Determination of Major and Trace Elements in Alloy Steels by Nanosecond and Femtosecond Laser Ablation ICP-MS with Non-matrix-matched Calibration

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ABSTRACT: Accurate elemental analysis of alloy steels is a prerequisite for providing high-quality product assurance. This study investigates the quantification capabilities of three laser systems: 257-nm femtosecond (300 fs), 213-nm Nd:YAG (3 ns), and 193-nm ArF* excimer (15 ns) lasers coupled with inductively coupled plasma mass spectrometry for the determination of major and trace elements in alloy steels. The results demonstrate that under typical operating conditions, the signal intensity of the 257-nm femtosecond (fs) laser system is approximately 10 and 3.6 times higher in comparison to the 193-nm ArF excimer and 213-nm Nd:YAG nanosecond (ns) lasers, respectively. The transient signals of the fs-laser also demonstrate greater stability compared to the ns-laser. In addition, significant differences in melting and elemental fractionation were observed among the three laser-ablation (LA) systems, with the highest observed for the 193-nm ns-LA. In contrast, calculated Fe-normalized elemental fractionation indices are close to 1 for most elements, and no significant melting was observed when employing the 257-nm fs-LA. In this work, internal standardization using ⁵⁷Fe and 100% normalization-calibration strategy were employed in combination with NIST 610 (silicate glass) as a non-matrix-matched external calibration material. The concentrations of the major and trace elements found in alloy-steel samples illustrate that a significant improvement in the analytical results was obtained with fs-LA using non-matrix-matched calibration.

INTRODUCTION

The elemental concentrations in alloy steels have a significant effect on its mechanical properties.¹ Hence, accurate elemental analysis in alloy steels is an essential prerequisite for providing high-quality product assurance. Since the first application of laser ablation sample introduction with ICP-MS by Gray in 1985,² laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has evolved as a powerful technique for the direct determination of trace element concentrations

and isotope ratios in various solid materials.^{3–10} The most striking features of LA-ICP-MS include high sensitivity, high spatial resolution, small sample size requirements, few sample preparation procedures, and rapid throughput, all of which facilitate the simultaneous acquisition of major and trace elements.^{6, 8, 11–13}

However, a major limitation of this technology is due to the occurrence of elemental fractionation, which represents the sum of all non-stoichiometric effects observed during ablation, transport, and ionization within

the ICP source. Therefore, matrix-matched calibration is often performed to compensate for this deficit. Unfortunately, the lack of suitable homogeneous standard reference materials has become a serious restriction for many matrices, especially with regard to alloy-steel samples, which are influenced by the metallurgical properties of the elements during manufacturing.^{14,15} Only a few studies have been performed for the quantitative analysis of major and trace elements in metallic samples using nanosecond (ns) LA-ICP-MS due to significant elemental fractionation.^{16,17} The application of ns-pulsed LA promotes the generation of a “heat-affected zone”, which is more problematic in metals owing to thermal diffusion into the target structure.^{18–20} Consequently, preferential vaporization of different elements can be observed within ablated metallic materials.²¹ To reduce these effects, the laser-pulse duration time needs to be shortened to less than the material-specific thermal relaxation time (approximately 10^{-13} s for metals).^{22,23}

Fortunately for femtosecond-pulsed ablation, the pulse duration time falls below the thermal relaxation time,^{19, 23–25} and the fs-LA process is significantly less thermal, even in metallic samples which have high thermal diffusivity.¹⁹ Moreover, compared to ns-LA, aerosols produced by fs-LA laser ablation consist of smaller particles in alloy samples,²⁶ unalloyed steel,²⁷ and glass.²⁸ Thus, aerosols produced by fs-LA demonstrate the potential to eliminate elemental fractionation and produce stoichiometric aerosols.^{28–30} For example, Horn *et al.*³¹ reported no elemental and isotopic fractionation in a

variety of matrices by utilization of ultraviolet fs-LA-MC-ICP-MS. Elimination of fractionation and matrix effects in fs-LA-ICP-MS can lead to improvement in analytical accuracy³² and produce non-matrix-matched calibrations successfully.^{33–35} In the case of metal and alloy samples, the use of ultraviolet fs pulses improved the accuracy and precision for the analysis of Pb compared with nanosecond laser ablation.²⁶ As reported by Bian *et al.*³⁶, using near-infrared fs-LA-ICP-MS in combination with non-matrix-matched standard reference materials, major and minor concentrations of Zn and Cu can be measured in metallic and dielectric standards. Možná *et al.*²⁷ employed non-matrix-matched calibration for the analysis of Fe-based samples using ultraviolet (265-nm) fs-LA. However, the concentrations of only a small number of elements (Al, Si, P, Cr, Mn, Fe, Ni, Cu, and Mo) were reported in their study. Wiltse *et al.*¹⁴ investigated the capabilities of infrared (795-nm) fs-LA-ICP-MS for the quantitative analysis of major, minor, and trace elements in steels and super alloys with both matrix- and non-matrix-matched standard calibrations using Cr, V, or Mn as the internal standard. However, the concentration of the internal standard should be homogeneous in the alloy steels and must be established from other sampling techniques prior to LA-ICP-MS analysis.¹⁴ To overcome this limitation, the calibration method based on 100 wt.% normalization of all elements was successfully applied for the LA-ICP-MS analysis of minerals (*e.g.*, silicates).¹² However, this 100% normalization method has to our knowledge never been employed for alloy-steel analyses.

Table 1. Summary of operating conditions for LA-ICP-MS measurements

Laser ablation system				ICP-MS	
Wavelength (nm)	193	213	257	Manufacturer	Agilent 7500a
Pulse length (ns)	15	3	0.3	RF power (W)	1350
Energy density (J/cm ²)	5.1–14.5	3.5–12.1	1.2–3.9	Plasma gas flow rate (L min ⁻¹)	15.0
Repetition rate (Hz)	6	6	6	Isotopes measured	¹¹ B, ²⁷ Al, ²⁹ Si, ³¹ P, ⁴⁹ Ti, ⁵¹ V, ⁵² Cr, ⁵⁵ Mn, ⁵⁷ Fe, ⁵⁹ Co, ⁶⁰ Ni, ⁶⁵ Cu, ⁶⁶ Zn, ⁹⁵ Mo, ¹¹⁸ Sn, ¹²¹ Sb, ¹⁸² W, ²⁰⁸ Pb & ²⁰⁹ Bi
Spot size (μm)	44	44	44	Dwell time per isotope (ms)	10
Wavelength (nm)	193	213	257	Detector mode	Dual

This study compares elemental fractionation, the morphologies of ablated craters, aerosol particles, and assesses the quantification capability of LA-ICP-MS analysis of stainless steel and middle-alloy samples using three types of lasers—193-nm ArF excimer (15 ns), 213-nm Nd:YAG (3 ns), and 257-nm Yb laser (300 fs). The same type of ablation cell and ICP-MS, as well as similar operating conditions, were used to avoid ambiguities when comparing the results from different laboratories. Furthermore, both the internal standardization (Fe used as internal standard) and the 100% normalization approach were used for data reduction. The comparison results provide a practical reference on the choice for the determination of the elements in alloy steels.

EXPERIMENTAL

Instruments. The experiments were performed using the Agilent 7500a ICP-MS instrument (Japan) in combination with three different pulse laser systems: an ArF excimer laser ($\lambda = 193$ nm) with 15 ns pulse duration (GeoLas 2005; MicroLas; Germany), a solid-state Nd:YAG laser ($\lambda = 213$ nm) with 3 ns pulse duration, and a Yb fs laser ($\lambda = 257$ nm) with 300 fs pulse duration (NWR-Femto Laser, Elemental Scientific Instruments, USA). Details of the instrumental operating conditions are listed in Table 1. Helium was used as the carrier gas in the ablation cell and merged with argon (make-up gas) behind the ablation cell via a "Y" junction downstream from the ablation cell.^{37,38} The carrier and make-up gas flows were optimized by ablating NIST SRM 610 to obtain the maximum signal intensity for $^{139}\text{La}^+$, while maintaining the ThO^+/Th^+ ratio below 0.3% and the U^+/Th^+ ratio close to 1. Each measurement consists of measuring the background signal (for 20 s), followed by 50 s for ablation of the samples.

Samples. To investigate the suitability of ns and fs LA-ICP-MS for the accurate determination of the elemental concentrations in steel alloys, nine alloy

samples were analyzed. Also used were international alloy steel standard reference materials (SRMs) obtained from the National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA: AISI 4340 Steel (NIST SRM 361), Chromium-Vanadium Steel (NIST SRM 363), and High-Carbon Steel (NIST SRM 364). The other alloy steel standards were obtained from the Central Iron and Steel Research Institute, Beijing, China: Stainless Steel GBW01395, Middle-Alloy (GBW01396, GBW01397, GBW01398, GBW01399 and GBW01400). In addition, Silicate Glass (NIST SRM 610) was used for the non-matrix-matched calibration material, since it is one of the most widely used and best-characterized reference materials for LA-ICP-MS analysis and contains many trace elements with relatively high concentrations (~500 ppm).³⁹ The working values for NIST SRM 610 were taken from Jochum et al.³⁹ and for the alloy steel samples from their certificate, respectively. To avoid oxidation of the alloy samples, all samples were polished using fine sandpaper, then ultrasonically treated in ultrapure alcohol prior to LA-ICP-MS analysis.

RESULTS AND DISCUSSION

Comparison of transient signal intensities. Fig. 1 shows the time-resolved LA-ICP-MS signal intensities of the selected elements (V, Cr, Mn, Fe, Co, Ni, and W) with ablation on an alloy sample (GBW01398) by three laser ablation systems. The laser fluence used in femtosecond laser ablation was about 3 J cm^{-2} , while the fluence used in 213 nm Nd: YAG laser and 193 nm ArF excimer laser was 8 J cm^{-2} and 10 J cm^{-2} , respectively. It can be seen that the signal intensities obtained by fs-LA were much higher than those acquired by using the ns-LA systems, namely 3.6 times greater than with the 213 nm Nd: YAG laser and 10 times larger than with the 193 nm ArF excimer laser, even with ablation at lower laser fluence. This enhanced signal intensity observed in fs-LA can be attributed to the fact that a higher number density of aerosol

Fig. 1 Time-resolved transient signal intensities for LA-ICP-MS ablation of alloy sample (GBW01398) using three laser ablation systems. (a): 193 nm ArF excimer nanosecond laser; (b): 213 nm Nd:YAG nanosecond laser; (c): 257 nm Yb femtosecond laser.

Fig. 2 SEM images of ablation craters obtained from alloy sample (GBW01398). (a) and (d): 193 nm ns-LA, at 10 J cm^{-2} ; (b) and (e): 213 nm ns-LA, at 8 J cm^{-2} ; (c) and (f): 257 nm fs-LA, at 3 J cm^{-2} .

particles ablated on the metallic samples^{26,27,40} and effectively digested in the ICP when employing fs-LA. In addition, Fig. 1 shows that the transient signal produced by fs-LA is more stable and demonstrates minimal spiking. A large number of instantaneous spikes can be observed in the ns-LA systems, especially with the 193-nm ArF excimer laser. This can be attributed to the presence of larger particles within the ICP during ns-pulsed LA compared to fs-LA.⁴¹ This increase in signal intensity and the improvement in signal stability with a decrease in pulse duration of the laser ablation systems indicates that pulse duration plays a significant role in the ablation of metallic samples.

Alloy sample ablation-crater morphology. Fig. 2 shows the scanning electron microscope (SEM) images of the morphology of ablation craters of the GBW01398 alloy-steel sample obtained using the three LA systems in single-spot ablation mode. As can be seen in Fig. 2a and 2d, abundant molten droplets exist around the craters formed with the 193-nm excimer ns-LA, where the large spherical aerosol particles with the tail moving away from the crater rim were deposited (Fig. 2d). These large droplets were formed by liquid ejection and vapor condensation.²⁴ In comparison, less molten ejecta and generation of small spherical droplets were generated with the 213 nm Nd:YAG laser (Fig. 2b and 2e). This could be attributed to the shorter pulse duration of the Nd:YAG laser (3 ns) compared to the 193 nm excimer laser (15 ns), which reduced the thermal effects. As can be observed in Fig. 2c and 2f, rough shaped fine particles were produced by 257 nm fs-LA and an enormous reduction of molten material was observed compared to ns-LA. These results further confirm that the observed degree of melting and ablation-crater morphologies significantly differs when performing ns- and fs-LA. Thermal processes are the dominant mechanisms of ns-LA for alloy steels, while fs-LA is less prone to thermal effects. Multiple sub-craters superimposed on the main ablation pit were observed when performing fs-LA.

This crater morphology was caused by the Gaussian energy distribution within the laser beam.²⁴ Additionally, typical ripple patterns were observed on the fs-LA crater walls, but they were largely erased on that of ns-LA. It can be explained as an effect of the interference between incident light and surface wave.^{22,35, 42–46}

Comparison of elemental fractionation in ns- and fs-LA-ICP-MS. Fig. 3 shows the calculated elemental fractionation indices (FIs) from the ablation of the steel sample (GBW01398) with the three laser ablation systems with different laser energy densities, respectively. The FIs for the investigated isotopes were calculated based on Fe as the internal standard, and 50 s transient signals were divided into equal time intervals, instead of 240 s, as reported by Fryer.⁴⁷ As described in Fig. 3a, the Fe-normalized FIs of most elements obtained with the 193 nm excimer ns-LA showed notable deviations from 1, especially at low laser energy densities. Additionally, it is worth noting that the deviations in calculated elements indicated that the FIs were significantly reduced with a high laser fluence of 10–14 J cm⁻². This is similar to the phenomenon reported by Li et al.³⁵ during ilmenite ablation. The calculated elemental fractionation indices were close to 1, especially when the laser energy densities were above 8.2 J cm⁻² with a 213 nm nanosecond ablation (Fig. 3b). In addition, the calculated elemental fractionation indices with the 257 nm femtosecond laser remain nearly close to 1 with the change of laser fluence from 1.8 J cm⁻² to 4.0 J cm⁻². However, the calculated elemental fractionation indexes of Pb and Bi with fs-LA also showed large deviations. This could be attributed to the heterogeneous distribution of Pb and Bi within the metal matrix, as confirmed by the transient signal intensities of V, Cr, Mn, Fe, Co, Pb, and Bi during fs-LA for the GBW01398 and SRM 364 alloy samples (Fig. 4). Fig. 5 shows the calculated elemental fractionation indices (FIs) from the ablation of nine steel samples using the three laser systems. As described in Fig. 5, the strongest deviation of calculated elemental

Fig. 3 The Fe-normalized fractionation indices obtained via fs- and ns-LA-ICP-MS of alloy sample (GBW01398) in different energy densities. Error bars represent the standard deviation (1 s) from three measurements.

Fig. 4 Time-resolved transient signal intensities for LA-ICP-MS ablation of SRMs using 257 nm fs-LA system. The laser fluence is at 3 J cm⁻². (a): Middle-alloy GBW01398; (b): High-Carbon Steel SRM 364.

Fig. 5 Calculated elemental fractionation indices (FIs) obtained by performing ablation of nine steel samples using three laser systems. (a): 193 nm ArF excimer laser, at 10 J cm^{-2} ; (b): 213 nm Nd:YAG laser, at 8 J cm^{-2} ; (c): 257 nm fs-laser, at 3 J cm^{-2} . Error bars represent the standard deviation (1 s) from three measurements.

Fig. 6 Relative deviations of average concentrations ($n = 11$) of nine alloy samples with respect to reference values calibrated against NIST SRM 60 and Fe as the internal standard. (a): 193 nm ArF excimer laser, 10 J cm^{-2} ; (b): 213 nm ns-LA, 8 J cm^{-2} ; (c): 257 nm fs-laser, 3 J cm^{-2} .

fractionation indices values from unity were observed during 193-nm ns-LA, whereas the 213-nm ns-LA demonstrated comparatively smaller deviations. With the application of 257-nm fs-LA, the calculated elemental fractionation indices closely approximated unity for most elements (Fig. 5c). The degree of elemental fractionation observed when employing the three laser systems was in good agreement with the corresponding melting effects as shown in Fig. 2. This implies that the pulse durations of the laser systems have a pronounced impact on the melting and fractionation of the metal samples.

Capability of non-matrix-matched calibration using three laser systems--Analysis of alloy steels using NIST 610 as reference material and Fe as internal standard. To investigate the non-matrix-matched calibration capabilities of ns- and fs-LA-ICP-MS for the quantification of alloy steel samples, the major and trace elements were determined using NIST SRM 610 as an external reference material. In addition, Fe was used as an internal standard to correct the mass bias and ablation yield between the reference material and the metal samples. Fig. 6 and Table S1 demonstrate relative deviations between the average concentrations ($n = 11$) determined in the nine alloy samples and the reference values. As can be observed in Fig. 6a, large discrepancies in relative deviations of most elements were observed using the 193 nm excimer laser ablation. The deviations of the measured contents from reference values were found in the range between 10–80%. An improved accuracy was observed when applying the 213-nm Nd:YAG ns-LA, where the relative deviations of the transition-metal elements (V, Cr, Mn, Co, Ni, and Cu) were within a 20% uncertainty for most alloy-steel samples. However, obvious discrepancies were observed for some elements (e.g., Al, Zn, Sn, Sb, Bi, and Pb). When performing fs-LA, the agreement between measured data and reference values was significantly better compared to that observed for both the 193-nm excimer and the 213-nm Nd:YAG ns-LA. As illustrated in

Fig. 7 Relative deviations in average concentrations ($n = 11$) of nine selected alloy samples with respect to reference values calibrated against NIST SRM 60 and 100% normalization calibration strategy by using (a): 193 nm ns-laser; (b): 213 nm ns-laser; (c): 257 nm fs-laser.

Fig. 5c, the relative deviations between observed data and reference values remained within 20% for most elements. The large deviations for Bi and Pb could be attributed to their heterogeneous distribution in alloy-steel samples (Fig. 4). Additionally, a dramatic systematic bias of the volatile element Zn was observed during both 193-nm and 213 nm ns-LAs, whereas an obvious improvement in Zn detection accuracy was observed when performing fs-LA. This may be attributed to the reduced thermal melting and elemental fractionation during fs-LA. The results presented here indicate that accuracy and precision were improved by using shorter laser pulse durations with NIST 610 Glass as the external standard and Fe as the internal standard.

Capability of non-matrix-matched calibration using three laser systems using NIST 610 as reference material and 100% normalization calibration. The concentration of the element used as the internal standard must be known a priori or determined using an

independent method prior to performing LA-ICP-MS analysis. Fortunately, the 100 wt.% normalization calibration method is a great improvement with ICP-MS elemental analysis. Fig. 7 and Table S2 show the calibrated results of steel alloy by applying 100% normalization in combination with NIST SRM 610 as the external reference material for both ns-LA and fs-LA. As can be seen, the relative deviations for most elements usually exceed 20% when performing 193-nm excimer and 213-nm Nd:YAG ns LA-ICP-MS. In contrast, use of the fs-LA-ICP-MS results in comparatively higher accuracy. When employing fs-LA, the measured values of most elements demonstrated good agreement (with 20 % uncertainty) with corresponding certified values. Additionally, the results obtained were comparable to those obtained using Fe as the internal standard (Fig. 7c). This indicates that using NIST SRM 610 as an external reference material in combination with the 100% normalization calibration strategy is also suitable for fs-LA-ICP-MS-based multi-element analysis of alloy steels.

CONCLUSIONS

The proposed study investigates the capabilities of ns-LA-ICP-MS (193-nm ArF and 213-nm Nd:YAG lasers) and fs-LA-ICP-MS (257-nm Yb laser) for the quantitative analysis of major and trace elements in alloy steels. As observed, the highest signal intensities and most stable signals were obtained during fs-LA-ICP-MS analysis, thereby demonstrating that the pulse duration of laser systems plays a significant role in melting and elemental fractionation of the metal samples. The strongest, intermediate, and non-significant melting phenomena were observed when applying the 193-nm ns-LA, 213-nm ns-LA, and 257-nm fs-LA, respectively. Consequently, minimum elemental fractionation was observed when using fs-LA. In addition, the quantitative analysis of the alloy-steel samples indicated that improved accuracy and precision were achieved using

shorter laser pulse durations by calibration with SRM NIST 610 Silicate Glass in combination with internal standard calibration or the 100% normalization calibration strategy. The use of fs-pulsed lasers provides much higher accuracy compared to ns-pulsed lasers when employing non-matrix-matched standards. The determined values of most elements found for the alloy-steel samples demonstrates good agreement with reference values and within a 20% uncertainty when employing fs-LA-ICP-MS with non-matrix-matched calibration.

ASSOCIATED CONTENT

Supporting Information

Please contact the corresponding author for Supporting Information. [Table S1](#): Element concentrations for alloy steels obtained by using NIST 610 as an external standard and Fe as an internal standard with LA-ICP-MS analysis; [Table S2](#): Element concentrations for alloy steels obtained by using NIST 610 as an external standard and 100% normalization calibration with LA-ICP-MS analysis.

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Notes

The authors declare no competing financial interest.

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