of aqua regia solution to approximately 250 mg of sample in a beaker. The beaker was covered with a watch glass and, after 10 min pre-digestion at room temperature, the solution was gradually heated on a hot-plate for approximately 30 min to 200 °C. After cooling for about 15 min, the sample digest

was made up to 100 mL with deionized water. Calibration blanks were prepared in the same mixed acid solution but without the addition of any Fe matrix. Calibration solutions were prepared by appropriate dilution from single element Cu, Cr and Ni stock solutions (1000 µg/ml, J.T. Baker). The analysis was performed on a Spectroflame ICP OES instrument.

RESULTS AND DISCUSSION

Calibration curves

Each LIBS spectrum was recorded by accumulation measurements of 40 consecutive spectra (at 40 different positions of the sample), taken from a plasma region 1.5 mm from the sample surface. For each sample, three sets of accumulated spectra were averaged. The relative standard deviation (*RSD* in %) of the measured LIBS intensities (shot-to-shot variation) was in the range 6–10 %.

Fig. 2 shows a typical LIBS spectrum of cast iron C3 reference sample in the spectral range of 300–360 nm. The same spectral lines of Fe, Ti, Mn, Cu, Cr, Ni and V as shown in Fig. 2 were identified in LIBS spectra of all other reference samples.
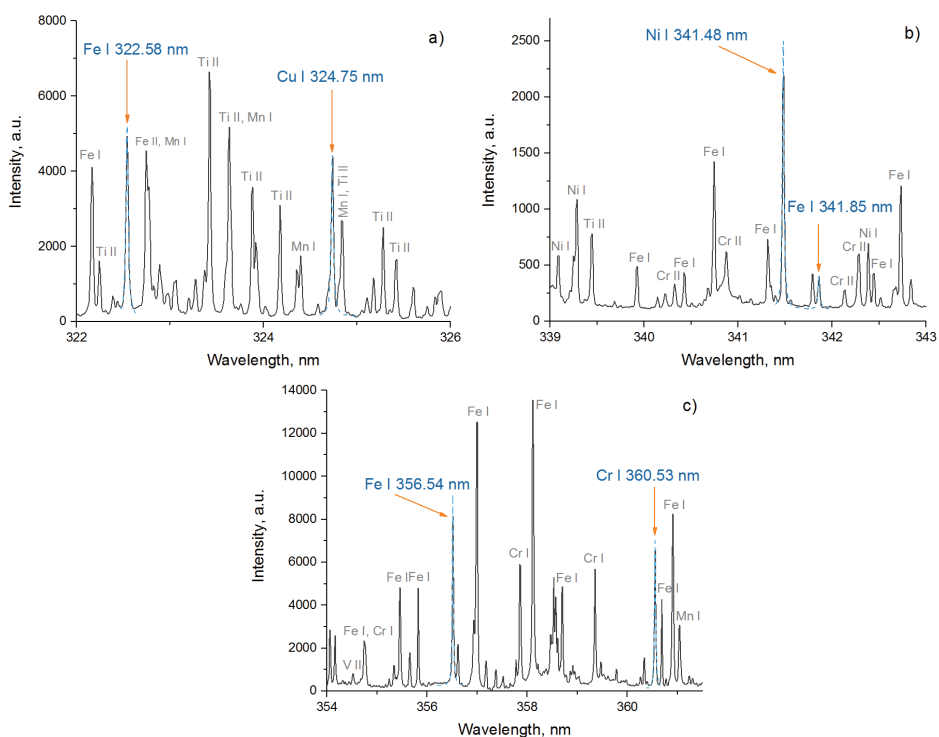

Fig. 2. LIBS spectrum of C3 cast iron alloy sample. Dashed lines are Lorentz fit of: a) Cu, b) Ni and c) Cr line used for calibration, together with Fe line used as internal standard.

As it may be seen from Fig. 2, the emission line profiles were reasonably well approximated by the Lorentz line shape. The intensities were calculated as the integrated peak area divided by the line width (FWHM). Calibration curves for Cu and Ni were constructed by plotting the emission intensity of the analyte line as a function of the concentration of analyte in the reference sample. In the case of Cr, the internal standardization procedure was applied to compensate statistical variations of the mass ablated and the plasma characteristics.[23,24] The intensity of Cr I 360.53 nm line (E_{exc} = 3.44 eV) was normalized to the intensity of the Fe I 356.54 nm line (excitation energy, E_{exc} = 4.43 eV). The wavelength range captured simultaneously by our detector was 10 nm. Because of that, for Cu and Ni, it was hard to find matching analyte-internal standard line pair with comparable E_{exc} and with sufficiently high intensity ratio.

As it may be seen in Fig. 3, the linearity of the calibration curves obtained for Cu, Ni and Cr was fairly good with correlation coefficients (R^2) better than 0.99. In the present case, the matrix effects are not expected to be very large because iron is the major component (> 92 %) both in calibration and control samples. The linear limit is valid for concentrations up to 1.2 % in the case of copper, 2.2 % for nickel and 0.3 % for chromium. Standards with concentrations of the analyte that produced saturation in the high-concentration region of the calibration curves (due to self-absorption of the emission lines) were excluded from calibration.
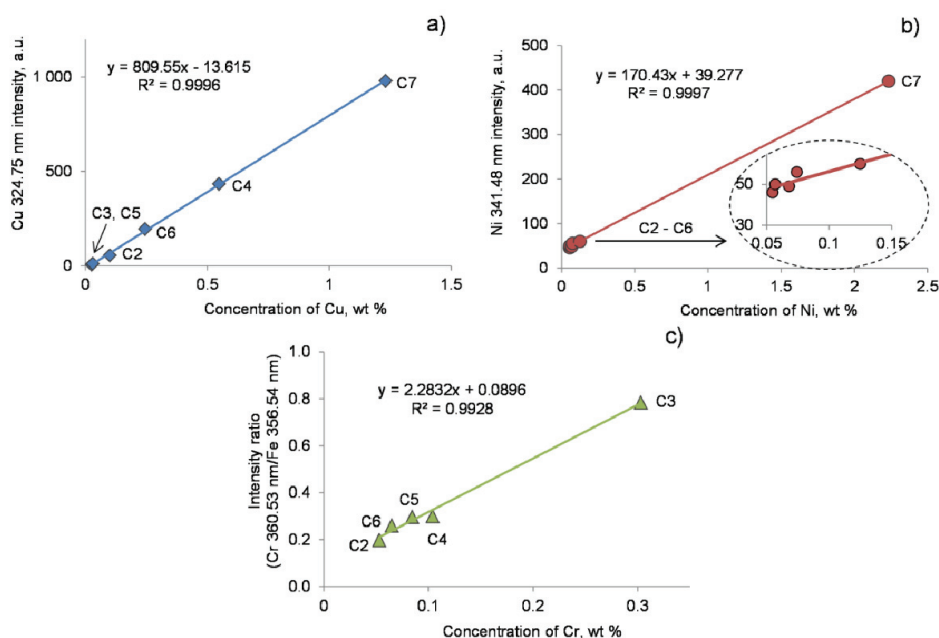

Fig. 3 Calibration curves of: a) Cu, b) Ni and c) Cr cast iron samples.

Calibration curves were used to determine the concentration of Cu, Ni and Cr in three samples of unknown composition. The obtained results together with results obtained with reference spectrochemical method (ICP-OES) are shown in Fig. 4.
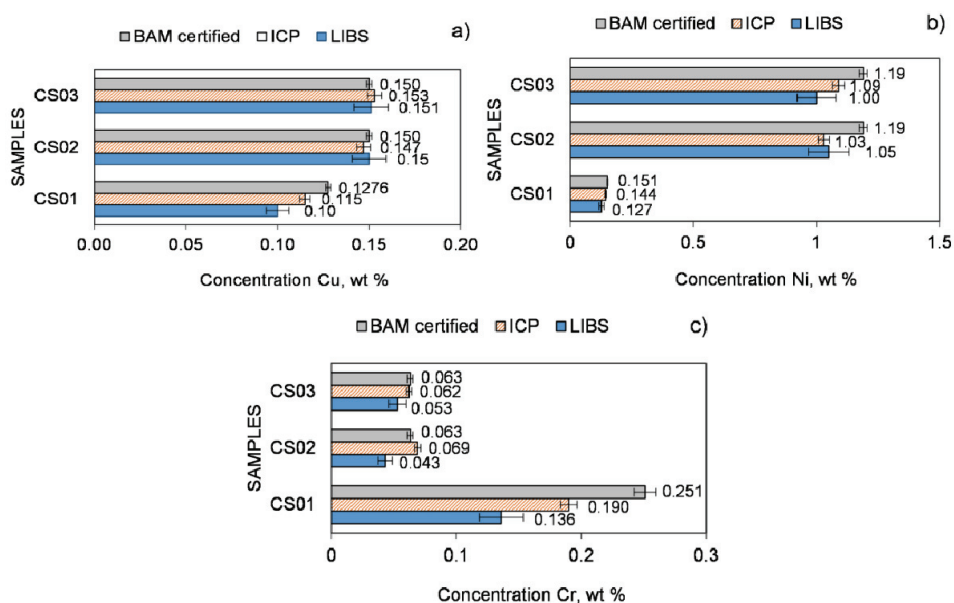

Fig. 4. Comparison chart of Cu, Cr and Ni concentrations in cast iron samples, measured by TEA CO_2 LIBS and ICP-OES. Numbers are wt. %, and errors bars correspond to the standard deviation of three replicate measurements (LIBS and ICP) and measurement uncertainties of true (certified) values reported by BAM.

To test the accuracy and precision of the LIBS measurements, two statistical parameters were evaluated and compared to those obtained by ICP analysis. Table II displays accuracy and precision results of the two techniques, given as average bias (or accuracy) and relative standard deviation (% *RSD*) defined by the equations,

$$\text{Average bais},\% = \frac{1}{N} \sum_{i=1}^{N} \frac{100\left(X_i - C_s\right)}{C_s}$$

$$RSD,\% = \frac{100 SD}{\overline{\overline{X}}}$$

where:

$$SD = \sqrt{\frac{\sum_{1}^{N}\left(X_i - \overline{X}\right)^2}{N-1}}$$

and

$$\overline{X} = \frac{\sum_{i=1}^{N} X_i}{N}$$

where N represents the total number of samples, X_i and $\overline{X}$ are measured and average concentrations, respectively, and C_s is true concentration value reported by BAM.

TABLE II. Comparison of precision and accuracy of the results obtained with LIBS and ICP-OES technique

Element	Precision, *RSD* / %		Accuracy, average bias, %	
	LIBS	ICP	LIBS	ICP
Cu	6.2	2.5	7.0	3.3
Cr	12.9	3.6	31.0	5.5
Ni	7.9	2.2	14.5	8.8

The correlation between the two analytical techniques was fairly good, however, as expected, higher accuracy and precision were obtained by ICP analysis (Fig 2, Table II). On the other hand, LIBS technique offers certain advantages like no need for sample preparation and fast on-line analysis with a level of accuracy and precision often sufficient for commercial industrial applications.

Limits of detection (*LOD*) for Cu, Cr and Ni were calculated according to formula $LOD = 3\sigma_B/s$, where σ_B is the standard deviation of the background and s is the sensitivity defined as a slope of calibration curve. The standard deviation of the continuum background was calculated by fitting a linear curve to the continuum intensity over narrow spectral regions (10 to 20 pixels or about 0.15 nm) on both sides of the atomic emission line, and then calculating the root mean square (*rms*) values based on the pixel-to-pixel variations from the linear fit. For each emission line of interest, the final *rms* noise was taken as the average of these two values. Table III lists the spectral lines used for calibration and *LOD* values obtained in this work, together with the *LOD* values reported in the literature.

Literature data refer to similar matrix composition, mainly steel, however, the results were obtained by using different LIBS configurations, (most commonly) based on Nd:YAG laser and time-gated detection. Obtained limits of detection are comparable to those reported in the literature despite differences in

laser wavelength, pulse duration, applied fluence, detection scheme, experimental arrangements (single or double pulse), and diversity of investigated iron-based alloys composition.

Table III. Comparison of LODs obtained in the present work with those reported in the literature; svsss – single spot sampling side-view scheme; svss – side-view scheme scanning sample; ofss – optical fibre single spot sample; sp – single pulse; dp – double pulse

Element	Cu	Ni	Cr
Wavelength, nm	324.75	341.48	357.87
LOD / %, present work	0.002	0.009	0.017
LOD / %, literature	0.02[12]; 0.006[25]; 0.0025[sp], 0.0004[dp].[26]	0.009[8];0.5[12]; 0.0006[23]; 0.01[sp], 0.001[dp26];0.007[27]	0.003[8];0.025[12];0.005[23]; 0.007[sp], 0.0025[dp26]; 0.021[27]; 0.009[svsss], 0.031[svss], 0.023[ofss28]

CONCLUSIONS

Laser-induced breakdown spectroscopy system based on TEA CO_2 laser was applied for the elemental characterization of cast iron samples. The analysis was performed in the air at atmospheric pressure with minimal preparation of samples. Time-integrated spatially-resolved detection system with prior optimization of plasma viewing region was used for the acquisition of emission spectra. The correlation between the LIBS signal and the concentration of analyte in the cast iron standard samples were linear in the concentration range 0.026–1.2 mass % for Cu, 0.053–0.3 mass % for Cr and 0.055–2.2 mass % for Ni, with correlation coefficients exceeding 0.99. Calculated detection limits were 20 ppm for Cu, 90 ppm for Cr and 170 ppm for Ni. The precision of LIBS determination was found to be (%, RSD) 6 for Cu, 13 for Cr and 8 for Ni, while the accuracy was 7, 31 and 14 % bias, for Cu, Cr and Ni, respectively. The analytical figures of merit of the studied LIBS system may be considered as satisfying for commercial industrial applications. The results of the present study open the possibility to construct a portable, non-gated LIBS system that can be used as analytical tool in the ferrous industry.

И З В О Д

ОДРЕЂИВАЊЕ КОНЦЕНТРАЦИЈЕ НИСКО ЛЕГИРАЈУЋИХ ЕЛЕМЕНАТА У ЛИВЕНОМ ГВОЖЂУ ПРИМЕНОМ СПЕКТРОСКОПИЈЕ ЛАСЕРСКИ ИНДУКОВАНЕ ПЛАЗМЕ НА БАЗИ ТЕА CO_2 ЛАСЕРА

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У овом раду испитиване су аналитичке могућности спектроскопије ласерски индуковане плазме за одређивање концентрације ниско-легирајућих елемената у ливеном гвожђу. Плазма је индукована озрачивањем мете у ваздуху, на атмосферском притиску, коришћењем инфрацрвеног угљендиоксидног ласера. За добијање емисионих спектара коришћена је временски интеграљена просторно разложена спектроскопија. Сет од десет узорака ливеног гвожђа у форми праха/честица обезбеђен је од ВАМ-а (Bundesanstalt für Material Forschung und Prüfung, Deutschland). Од овог сета, седам узорака је коришћено за калибрацију, а три су третирана као непознати узорци. За бакар, хром и никл добијене су линеарне калибрационе криве са коефицијентом корелације већим од 0,99. Процењена прецизност и тачност методе упоређена је са вредностима добијеним анализом истих узорака методом спектроскопије индуктивно спрегнуте плазме. Одређене границе детекције за Cu, Cr и Ni упоређене су са расположивим литературним подацима. Узимајући у обзир предности које пружа спектроскопија ласерски индуковане плазме (LIBS), као што су економична и брза анализа без потребе за предходном припремом узорака, као и могућност за анализу у реалном времену на лицу места, аналитичке карактеристике испитиваног LIBS система могу се сматрати задовољавајућим.

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REFERENCES

1. U.S. Geological SurveyNational Minerals Information Center, https://minerals.usgs.gov/ /minerals/pubs/commodity/iron_&_steel_scrap/index.html#mcs (accessed 28/02/2017)
2. ASTM E351-13, Standard Test Methods for Chemical Analysis of Cast Iron—All Types, ASTM International, West Conshohocken, PA, 2013, www.astm.org (accessed 28/02/2017)
3. ISO 13898-1:1997(en) Steel and iron — Determination of nickel, copper and cobalt contents — Inductively coupled plasma atomic emission spectrometric method — Part 1: General requirements and sample dissolution, https://www.iso.org/standard/23268.html (accessed 28/02/2017)
4. ASTM E1999-11, Standard Test Method for Analysis of Cast Iron by Spark Atomic Emission Spectrometry, ASTM International, West Conshohocken, PA, 2011, www.astm.org (accessed 28/02/2017)
5. ASTM E322-12, Standard Test Method for Analysis of Low-Alloy Steels and Cast Irons by Wavelength Dispersive X-Ray Fluorescence Spectrometry , ASTM International, West Conshohocken, PA, 2012, www.astm.org (accessed 28/02/2017)
6. *Laser-Induced Breakdown Spectroscopy (LIBS), Fundamentals and Applications*, A. W. Miziolek, V. Palleschi, I. Schechter, Eds., Cambridge University Press, Cambridge, 2006
7. F. Boué-Bigne, *Spectrochim. Acta,* B **63** (2008) 1122

8. C. Lopez-Moreno, K. Amponsah-Manager, B. W. Smith, I. B. Gornushkin, N. Omenetto, S. Palanco, J.J. Laserna, J.D. Winefordner, *J. Anal. At. Spectrom*. **20** (2005) 552
9. R. Sattmann, V. Sturm, R. Noll, *J. Phys., D: Appl. Phys*. **28** (1995) 2181
10. J. Vrenegor, R. Noll, V. Sturm, *Spectrochim. Acta, B* **60** (2005) 1083
11. I. Bassiotis, A. Diamantopoulou, A. Giannoudakos, F. Roubani-Kalantzopoulou, M. Kompitsas, *Spectrochim. Acta, B* **56** (2001) 671
12. M. O. Vieitez, J. Hedberg, O. Launila, L-E. Berg, *Spectrochim. , B* **60** (2005) 920
13. N. Idris, K. Kagawa, F. Sakan, K. Tsuyuki, S. Miura, *Appl. Spectrosc*. **61** (2007) 1344
14. A. Khumaeni, Z. S. Lie, H. Niki, Y. I. Lee, K. Kurihara, M. Wakasugi, T. Takahashi, K. Kagawa, *Appl. Opt*. **51** (2012) B121
15. J. Savovic, M. Stoiljkovic, M. Kuzmanovic, M. Momcilovic, J. Ciganovic, D. Rankovic, S. Zivkovic, M. Trtica, *Spectrochim. Acta, B* **118** (2016) 127
16. S. Zivkovic, M. Momcilovic, A. Staicu, J. Mutic, M. Trtica, J. Savovic, *Spectrochim. Acta, B* **128** (2017) 22
17. M. Momcilovic, M. Kuzmanovic, D. Rankovic, J. Ciganovic, M. Stoiljkovic, J. Savovic, M. Trtica, *Appl. Spectrosc*. **69** (2015) 419
18. M. Momčilović, J. Ciganović, D. Ranković, U. Jovanović, M. Stoiljković, J. Savović, M. Trtica, *J. Serb. Chem. Soc*. **80** (2015) 1505
19. S. Zivkovic, J. Savovic, M. Trtica, J. Mutic, M. Momcilovic, *J. Alloys Cmpds.* **700** (2017) 175
20. M. S. Trtica, B. M. Gakovic, B. B. Radak, S. S. Miljanic*, Proc. SPIE* **4747** (2002) 44
21. A. Matsumoto, A. Tamura, K. Fukami, Y.H. Ogata, T. Sakka, *Anal. Chem*. **85** (2013) 3807
22. M. Khater, P van Kampen, J. T. Costello, J-P Mosnier, E. T. Kennedy, *J. Phys., D: Appl. Phys*. **33** (2000) 2252
23. C. Aragon, J. A. Aguilera, F. Penalba, *Appl. Spectrosc*. **53** (1999) 1259
24. V. Karki, A. Sarkare, M. Singh, G. S. Mauryarohit, R. Kumar, A. K. Rai, S. K. Aggarwal, *Pramana* **86** (2016) 1313
25. M. A. Ismail, H. Imam, A. Elhassan, W. T. Youniss, M. A. Harith, *Anal. At. Spectrom*. **19** (2004) 489
26. M. A. Ismail, G. Cristoforetti, S. Legnaioli, L. Pardini, V. Palleschi, A. Salvetti, Elisabetta Tognoni, M. Harith, *Anal. Bioanal. Chem*. **385** (2006) 316
27. C. B Stipe, B. D Hensley, J. L Boersema, S. G Buckley, *Appl. Spectrosc*. **64** (2010) 154
28. V. Lednev, S. M. Pershina, A. F. Bunkina, *J. Anal. At. Spectrom*. **25** (2010) 1745.