Direct Determination of Trace Elements in Steel by Laser Ablation/ICP-MS[†]

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Abstract:

Elemental fractionation (non-stoichiometric generation of vapor species) can be canceled with repeated laser irradiation in an adequate area without vacant space by a developed laser ablation (LA) system. Particles generated with this system were induced to inductively coupled plasma mass spectrometry (ICP-MS) for quantitative determination of trace elements (B, As, Sb, Pb) in steel samples. Analytical performance of the developed LA-ICP-MS was investigated with standard reference materials of iron. The analytical results showed that this method has sufficient precision, sensitivity and accuracy for the analysis of steel samples in the µg/g level concentration of trace elements. This system can reduce much time for the determination of trace elements compared with solution ICP-MS or electrothermal vaporization atomic absorption spectrometry.

1. Introduction

Diverse techniques ranging from instrumental analyses, such as spark discharge emission spectrography and X-ray fluorescence analysis, to wet chemical analyses such as titration are used in performing steel analyses. In general, high sensitivity and rapid analysis time are mutually exclusive, and the appropriate methods need to be chosen to best meet the purpose and necessity. For example, instrumental analyses capable of directly analyzing solid samples are widely used as process management analyses in the manufacturing processes of metals because of excellent rapidity. However, because instrumental analyses lack sensitivity for analyses of trace elements, inductively coupled plasma mass spectrometry (ICP-MS) and electro-thermal vaporization/cold vapor atomic absorption spectrometry are used in performing analyses requiring higher sensitivity. On the other hand, these analysis methods are slow because sample solutions are handled and it is necessary to melt solid samples. In order to simultaneously meet the two needs for high sensitivity and rapidity that are demanded at manufacturing locations, it is necessary to use new engineering elements and the laser ablation (LA) method is attracting attention as one such new engineering element.

In the LA method, a solid sample is directly irradiated with laser beams and part of the sample is ablated into fine particles instead of being dissolved into a sample solution. Because vaporized fine particles thus generated are transferred to an analyzer and can be instantaneously analyzed, the time required by pretreatment can be substantially shortened compared to when a sample is dissolved into a sample solution. Since the study by Gray[1], many reports have been made[2,3] on LA-ICP-MS, in which LA is applied to ICP-MS. Problems that have been known for a long time include (1) the fractionation problem where the generated fine particles and base material samples have different chemical compositions[4] and (2) the problem of the quantity and stability of vaporized fine particles. In recent years, it has become apparent that the excitation efficiency of plasmas differs depending on the size of the generated fine particles[5]. To solve these problems, many studies on energy irradiation means, including the kinds of lasers, have been reported on and particularly recently, there have also been many reports on the effectiveness of LA in which a short-wavelength laser is used[6–10]. However, there is scarcely

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any example in which these methods are applied to the analyses of trace components in steel at or below μg/g level.

At JFE Steel, the development of a laser ICP atomic emission spectrometry was carried out in 1987 and this analysis method was applied to uses such as component analysis and defect analysis[11]. The basic principle of this method is a JFE-specific engineering element called "repeated laser irradiation to the same area," which is characterized by a beam scanning method. That is, an LA system that generates fine particles whose composition is the same as that of the base material sample was developed by combining a pulse laser having a high repetitive frequency and a galvanometer scanner. Also for LA-ICP-MS, in which this LA is applied to ICP-MS, its applicability to many elements was verified and the basic characteristics of LA-ICP-MS was reported on[12]. This time, an examination was made into the application of LA-ICP-MS to the four elements B, As, Sb, and Pb, for which analyses in trace amounts are required in terms of work processes from the standpoints of quality, environment and the like at steel works, and a method was developed capable of the quantitative determination of these trace elements in steel with high precision up to an infinitesimal concentration region of at or below the μg/g level.

2. Experiment

2.1 Apparatus

(1) Laser Ablation System

An outline of the system is shown in **Fig. 1**. An Nd:YVO4 laser of the Q-switched type capable of oscillating with a maximum average output of 10 W at a pulse frequency of 50 kHz (wavelength: 1 064 nm, T40-Z20-106Q, made by Spectra-Physics, Inc.) was used as the system laser. The output of the laser was controlled by the electric current applied to the laser diode within the laser and the power measured by a power meter (TPM300CE made by Gentec Electro-Optics, Inc.). An optical system of beam irra-
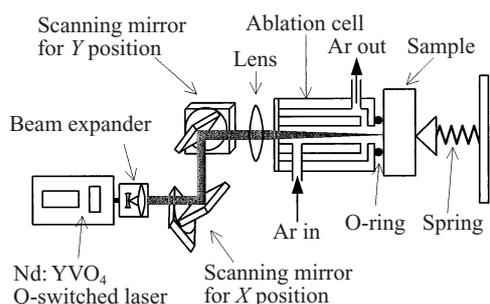
diation, which is composed of a beam expander, two galvanometer scanners (M2S made by GSI Group.) and a condenser lens, was adjusted so that the spot diameter of the laser became 50 μm or less. The ablation cell is of a coaxial double tube construction; a quartz window for transmission is installed on the incoming side of the laser light and an opening is provided on the opposite side. Ar gas for transferring vaporized fine particles is introduced from the window side of the inner tube and discharged from an opening of the outer tube. A sample is set in the opening via an O-ring.

(2) ICP-MS

A VG PQ ExCell (made by Thermo Electron K.K) was used. NIST SRM 1765 (a low-alloy steel, Co = 0.006%: reference value, NIST: National Institute of Standards and Technology, SRM: Standard Reference Materials) was used for the analysis of LA samples and the sensitivity was adjusted by using ^{59}Co.

2.2 Experimental Method

2.2.1 Measurements by LA-ICP-MS

Sample surfaces were polished using a zirconium-based abrasive belt (Z76X, grain size: 60, made by Riken Corundum Co., Ltd.). The laser pre-irradiation time was set at 30 s, the total integration time per ion was set at 3 s, and the cleaning time after the finish of an analysis was set at 30 s. The analytic conditions are shown in **Table 1**. The analytical performance of LA-ICP-MS was investigated using the steel standard reference materials shown in **Table 2**. Although in high boiling point components such as Mo and W, it is necessary to set the laser pre-irradiation time at 120 s or so, sufficient analysis precision could be obtained with 30 s for the four elements analyzed this time.

2.2.2 Chemical analyses of steel samples

Chips were sampled from the steel standard reference materials and after the acidolysis of the samples, B was analyzed by solvent extraction/curcumin absorptiometry and the other elements were analyzed by electrothermal vaporization AAS.

3. Experimental Theory[12]

When the output of a laser that radiates beams on a sample, is not so large as to cause a breakdown, the energy of the laser is converted into thermal energy. Because thermal characteristics differ from element to element, the composition of a vaporized substance is not the same as that of the original sample. This non-uniformity is an unavoidable phenomenon. However,

Fig.1[12] Schematic diagram of the developed LA system

Table 1 Apparatus and analytical conditions for the developed LA-ICP-MS

Laser ablation	
Laser	Nd: YVO$_4$
Wavelength	1 064 mm
Average power	0.6 W
Pulse frequency	10 kHz
Pulse width	10 ns
Beam expander	× 5
Focal length	100 mm
Spot diameter	50 μm
X-scan length	2.0 mm
Y-scan length	2.0 mm
X-scan frequency	43 Hz
Y-scan frequency	2.5 Hz
Ar flow	1.0 l/min
Diameter of O-ring	22 mm
ICP	
Coolant gas flow	12 l/min
Auxiliary gas flow	1.0 l/min
RF power	1.4 kW
Carrier gas flow (for solution analysis)	0.4 l/min
Mass spectrometer	
Dwell time	10 ms/channel
Channels per mass	3
Sweeps	100
Laser pre-irradiation	30 s
Cleaning	30 s
Monitor for tuning	
Solution-ICP-MS	In (1 ng/ml)
LA-ICP-MS	Co (NIST 1765)

Table 2 Composition of NIST, Brammer and JSS SRM samples

Sample	B	As	Sb	Pb
(a)				
NIST 1765	0.000 9	0.001 0	0.001 0	0.000 3
NIST 1766	0.000 4	0.003 5	0.000 5	0.003
NIST 1767	0.001 0	0.000 5	0.002 0	<0.000 1*
(b)				
BS61C	0.000 05**			
NIST 1265a	0.000 13			
NIST 1261a	0.000 5			
BCS/SS 112	0.000 7			
NIST 1767	0.001 0			
(c)				
BS 250		0.003	0.000 4	
NIST 1768	<0.000 2*	<0.000 1*	<0.000 1*	<0.000 1*
JSS 1000-1	0.000 02*	<0.000 2*	<0.000 02*	<0.000 01*
(d)				
NIST 1265a	0.000 13	0.000 2*		0.000 01
BS 250		0.003	0.000 4	
BS 3941		0.003	0.000 7*	0.001 0
BS 61C	0.000 05**	0.003	0.000 4	0.000 03
BS 61D	0.000 4	0.005		0.000 3
BCS/SS 112	0.000 7	0.002 1		
ECRM 097-1D	0.000 3	0.051		

   * Not certified but informed value
** Analytical value by conventional method

if thermal irradiation is repeated on the same area of a sample, this non-uniformity will be gradually eliminated.

For the sake of simplicity, the following assumptions are made. (1) The heated area is large enough to be able to neglect the effect of a side area (an area which is formed around a crater due to the pressure of the vapor generated during laser irradiation and in which a melted part deposits); and (2) during laser irradiation, the irradiation with thermal energy is uniformly performed in terms of time and place.

A sample initially consists of an element, S and a matrix element, m.

$C_S(0)$ is the initial concentration of S in a solid.

$$C_S(0) = X_0/V_0 \cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where V_0 is the quantity of the thermally-affected zone in the solid (= a vaporized part V_v + a melted part V_m), and X_0 is the quantity of the component to be analyzed S

in V_0.

The vaporized part and the melted part are generated by the first irradiation. That is, X_0 is divided into X_v and X_m. X_0 is the quantity of the component to be analyzed S in the vaporized part V_v and X_m is the quantity of the component to be analyzed S in the melted part V_m. The value of X_v/V_v differs from $C_S(0)$ because fractionation occurs. Therefore, the fractionation coefficient, f defines the degree of non-uniformity.

$$f = (X_v/V_v)(X_0/V_0) \cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

The difference of the vaporized quantity from the original quantity remains in the melted part.

$$f = X_0 - X_v = X_0 \cdot (1 - f \cdot V_v/V_0) \cdots\cdots\cdots (3)$$

Because the thermal energy that is given is constant, the same quantity as in the first radiation is thermally affected also in the second laser irradiation. That is, in addition to the quantity of the melted part V_m that remained after the first laser irradiation, a quantity corresponding to the vaporized quantity V_v in the base material not previously thermally affected is newly thermally affected. The quantity of the element $X_0(2)$ present

in the new thermally-affected zone due to this second laser irradiation is given by the following equation:

$$X_0(2) = X_m(1) + C_S(0) \cdot V_v$$
$$= X_0(1) \cdot (1 - f \cdot V_v/V_0) + X_0(0) \cdot V_v/V_0 \cdots\cdots(4)$$

Hence, the quantity of X that is vaporized, $X_v(2)$, and the quantity that remains in the melted part, $X_m(2)$, are respectively given as follows:

$$X_v(2) = f \cdot X_0(2) \cdot V_v/V_0 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(5)$$

$$X_m(2) = X_0(2) - X_v(2) = X_0(2) \cdot (1 - f \cdot V_v/V_0)$$
$$= X_0(1) \cdot (1 - f \cdot V_v/V_0)^2 + X_0(0) \cdot V_v/V_0(1 - V_v/V_0)$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(6)$$

When the inductive method is adopted, the quantity of the element S that is affected by the $(n + 1)$th laser irradiation, $X_0(n + 1)$, is given as follows:

$$X_0(n + 1) = X_m(n) + C_S(0) \cdot V_v$$

$$= X_0(1) \cdot (1 - f \cdot V_v/V_0)^n + X_0(0) \cdot V_v/V_0 \cdot \sum_{k=0}^{n-1}(1 - f \cdot V_v/V_0)^k$$

$$= X_0(1) \cdot (1 - f \cdot V_v/V_0)^n$$
$$+ X_0(0) \cdot V_v/V_0 \cdot \{1 - (1 - f \cdot V_v/V_0)^n\}/(f \cdot V_v/V_0) \cdots\cdots(7)$$

$$X_v(n + 1) = f \cdot X_0(n + 1) \cdot V_v/V_0$$
$$= X_0(1) \cdot (1 - f \cdot V_v/V_0)^n \cdot f \cdot V_v/V_0$$
$$+ X_0(0) \cdot V_v/V_0 \cdot \{1 - (1 - f \cdot V_v/V_0)^n\} \cdots\cdots\cdots(8)$$

Because $|(1 - fV_v/V_0)| = |1 - Xv/X_0| < 1$, $(1 - fV_v/V_0)^n$ approaches 0 as n increases. Therefore, $X_v(n + 1)$ can be approximated to $X_0(0) \cdot V_v/V_0$. It follows that the fractionation coefficient, f converges gradually to 1 as thermal irradiation is repeated.

The above equations hold only when a region, in which a melted part remaining after laser irradiation, and a base material that has not been thermally affected, coexist, is subjected to the next laser irradiation. On the other hand, in the case where laser irradiation is repeated on a sample surface in a dotted manner or linearly, almost all the melted part deposits surround a crater due to the vapor pressure generated by vaporization. At this time, regions where melted part and base material coexist rarely occur and the above equations do not hold. In contrast to this, in the case where a laser performs two-dimensional laser scanning in a planar manner without any vacant regions, all the in-plane area provides a region in which a melted part and a base material coexist. A melted part is present also around a planar crater. However, by ensuring that a region sufficiently wide for the spot diameter of the laser is scanned, the effect of any side area where melted part deposits exist can be substantially neglected and the above equations hold.

On the other hand, in order to ensure that all substances are vaporized, it is necessary that the heated spot reach to a sufficiently high temperature of 6 000 K or more. If the temperature is low, the irradiated surface with repeated laser irradiation becomes covered with components that are not vaporized, and eventually comes to a state that is not ablated.

From the foregoing, the authors thought that it is possible to eliminate fractionation in LA by irradiating a sufficiently wide region by a pulse laser having an appropriate output repeatedly and without a vacant space. As a result of thermal conductivity simulation, it could be estimated that an appropriate laser output for steel materials is several megawatts per millimeter square or so when the pulse width is 10 ns. If laser irradiation of an area of 1 square millimeter or more is performed when the focused area of a laser on a sample surface is 50 μmΦ, the region that overflows to the side area becomes not more than 5% of the region which is vaporized and it is possible to consider this region to be sufficiently wide.

4. Results and Discussion

4.1 Investigation of Stability of Ion Intensity

Changes with time in ^{57}Fe ion intensity obtained by the developed LA-1CP-MS are shown in **Fig. 2** compared with the results of a solution analysis method. Each of the data was sampled for each 25 ms by integrating the ion intensity of ^{57}Fe for 10 ms. When the scanning conditions of the laser spot were inappropriate, the variations and waviness became large. Owing to the use of the galvanometer scanners and a control system of very good position control capability and the optimization of conditions such as scanning speed, the dispersion of ion intensity in LA-ICP-MS became 2.4% as a relative standard deviation (RSD) and almost reaches the stability as in the solution analysis method.
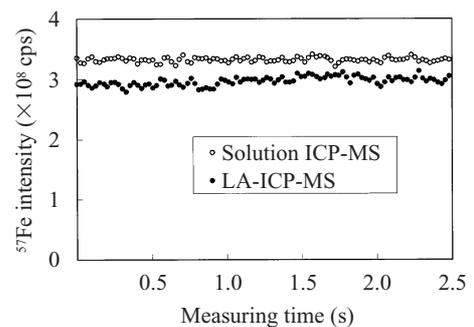

Fig.2[12]) Intensity-time profile of ^{57}Fe measured by the developed LA-ICP-MS compared with solution ICP-MS

4.2 Precision and Sensitivity of LA-ICP-MS

To verify the analytical precision and sensitivity of LA-ICP-MS for steel samples, the correlation between the contents and ion intensities or intensity ratios of each element to ^{57}Fe was investigated using the steel standard reference materials NIST 1765, 1766 and 1767 (Table 2(a)). The results of the investigation are shown in **Fig. 3**. In the LA method, the ion intensity of Ar gas was used as a blank value, and the intensity ratio was found after the subtraction of the ion intensity of the Ar gas for each sample from the ion intensities of the elements to be analyzed and of ^{57}Fe. Although the repetitive analytical precision is indicated by an error bar (1σ, $n = 5$) in Fig. 3, the ion intensity ratio to Fe showed a smaller dispersion and the Fe internal standard method was effective.

For B, the coefficient of correlation between the concentration and ion intensity ratio in the trace concentration region of 4 to 10 μg/g was 0.999 3 and a good linear relationship was thus obtained. RSD of 4% or less were obtained in the ion intensity ratio to ^{57}Fe, although some samples showed variations of 6% in RSD for ion intensity.

For As, the coefficient of correlation was 0.999 1 in the region of 5 to 40 μg/g and the RSD of the ion intensity ratio was 2% or less.

For Sb, the coefficient of correlation between the certified value in the region of 5 to 20 μg/g and ion intensity ratio was 0.989 and the linear relationship was somewhat poor compared to the other elements, although the repetitive measurement precision of the ion

O: Ion intensity
●: Intensity ratio to ^{57}Fe

Fig.3[12)] Correlation between contents and ion intensities or intensity ratios of each element to ^{57}Fe

Table 3 Lower limits of determination in steel by LA-ICP-MS

(μg/g)

Element	LLD of LA-ICP-MS
B	0.06
As	0.02
Sb	0.004
Pb	0.005

intensity ratio was 2%, which is good in terms of RSD. However, when chips were taken from block samples, and the analytical values were found from electro-thermal vaporization AAS after the dissolution of the chips in an acid, and the analytical values were plotted as abscissa, the coefficient of correlation improved to 0.996. Thus, a linear relationship that substantially intersects the origin was obtained.

For Pb, both the linear relationship of the correlation curve in the range of 1 to 30 μg/g (the coefficient of correlation: 0.999 4) and the repetitive analytical precision (RSD < 2%) were good.

The lower limit of determination of each element was calculated. The samples prepared as high-purity irons, which are shown in Table 2(c), were analyzed by using the correlation shown in Fig. 3 as the calibration curve, and a value that is ten times as high as the standard deviation (10σ) was regarded as the lower limit of determination. The steel standard reference materials BS 250 for B, NIST 1768 for Sb and JSS 1000-1 for As and Pb were used as low-concentration samples for calculating the lower limits of determination. The results are shown in **Table 3**. It became apparent that the determination is possible with high sensitivities, which are on the level of several tens of nanograms/g for B and As and several nanograms/g for Sb and Pb. Furthermore, it can be said that in LA-ICP-MS, to prevent the effect of the pollution by acids for decompose and from the environment, the ion intensity during blank determination and the background intensity due to the generation of molecular ions ascribable to water are low compared to solution samples dissolved in an acid, making it possible to analyze trace components with high sensitivity.

4.3 Accuracy of Analytical Values in LA-ICP-MS

In order to verify the accuracy of the analyses of trace elements in steel by this method, steel standard reference materials were analyzed. The samples shown in Table 2(d) were determined by using the calibration curves prepared in section 4.2 above. The results are shown in **Fig. 4**. Incidentally, it might be thought that some certified values would have large dispersions during the analysis for the determination of the certified values and lack effective values for the verification of
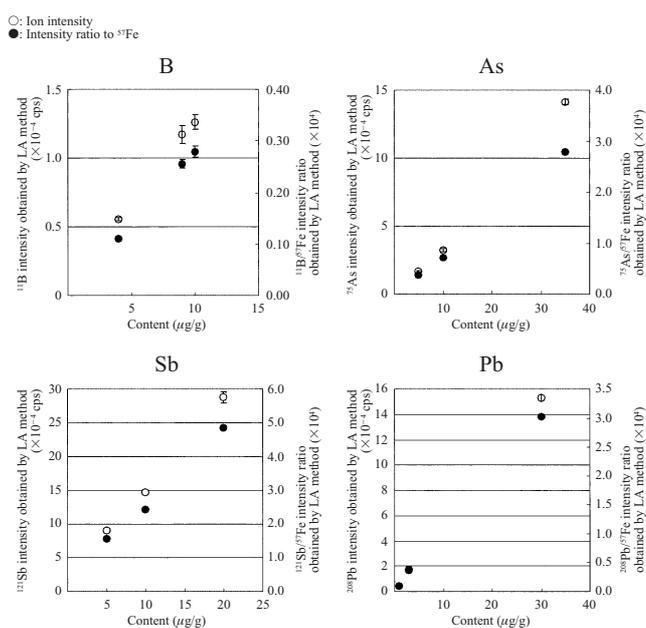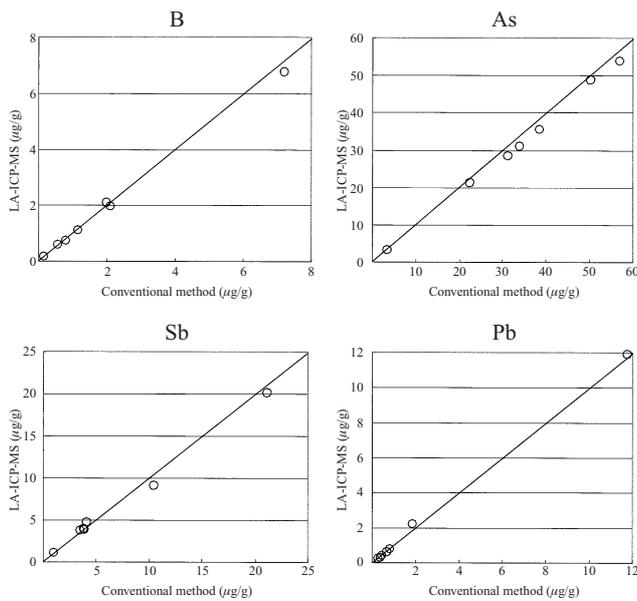
Fig.4[12) Correlation of analytical value between conventional method and LA-ICP-MS

the accuracy of the LA method with respect to the determination and analysis on the order of μg/g. For this reason, the samples used in the LA method were chemically analyzed by the method described in paragraph 2.2.2 above, the analytical values were plotted as abscissa, and the correlation to these values was found.

In all of the elements, a good correlation of 0.995 or more in terms of the coefficient of correlation was observed between the two kinds of analytical values. This shows that the direct determination by this method is possible for elements that have hitherto been determined after the dissolution of samples in an acid. The value of σ_d obtained was 0.2 μg/g for B and Pb, 1.4 μg/g for As, and 0.7 μg/g for Sb. Although the values σ_d of As and Sb were large compared to those of B and Pb, this is because the concentration range differs and it can be judged that for all of the elements, an accurate analysis is possible in trace concentration regions.

4.4 Evaluation of Practicality of Boron Analysis

Among the four elements, the analysis of trace amounts of B requires the longest time to perform. Particularly in the region of infinitesimal amounts of 2 μg/g or less, it is necessary to perform the separation of B by its distillation from other components. This preparation requires half a day or a whole day. With direct analysis by LA-ICP-MS, the measuring time is only a minute or so for each sample, and it is possible to complete the analysis within 1 h, including the time required for pretreatment (polishing work) to obtain a smooth surface and the preparation of calibration curves. Therefore, the direct analysis by LA-ICP-MS can contribute greatly to the shortening of the analysis time if satisfactory analytical precision can be obtained. Accordingly, the analysis

precision of the LA method was compared with the tolerance of repeatability described in "curcumin absorptiometry by distillation and separation in methyl borate" in accordance with JIS G 1227, "Iron and Steel-Methods for Determination of Boron Content." The results are shown in **Table 4**. For the precision of the LA method, the difference R, in the analytical value obtained when the same sample is repeatedly analyzed was twice at a short interval as was shown.

Values below the tolerance are obtained at or below the 5 μg/g level, whereas R is larger than the tolerance in the concentrations of 0.5 μg/g and 1.3 μg/g. In the sample having a concentration of 1.3 μg/g, the dispersion is larger than in the sample of 10 μg/g and it might be thought that there is a possibility that B exists nonuniformly within the sample. For this reason, a trial was made to reduce the effect of segregation by increasing the area through which beams are caused to scan to 4 times the usual area (4 mm $\times$ 4 mm). The results are also shown in Table 4. Incidentally, in order to realize the method of eliminating fractionation described in section 3 above, also the laser pre-irradiation time was increased to 120 s, four times as long as the usual pre-radiation time. For all of the samples shown in this table, good precisions were obtained compared to samples under the usual analytic conditions. Particularly in the sample of 1.3 μg/g, R could be reduced to 1/6 and almost the same precision as the tolerance of repeatability (that is shown in JIS G 1227) was obtained.

When a comparison is made in terms of the representativeness of samples between curcumin absorptionometry and the LA-ICP-MS method, it is found that the former uses a sample of 0.5 g (0.1 g is allowed on the level of 10 μg/g) as an object of analysis, whereas the amount of an object of analysis that is calculated from the fine particle generation rate and the integration time of ICP-MS is 1.5 μg or so. That is, because in some ways with laser irradiation, only a small part of the region of a sample is analyzed, it might be thought that it is necessary to optimize the analytic conditions when elements that are apt undergo segregation are analyzed.

Table 4 Comparison of repeatability between conventional method and LA-ICP-MS

B concentration (μg/g)	Repeatability (μg/g)		
	JIS G 1227	LA-ICP-MS	
		2 mm $\times$ 2 mm	4 mm $\times$ 4 mm
0.5	0.01	0.02	0.01
1.3	0.04	0.42	0.07
5	0.31	0.17	0.07
7	0.51	0.25	0.11
10	0.85	0.33	0.17

5. Conclusions

A technique for rapidly determining levels of trace elements in steel with high sensitivity was developed by introducing fine particles generated by the "repeated laser irradiation to the same area" that reduces the effect of fractionation into ICP-MS, which is a high-sensitivity technique. Particularly for B, As, Sb and Pb that have great analytic needs, the precision, sensitivity and accuracy of the LA method was evaluated and the following knowledge was obtained:

(1) Analytical Precision: When the internal standard method that uses the ion intensity ratio to ^{57}Fe is adopted, in the trace concentration region of the level of μg/g in steel, it is possible to analyze B with an RSD of 3% or so and the other elements with an RSD of 2% or so. For B, some samples showed large dispersions in the infinitesimal concentration region of 2 μg/g or lower. However, because almost the same precision as in the JIS method was obtained by increasing the area radiated by the laser, it was judged that this is the effect of segregation.

(2) Sensitivity: The lower limit of determination is on the order of several tens of nanograms/g for B and As and on the order of several nanograms/g for Sb and Pb, and high-sensitivity analysis is possible.

(3) Accuracy of Analytical Values: A comparison was made between the measured values of the chemical analysis method and those of LA-ICP-MS and a high correlation with values of the coefficient of correla-

tion of 0.995 or more was obtained.

As described above, an investigation was made into the application of LA-ICP-MS to the determination of trace amounts of B, As, Sb, and Pb in steel samples and satisfactory results were obtained. JFE Steel consider that this method can contribute to the rapid evaluation of products and an improvement in productivity by shortening the analysis time thanks to the high sensitivity and rapidity of the method.

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