

L. M. Cabalín · D. Romero · C.C. García · J. M. Baena  
J. J. Laserna

## Time-resolved laser-induced plasma spectrometry for determination of minor elements in steelmaking process samples

Received: 3 May 2001 / Revised: 27 August 2001 / Accepted: 7 September 2001 / Published online: 20 December 2001  
© Springer-Verlag 2001

**Abstract** A pulsed Nd:YAG laser operating on the fourth (266 nm) and second (532 nm) harmonics has been used to generate plasmas on the target surface in air at atmospheric pressure. The influence of wavelength on quantitative analysis of 4 minor elements in stainless steel samples (Si, Ti, Nb and Mo) was investigated. Stainless steel samples with different elemental concentrations were prepared and analyzed by laser-induced plasma spectrometry (LIPS). The effect of laser wavelength on analytical figures of merit (calibration curves, correlation coefficients, linear dynamic ranges, analytical precision, and accuracy values) was found to be negligible when internal standardization (an Fe line) and time-resolved laser-induced plasma are employed. For both wavelengths, the calibration curves presented a good linearity and an acceptable linear dynamic range in the concentration interval investigated. For the four elements studied, limits of detection lower than  $150 \mu\text{g g}^{-1}$  were achieved. To evaluate the influence of wavelength on precision and accuracy, a set of fifteen high-alloyed steel samples from different stages of steelmaking process have been analyzed. Finally, the long-term stability of the analytical measurements for Mo with 532 nm wavelength has been discussed. RSD values were lower than 5.3% for the elements studied.

**Key words** Laser-induced plasma spectrometry (LIPS) · Stainless steel · Quantitative analysis

### Introduction

Stainless steels are iron-based alloys with a carbon content generally below 1.2% and at least 10.5% Cr as well

as other elements such as nickel, silicon, titanium, niobium, molybdenum and so on. Stainless steel with different properties and characteristics can be achieved by varying the chemical composition and adapting the steelmaking process. In industrial steelmaking, chemical analysis plays an important role during production. Consequently, it is essential to keep the content of the different elements under rigorous control during all transformation steps from raw materials to the final products in order to be sure that the composition of the stainless steel falls within an established range of acceptability. The way to determine the chemical composition has changed in the recent years, with successive improvements in both precision and speed. In the last decade, the existing instrumental analysis techniques have been improved and new approaches have been developed for rapid, reliable, and accurate analytical results, allowing real-time monitoring of steel production [1].

Laser-induced plasma spectroscopy (LIPS) has been applied successfully to the chemical analysis of stainless steel samples. In contrast to conventional analytical methods like flame atomic absorption spectrometry (FAAS), inductively coupled plasma-atomic spectrometry (ICP-AES) and X-ray fluorescence spectrometry (XRF), LIPS permits fast, in-situ and on-line analysis of materials without sample preparation, eliminating the need for sampling, transportation to a central analysis facility and surface preparation. Direct multi-element analysis of major and minor constituents of stainless steel represents one application for which these characteristics are of great importance. Several publications in the literature deal with this topic [2, 3, 4, 5, 6, 7].

Cremers [8] first reported on the use of fiber optics for LIPS remote elemental analysis. The figures of merit for minor constituents of steel were measured at distances between 0.5 and 2.4 m by use of a focusing lens and collecting the emitted light. Davies et al. [9] used a 100-m fiber optic pair to perform remote LIPS on ferrous targets in an operating nuclear reactor. Detection limits of  $200 \mu\text{g g}^{-1}$  or less were found for Cr, Cu, Mn, Mo, Ni, Si and V. Lorenzen et al. [10] developed an industrial device for on-

L.M. Cabalín · D. Romero · C.C. García · J.J. Laserna (✉)  
Department of Analytical Chemistry, Faculty of Sciences,  
University of Málaga, 29071 Málaga, Spain  
e-mail: laserna@uma.es

J.M. Baena  
Acerinox S.A., Palmones, Los Barrios, 11379 Cádiz, Spain

line analysis of liquid steel using optical fiber, time-resolved optical multichannel analyzer and a fast computer. Recently, LIPS has been evaluated for stainless steel samples at high temperatures [11]. The steel sample was 51.5 cm from the focusing lens and was placed inside a laboratory oven. Studies were carried out at temperatures ranging from 25 to 1200 °C. A noticeable dependence of signal emission intensity on sample temperature was found.

LIPS has been also applied for direct analysis of elemental content in steel and in melted steel samples [12, 13, 14]. Ernst et al. determined Cu in steel for the assessment of radiation embrittlement [15]. Concentrations from 0.01% to 5% were examined. Results were compared with AAS analysis and were found to be satisfactory.

Numerous experimental optimizations have been proposed to achieve better analytical performance. They included the study of the effect of focusing distance and laser-pulse energy on accuracy and limit of detection [16, 17], the influence of sample surface topography [18, 19] on spectral emission and analytical precision, the observation of plasma in a low-pressure atmosphere [20, 21] and the application of double-pulse excitation to increase the removal material and, consequently, to improve the limit of detection [21, 22, 23, 24].

However, the main limitations of LIPS in the analysis of complex matrices such as stainless steel are related to matrix effects and to signal fluctuations due to different plasma characteristics and the nature of the ablation process, which results in a poor reproducibility. Several methods have been developed to overcome this drawback [25, 26, 27]. Gornushkin et al. [28] proposed a correlation method for the rapid identification of series of stainless steel and cast iron standards with similar chemical composition. Recently, a fully automated prototype capable of analyzing and classifying a reduced set of steel components in less of 36 s without prior sample preparation has been described [29]. This method is based on multivariate calibration of elements for the correction of matrix effects and spectral interferences.

In the present work, the applicability of LIPS for direct analysis of stainless steel is evaluated. To improve the analytical performance of LIPS, the ultraviolet (266 nm) and the visible (532 nm) wavelengths of a Nd:YAG laser have been compared for the quantitative analysis of 4 minor elements in stainless steel. The figures of merit (calibration curves, correlation coefficients, linear dynamic ranges, analytical precision and accuracy values) for both wavelengths are discussed. In this case, an Fe line was used as internal standard for compensating the signal fluctuations and for improving analytical precision and accuracy values. A long-term stability test of analytical measurements for Mo in stainless steel at 532 nm is presented.

## Experimental

### Instrumentation

The experimental set-up used in this study has been described in previous works [17, 18]. Briefly, it consists of a Q-switched Nd:YAG laser (Continuum, model Surelite SLI-20, pulse width= 5 ns) operating at its fourth or second harmonic (266 nm or 532 nm, respectively). The laser pulse energy was measured with a pyroelectric joulemeter (Gentec, model ED-200, with a nominal sensitivity of 9.86 V J<sup>-1</sup>) coupled with a digital oscilloscope. Samples were irradiated in air at atmospheric pressure. The laser beam was guided with a quartz prism and focused, at normal incidence, on the sample surface with a planoconvex quartz lens with a focal length of 100 mm. Beam diameters were measured by displacing a slit through the focal position and measuring the transmitted light with a joulemeter. Laser spot diameters were estimated to be approximately 62 μm and 125 μm at 266 nm and 532 nm, respectively. The laser-induced plasma emission was collected by a planoconvex quartz lens with focal length of 100 mm into the entrance slit of a 0.5 m focal-length Czerny-Turner spectrograph (Chromex, model 500 IS, with three indexable gratings of 300, 1200 and 2400 grooves mm<sup>-1</sup>). Light was dispersed using the 2400 grooves mm<sup>-1</sup> grating. The reciprocal linear dispersion was 2.5 nm mm<sup>-1</sup>. The entrance slit was 10 μm wide and 10 mm high. The dispersed plasma light was detected using a two-dimensional charge-coupled device (CCD) detector (Stanford Computer Optics, model 4Quik 05) equipped with an intensifier system. The CCD consisted of 768(h)×512(v) elements. The photoactive area was 6×4.5 mm<sup>2</sup>. In this configuration, each spectrum covered approximately 15 nm. Operation of the detector was controlled by

**Table 1** Percentage composition of the Acerinox in-house stainless steel samples used in this work

Sample Reference	Elemental concentration (%)							
	Mn	Ni	Nb	Mo	Si	P	Ti	Cr
ACX-P01/97	0.474	0.100	0.002	1.418	0.262	0.026	0.007	1.155
ACX-P02/97	0.209	0.112	0.001	0.642	0.302	0.024	0.006	4.940
ACX-P08/97	1.158	8.608	0.004	0.508	1.010	0.023	0.007	17.959
ACX-P10/97	1.48	11.240	0.034	2.160	0.485	0.024	0.006	17.180
ACX-P11/97	3.130	9.919	<0.001	0.205	0.505	0.025	0.005	13.720
ACX-P13/97	1.613	20.022	0.008	0.399	1.341	0.020	0.009	24.976
ACX-P14/97	0.700	21.689	0.016	0.073	1.987	0.020	0.016	23.527
ACX-P15/97	0.743	39.745	0.011	3.105	0.581	0.018	0.007	28.340
ACX-P16/99	0.180	0.170	0.410	0.010	0.490	0.020	0.099	17.880
ACX-P17/99	1.380	11.110	0.040	2.110	0.640	0.028	0.347	16.950
ACX-P18/99	1.360	11.220	0.053	2.240	0.560	0.020	0.388	17.100
ACX-P19/99	1.460	11.310	0.046	2.160	0.430	0.020	0.476	16.950
ACX-P20/99	0.280	0.200	0.527	0.040	0.410	0.020	0.180	17.860
ACX-P21/99	1.270	10.770	0.045	2.100	0.340	0.026	0.037	17.240

**Table 2** Percentage composition of the Acerinox steelmaking process samples used in this work

Sample Reference	Elemental concentration (%)							
	Mn	Ni	Nb	Mo	Si	P	Ti	Cr
7B44C1	0.704	17.486	0.012	0.213	0.328	0.023	0.018	24.537
7B44R1	1.448	19.256	0.009	0.225	0.531	0.025	0.003	24.823
7B44F1	1.453	19.349	0.008	0.216	0.524	0.025	0.008	24.729
6T74C1	0.177	0.144	0.003	0.012	0.050	0.021	0.004	14.397
6T74R1	1.134	0.168	0.007	0.012	0.235	0.023	0.007	16.240
6T74F1	0.162	0.175	0.525	0.013	0.322	0.024	0.009	16.402
7C81C1	1.086	7.446	0.011	0.926	0.291	0.031	0.008	18.645
7C81R2	1.519	11.363	0.007	2.055	0.140	0.029	0.003	16.733
7C81F2	1.589	11.241	0.008	2.164	0.432	0.030	0.314	16.688
7B10C2	0.496	0.105	0.004	0.013	0.178	0.025	0.005	10.291
7B10R1	0.392	0.142	0.004	0.014	0.238	0.026	0.006	16.271
7B10F1	0.411	0.144	0.004	0.012	0.379	0.026	0.008	16.256
7C80C1	0.776	6.178	0.009	0.278	0.201	0.030	0.009	18.737
7C80R1	1.606	8.012	0.006	0.238	0.382	0.030	0.002	17.985
7C80F1	1.651	8.146	0.006	0.238	0.298	0.031	0.015	18.283

4 Spec 1.20 software. The emission signal was corrected by subtraction of the dark signal of the detector, which was separately measured for the same exposure time. Each pulse was stored as a file containing spectral and spatial information. Calibration of the detector system was carried out by using several spectral lines emitted from a laser-induced plasma of titanium.

A sample holder was designed and manufactured in our laboratory. This sample holder enabled accommodation of different sample thicknesses so that its surface was always at a fixed distance from the focusing lens. The sample holder was mounted on a manual X–Y–Z translation stage, which made possible sample manipulation as desired.

### Samples

The samples consisted of stainless steel standards, which were provided by Acerinox, S.A. A set of twenty-one steel samples was prepared covering a very wide range of concentrations. Such a set of secondary standard samples (in-house samples) came from Acerinox standard materials or, in some cases, they were manufactured in a pilot induction furnace (40 kg nominal capacity). When the samples were made in this furnace, they underwent special metallurgical treatment in terms of forging, hot and cold rolling, heat treatment, and pickling in order to achieve homogenous crystalline structures. The chemical composition of the samples was measured by several conventional analytical methods both by wet chemistry and non-destructive spectrometric techniques. The results of the chemical analysis are summarized in Table 1. Table 2 shows the percentage concentration of steelmaking process samples.

## Results and discussion

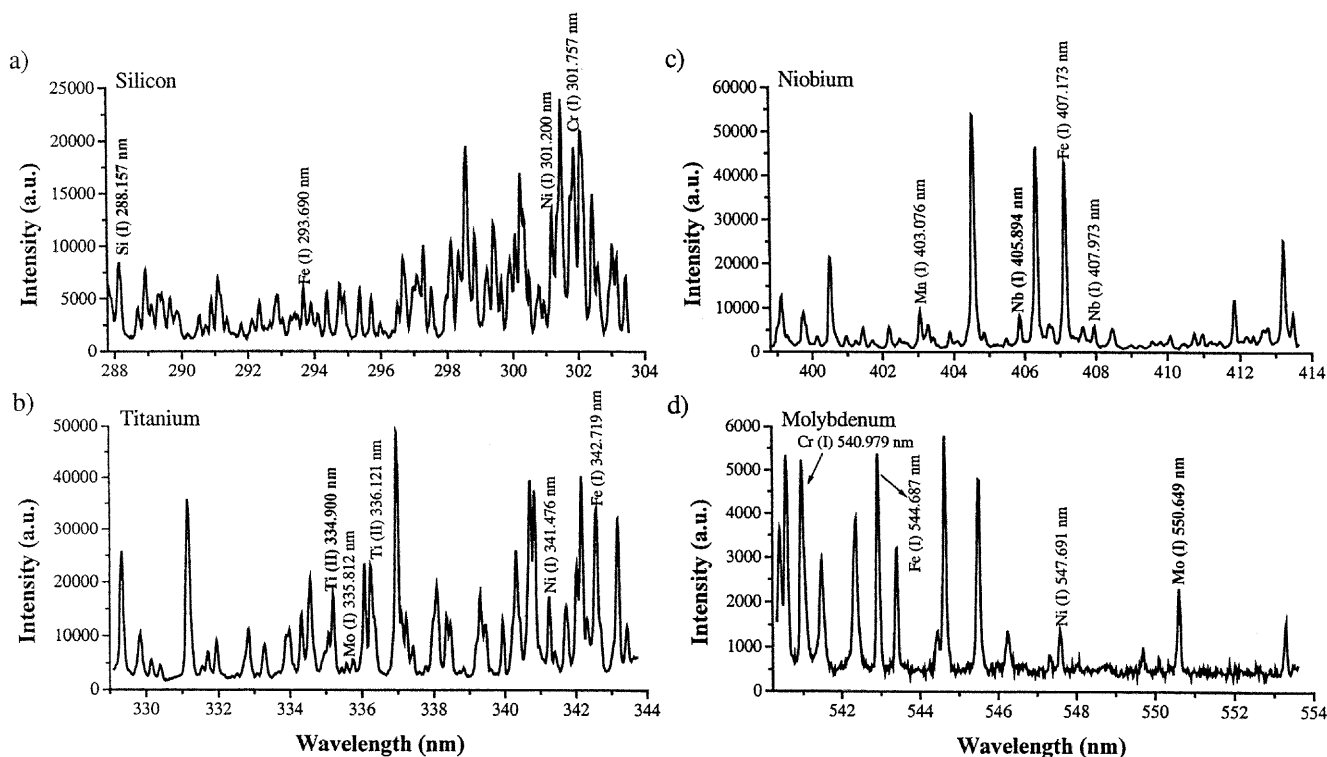
### Spectral analysis of stainless steel

A preliminary spectral study was carried out in order to select the most sensitive emission lines of the 4 minor elements in stainless steel samples (Si, Ti, Nb and Mo). Accordingly, four spectral windows in the wavelength ranges 288–304 nm, 329–344 nm, 399–414 nm and 540–554 nm were chosen to observe specifically Si, Ti, Nb and Mo, respectively. Those spectral regions were selected because line emission of the elements studied are well resolved

and free from spectral interference. Fig. 1 shows the LIP emission spectra for an AISI 316 stainless steel. For each wavelength interval, spectral lines of several major elements could be simultaneously observed which provided the possibility of using an internal standard. The spectral lines of the relevant elements are also labeled in each spectrum. For instance, Fig. 1a shows the spectral characteristics of a stainless steel sample with a silicon concentration of 2%. The spectral line corresponding to Si (I) 288.157 nm together with several spectral lines for Fe, Ni and Cr can be seen. Spectra were acquired by accumulating a total of five laser shots in the same sample location. On the basis of previous investigations [17], the experimental conditions suitable for analysis of stainless steel were an acquisition time of 1  $\mu$ s and a delay time of 1.5  $\mu$ s after plasma formation; the beam was focused 1 mm inside the sample in order to improve the ablation efficiency.

### Influence of laser wavelength on analytical figures of merit

The effect of ultraviolet and visible wavelengths of the Nd:YAG laser on the analytical figures of merit (AFOM) has been evaluated using fourteen stainless steel samples with variable concentrations of the elements of interest (Table 1). Fig. 2 shows a comparison of the calibration curves for Si, Ti, Nb and Mo using the wavelengths of 266 nm and 532 nm. Calibration curves were constructed using an internal standard. The net signals of each element were normalized to an adjacent Fe line. The vertical bars in the figure correspond to the signal range of five replicate measurements each on a fresh sample position. As shown, similar analytical results have been obtained with the two wavelengths, indicating that the dependence of AFOM on wavelength is nearly negligible when internal standardization is used. The exception was with Nb (I) at 532 nm; for this the data are indicative of a significant



**Fig. 1** LIP spectra of a type 316 stainless steel sample showing emission lines of (a) silicon, (b) titanium, (c) niobium, and (d) molybdenum. The spectra were obtained by accumulating five laser shots in the same position. Laser energy was 4 mJ pulse<sup>-1</sup>. Delay time and acquisition time were 1.5  $\mu$ s and 1  $\mu$ s, respectively

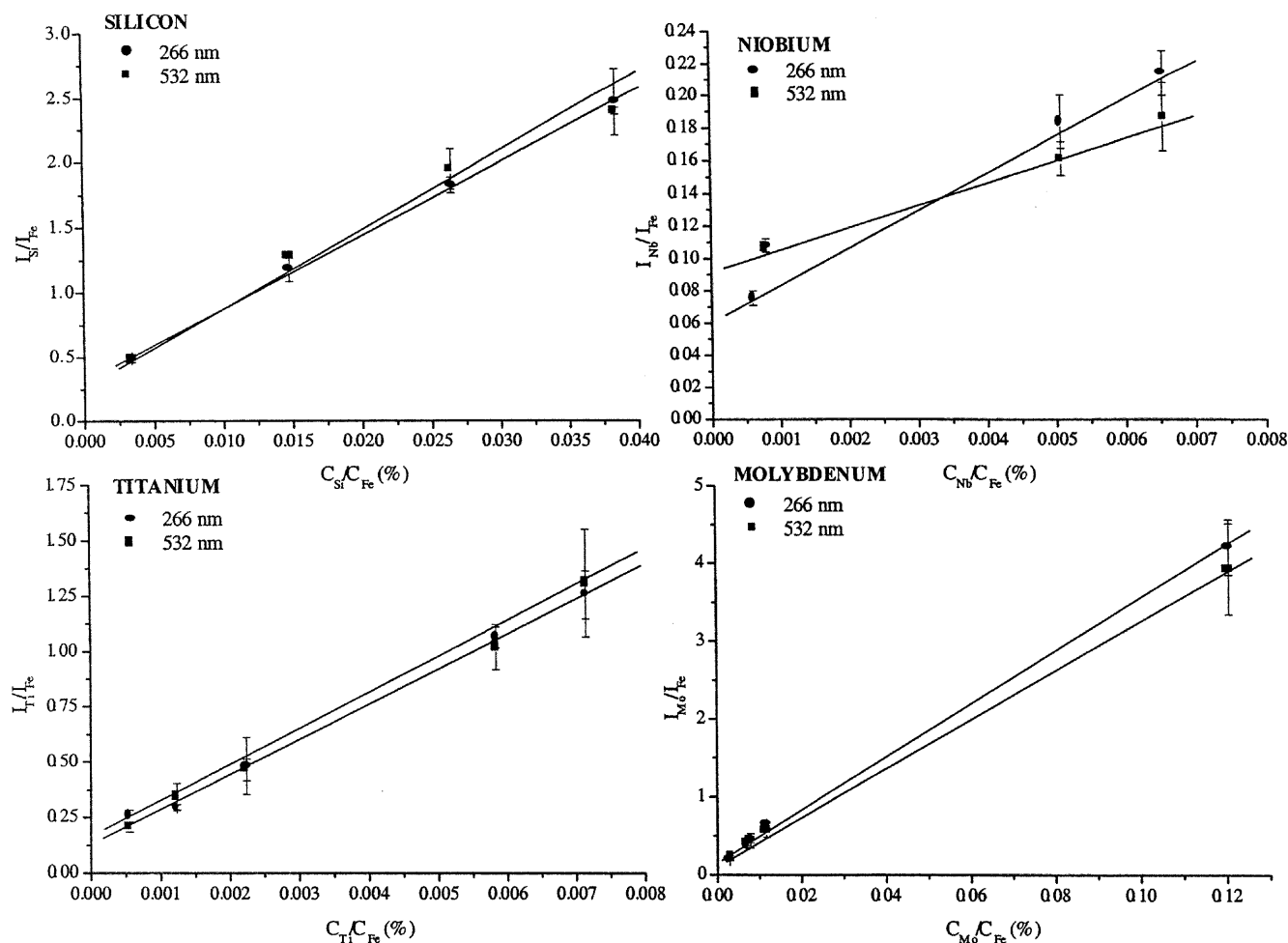
difference for both laser wavelengths. The slopes, the correlation coefficients and the linear dynamic range values from calibration curves obtained at 266 nm and 532 nm are summarized in Table 3. The linearity of calibration curves for the four elements was excellent with an average value of  $R^2$  of 0.996 and 0.992 for the ultraviolet and visible radiation, respectively, except for Si (I) 288.157 nm at 532 nm with a correlation coefficient of 0.981.

Table 4 illustrates a comparison of the limits of detection (LODs) measured with 266 nm and 532 nm for four elements in stainless steel. A type 304 stainless steel sample with a nominal content of 1.41% Mn, 8.13% Ni, 0.014% Nb, 0.32% Mo, 0.34% Si, 0.033% P, 0.009% Ti and 18.44% Cr was used. LOD values were acquired by accumulating 10 laser shots in the same position. Each sample was measured fifteen times. The relative standard deviation of the background and the signal-to-background ratios are also presented. The background signal could be obtained using a blank sample at the same wavelength as the signal; however, in practice, it is very difficult to obtain such a blank sample for use in solid-sampling LIPS. For this reason, the background signal was considered as the lowest signal value measured at either side of the spectral peak. As shown, S/B values range from 4.6 to 7.9 and no significant effect was observed when changing from visible to ultraviolet breakdown. This observation could indicate that the breakdown regime is thermal rather

than photochemical in nature. The limits of detection at 266 nm were of 78, 54, 24 and 61  $\mu$ g g<sup>-1</sup> for Si, Nb, Ti and Mo, respectively. Those values are in agreement with those reported by other authors [9, 16, 20, 30, 31]. The only appreciable difference in LODs appears for Mo, which has LOD values of 61  $\mu$ g g<sup>-1</sup> and 144  $\mu$ g g<sup>-1</sup> at 266 nm and at 532 nm, respectively.

It should be noted that LIPS precision was better than 10% with breakdown at the two wavelengths for the four elements studied, which indicates acceptable method reproducibility. On the other hand, RSD values of background were better than 3.50%.

To determine the effect of laser wavelength on analytical precision and accuracy a set of fifteen high alloyed steel samples coming from different stages of steelmaking was analyzed. The chemical compositions were determined by X-ray fluorescence spectrometry (XRF) (Table 2). The quantitative analysis of those steelmaking process samples were conducted using the ultraviolet and visible wavelengths of the Nd:YAG laser. After preparation of calibration curves for each element, 15 replicate measurements for each sample were made and the averaged concentration of each element was determined. The relative error and relative standard deviation of the measurements were also calculated. The corresponding results are shown in Tables 5 6 7 8 for Si, Nb, Ti and Mo, respectively. It should be noted that the concentrations found, for all elements at both wavelengths, agree quite reasonably with those given by XRF and only the composition of some elements in steelmaking process samples exhibit a significant difference compared with the XRF content. Relative errors vary widely depending on the concentration measured. Thus, for minor elements at concentrations close to the limits of detection the relative errors can be as large as



**Fig. 2** Comparison of LIPS calibration curves for Si, Nb, Ti and Mo using internal standard with breakdown at 266 nm and 532 nm. The spectra were obtained by accumulating five laser shots. Five

replicate measurements were made each on a fresh sample position. Laser energy was 4 mJ pulse<sup>-1</sup>. Delay time and acquisition time were 1.5 μs and 1 μs, respectively

**Table 3** Analytical figures of merit of emission lines used for the analysis of stainless steel standards using internal standard with breakdown at 266 nm and 532 nm

Element	Breakdown at 266 nm			Breakdown at 532 nm		
	Slope	Corr. coefficient (R <sup>2</sup> )	LDR <sup>a</sup> (Conc. %)	Slope	Corr. coefficient (R <sup>2</sup> )	LDR <sup>a</sup> (Conc. %)
Si <sub>288.157</sub> /Fe <sub>293.690</sub>	56	0.999	0.1–2.00	54	0.981	0.1–2.00
Nb <sub>405.894</sub> /Fe <sub>407.173</sub>	18	0.999	0.05–0.50	13	0.995	0.05–0.50
Ti <sub>334.900</sub> /Fe <sub>342.719</sub>	156	0.997	0.030–0.50	160	0.996	0.030–0.50
Mo <sub>550.649</sub> /Fe <sub>544.687</sub>	33	0.991	0.01–3.00	31	0.999	0.01–3.00

<sup>a</sup>Linear dynamic range determined as 5% drop off from linearity

**Table 4** Analytical figures of merit of the LIPS method for the analysis of AISI 304 stainless steel using internal standard. The data were obtained by accumulating ten laser shots and averaging fifteen replicate measurements each on a fresh sample position

Element	Wavelength (nm)	Breakdown at 266 nm			Breakdown at 532 nm		
		RSD <sub>b</sub> <sup>a</sup> (%)	S/B <sup>b</sup>	C <sub>LOD</sub> <sup>c</sup> (μg g <sup>-1</sup> )	RSD <sub>b</sub> <sup>a</sup> (%)	S/B <sup>b</sup>	C <sub>LOD</sub> <sup>c</sup> (μg g <sup>-1</sup> )
Si	288.157	2.6	5.8	78	2.0	4.6	77
Nb	405.894	2.8	6.6	54	2.5	5.4	56
Ti	334.900	3.1	7.1	24	3.5	7.1	26
Mo	550.649	2.5	7.7	61	2	7.9	144

<sup>a</sup>Precision expressed as RSD (%) of the background for 15 replicate measurements

<sup>b</sup>Signal-to-background ratio for the concentration used in the C<sub>LOD</sub>

<sup>c</sup>Limit of detection calculated from the equation: C<sub>LOD</sub>=(3×C×RSD<sub>b</sub>)/S/B [31]

**Table 5** Quantitative analysis for silicon in steelmaking process samples with breakdown at 266 nm and 532 nm

Sample	Si Nominal content <sup>a</sup> (%)	Breakdown at 266 nm			Breakdown at 532 nm		
		Found content (%)	Relative error (%)	RSD (Cont. %)	Found content (%)	Relative error (%)	RSD (Cont. %)
7B44C1	0.328	0.329	0.30	8.32	0.334	1.83	7.10
7B44R1	0.531	0.519	2.26	6.93	0.498	6.21	8.13
7B44F1	0.524	0.520	0.76	8.47	0.520	0.76	10.93
6T74R1	0.235	0.312	32.77	6.01	0.284	20.85	3.16
6T74F1	0.322	0.341	5.90	3.60	0.323	0.31	3.66
7C81C1	0.291	0.333	14.43	4.99	0.302	3.78	4.83
7C81F2	0.432	0.409	5.32	9.32	0.397	8.10	6.22
7C10C2	0.178	0.286	60.67	5.01	0.257	44.38	3.77
7C10R1	0.236	0.372	57.63	5.87	0.293	24.15	4.75
7C10F1	0.379	0.414	9.23	3.72	0.388	2.37	6.69
7C80C1	0.201	0.349	73.63	7.02	0.265	31.84	5.84
7C80R1	0.382	0.409	7.07	6.00	0.381	0.26	5.67
7C80F1	0.298	0.373	25.17	5.94	0.297	0.34	7.93

<sup>a</sup>Concentration measured by XRF expressed as (%)**Table 6** Quantitative analysis for niobium in steelmaking process samples with breakdown at 266 nm and 532 nm

Sample	Nb Nominal content <sup>a</sup> (%)	Breakdown at 266 nm			Breakdown at 532 nm		
		Found content (%)	Relative error (%)	RSD (Cont. %)	Found content (%)	Relative error (%)	RSD (Cont. %)
7B44C1	0.012	0.063	425.00	15.38	0.032	166.67	7.37
6T74C1	0.003	0.012	300.00	16.56	0.029	866.67	10.80
6T74F1	0.525	0.382	27.24	9.58	0.450	14.29	5.74

<sup>a</sup>Concentration measured by XRF expressed as (%)**Table 7** Quantitative analysis for titanium in steelmaking process samples with breakdown at 266 nm and 532 nm

Sample	Ti Nominal content <sup>a</sup> (%)	Breakdown at 266 nm			Breakdown at 532 nm		
		Found content (%)	Relative error (%)	RSD (Cont. %)	Found content (%)	Relative error (%)	RSD (Cont. %)
7B44C1	0.018	0.033	83.33	4.02	0.033	83.33	6.64
7C81C1	0.008	0.017	112.50	7.33	0.006	25.00	35.24
7C81F2	0.314	0.320	1.91	4.04	0.290	7.64	2.86

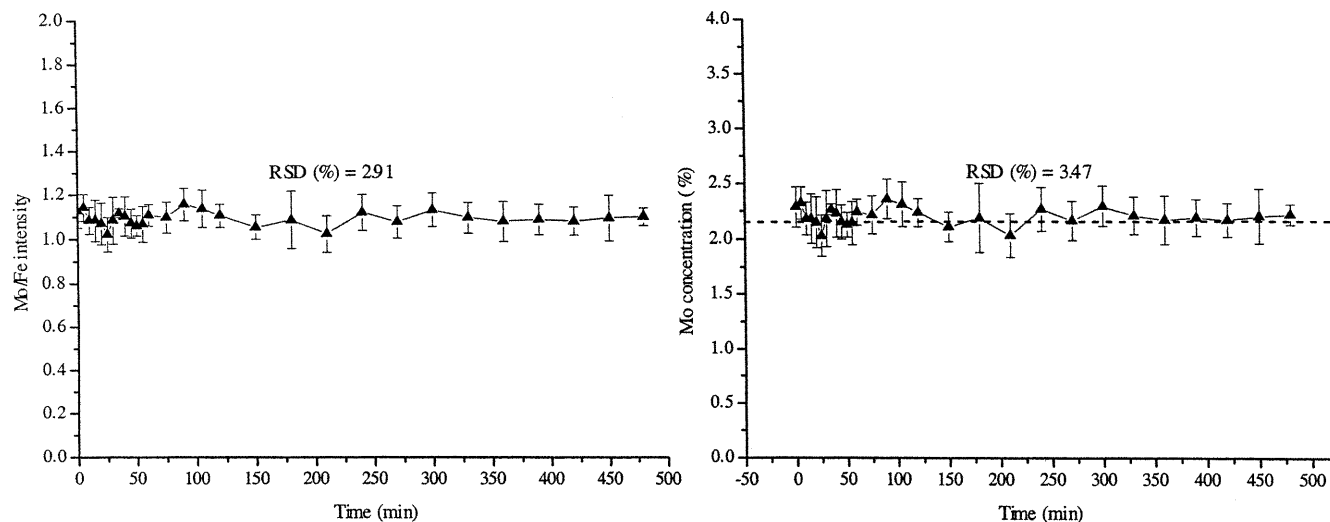
<sup>a</sup>Concentration measured by XRF expressed as (%)**Table 8** Quantitative analysis for molybdenum in steelmaking process samples with breakdown at 266 nm and 532 nm

Sample	Mo Nominal content <sup>a</sup> (%)	Breakdown at 266 nm			Breakdown at 532 nm		
		Found content (%)	Relative error (%)	RSD (Cont. %)	Found content (%)	Relative error (%)	RSD (Cont. %)
7B44C1	0.213	0.174	18.31	7.86	0.165	22.54	12.60
7B44R1	0.225	0.210	6.67	8.13	0.298	32.44	7.57
7B44F1	0.216	0.196	9.26	7.53	0.219	1.39	9.43
7C81C1	0.926	0.833	10.04	5.82	0.961	3.78	6.00
7C81R2	2.055	2.108	2.58	6.08	2.170	5.60	6.70
7C81F2	2.164	2.230	3.05	7.19	2.247	3.84	7.34
7C80C1	0.278	0.242	12.95	7.81	0.163	41.37	10.32
7C80R1	0.238	0.197	17.23	8.16	0.236	0.84	11.26
7C80F1	0.238	0.198	16.81	12.13	0.289	21.43	7.75

<sup>a</sup>Concentration measured by XRF expressed as (%)

866%. Large analyte concentrations can be measured with relative errors of the order of ~0.30%. The RSD (%) of 15 replicate measurements each one of 10 accumulated laser shots varied from 3.60 to 16.56 at 266 nm and from 3.66 to 35.24 at 532 nm. Those measurements are within

typical reproducibility levels provided by LIPS. It should be noted that in all samples studied, for the four elements, RSD values with the ultraviolet and visible wavelengths, increased as the elemental concentration decreased. For instance with breakdown at 532 nm, the Nb (I) RSD (%)



**Fig. 3** Long-term stability of the ratioed intensity and the found concentration value with breakdown at 532 nm for Mo. The dashed line indicates the value corresponding to a stainless steel nominal concentration

of sample 6T74C1 is lower than that corresponding to sample 6T74F1 by a factor of about 2. This is also the reason for the poor precision for Ti, which presents an elemental concentration close to the method LOD. These analytical results obtained in all samples are similar when using the fourth and second harmonics of the Nd:YAG laser. However, the accuracy seems to be better with visible radiation, while the analytical precision appears to be better at ultraviolet wavelengths.

#### Long-term stability and repeatability

In order to check for long-term stability of the analytical system, the temporal behavior of the LIP ratioed intensity and the found concentration for one of the minor elements (Mo (I) 550.649 nm) has been investigated. As the ablation behavior was found to be similar for the ultraviolet and visible wavelengths, only the second harmonic of the Nd:YAG laser was evaluated. The repeatability study was carried out during a period of 8 h. During this period of time, five measurements were made, each one of them accumulating ten laser shots. In the first hour, data were acquired every 5 min; during the second hour, the values were obtained every 15 min and in successive hours the data were taken every 30 min. The long-term stability for the element evaluated is presented in Fig. 3. In the figure, the dashed lines indicate the corresponding nominal concentration in the stainless steel. In all the cases, RSD (%) values lower than 5.3% have been achieved under routine conditions, demonstrating satisfactory stability and the absence of significant drift.

#### Conclusions

The capability of LIPS for the direct analysis of stainless steel has been demonstrated. The fourth and second harmonics of the Nd:YAG laser have been compared to evaluate the influence of the wavelength on quantitative analysis of stainless steel. The analytical figures of merit in terms of calibration curves, correlation coefficients, linear dynamic ranges, limits of detection and analytical precision and accuracy values for four minor elements in stainless steel have been calculated. It has been demonstrated that when an internal standard is used, the ultraviolet and visible wavelengths provide similar analytical results and the effect on wavelengths for quantitative purposes is not significant. For both wavelengths, the limits of detection for all elements were lower than  $150 \mu\text{g g}^{-1}$ . Those values are in good agreement with the general needs of steelmaking process analysis.

The long-term stability of the signal measurements were better than 5.3% for Mo with the Nd:YAG system operating on the visible harmonic demonstrating the analytical capability of LIPS for analysis of stainless steel samples comparable with other conventional techniques. Laser-induced plasma spectrometry appears to be a promising method with enormous applications in industrial fields where information on the quality of materials during the production process is necessary.

**Acknowledgements** This work is supported by the ECSC under the project 7210.PB/041. One of authors (L.M.C) thanks the Spanish Secretaría de Estado de Universidades, Investigación y desarrollo for providing a fellowship. This work was also supported by Project PB97-1107 of the Dirección General de Investigación Científica y Técnica (Ministry of Education and Science, Madrid, Spain).

#### References

1. Dulski TR (1993) *Anal Chem* 65:29R-39R
2. Darker SA, Tyson JF (1993) *J Anal At Spectrom* 8:145-209
3. Russo RE (1995) *Appl Spectrosc* 49:A14-A28

4. Schechter I (1997) *Anal Chem* 16:173–297
5. Sneddon J, Lee YI (1999) *Anal Lett* 32:2143–2162
6. Rusak DA, Castle BC, Smith BW, Winefordner JD (1997) *Crit Rev Anal Chem* 27:257–290
7. Winefordner JD, Gornushkin IB, Pappas D, Matveev OI, Smith BW (2000) *J Anal At Spectrom* 15:1161–1189
8. Cremers DA (1987) *Appl Spectrosc* 41:572–579
9. Davies CM, Telle HH, Montgomery DJ, Corbett RE (1995) *Spectrom Chim Acta B* 50:1059–1075
10. Lorenzen CL, Carlhoff C, Hahn U, Jogwich M (1992) *J Anal Atom Spectrom* 7:1029–1035
11. Palanco S, Cabalin LM, Romero D, Laserna JJ (1999) *J Anal At Spectrom* 14:1883–1887
12. Gonzalez A, Ortiz M, Campos J (1995) *Appl Spectrosc* 49:1632–1635
13. Aguilera JA, Aragón C, Campos J (1992) *Appl Spectrosc* 46:1382–1387
14. Aguilera JA, Aragón C, Campos J (1993) *Appl Spectrosc* 47:606–608
15. W.E. Ernst WE, D. F. Farson DF, Sames DJ (1996) *Appl Spectrosc* 50:306–309
16. Aguilera JA, Aragon C, Peñalba F (1999) *Appl Spectrosc* 53:1259–1267
17. Cabalin LM, Romero D, Baena JM, Laserna JJ (1999) *Frese-nius J Anal Chem* 365:404–408
18. Cabalin LM, Romero D, Baena JM, Laserna JJ (1999) *Surf In-terface Anal* 27:805–810
19. Mao X, Chan WT, Russo RE (1997) *Appl Spectrosc* 51:1047–1054
20. Thiem TL, Salter RH, Gardner JA, Lee YI, Sneddon J (1994) *Appl Spectrosc* 48:58–64
21. Sturm V, Peter L, Noll R (2000) *Appl Spectrosc* 54:1275–1278
22. St-Onge L, Sabsabi M, Cielo P (1998) *Spectrochim Acta B* 53:407–415
23. Sattmann R, Sturm V, Noll R (1995) *J Phys D: Appl Phys* 28:2181–2187
24. Strakis DN, Eland KL, Angel SM (2000) *Appl Spectrosc* 54:1270–1274
25. Ciucci A, Corsi M, Palleschi V, Salvatti A, Tognoni E (1999) *Appl Spectrosc* 53:960–964
26. Chaléard C, Mauchien P, Andre N, Uebbing J, Lacour JL, Geertsen C (1997) *J Anal At Spectrom* 12:183–188
27. Noll R, Peter L, Mönch I, Sturm V (1998) in *Proc 5th Int Conf Progress in Analytical Chemistry in the Steel and Metals In-dustries*. Office for Official Publications of the European Com-munities, L2985 Luxembourg, p 345
28. Gornushkin IB, Smith BW, Nasajpour H, Winefordner JD (1999) *Anal Chem* 71:5157–5164
29. Palanco S, Laserna JJ (2000) *J Anal At Spectrom* 15:1321–1327
30. Nemet B, Kozma L (1995) *J Anal At Spectrom* 10:631–636
31. Boumans PWJM (1991) *Spectrochim Acta B* 46:431–445