

Direct Quantification of Mn Concentration in Molten Steel Utilizing a Wavelength-Variable Laser

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A method for the on-line quantification of Mn concentration in molten steel was examined. Application of atomic absorption spectrometry using a wavelength-variable laser as the light source was attempted. When the laser emission wavelength was set to the absorption center wavelength in a laboratory melting furnace experiment, it was difficult to measure Mn concentrations of more than 1.0% in the molten steel. Investigation on the relationship between the laser emission wavelength and absorbance was performed using an atomic absorption burner and it was found that the absorption sensitivity could be adjusted by shifting the wavelength from the absorption center wavelength. We reduced the absorption sensitivity to about 1/10 by shifting the laser emission wavelength about 0.015 nm from the absorption center to the longer wavelength side, and performed a melting furnace experiment again. Possibility of directly quantifying Mn concentrations of up to 1.5% or higher was demonstrated.

KEY WORDS: atomic absorption spectrometry; laser light source; wavelength-variable laser; direct quantification; molten steel; manganese.

1. Introduction

Atomic absorption spectrometry has long been known as a technique that allows high-sensitivity elemental analysis with a relatively simple system configuration, and is an official analysis technique that has been widely used for analysis of elements in steels. It has an advantage that it is not easily affected by coexisting elements. However, under fixed analysis conditions, it has a disadvantage that it has a narrower dynamic range than ICP emission spectrometry et cetera. Because of this, quantitative analysis requires processes such as diluting the solution to be measured to an appropriate concentration and adjusting the burner angle. The reason for this is as follows: To obtain the concentration C in the light-absorbing layer using theoretical absorbance Eq. (1), the absorbance given by Eq. (2) can be measured only up to 2 because the light intensity after absorbance becomes weaker.

$$-\log(I/I_0) = k\mu LC \quad \text{..... (1)}$$

where T : light intensity after absorption, T_0 : light intensity before absorption, k : instrumental constant, μ : absorption sensitivity, L : thickness of the light-absorbing layer, C : concentration in the light-absorbing layer.

$$A = -\log(I/I_0) \quad \text{..... (2)}$$

Studies have been conducted to extend the dynamic range of atomic absorption spectrometry using a laser light source to compensate for this disadvantage.^{1,2)} Extending the dynamic range is an idea mainly to detect low light intensity and an effort to improve the measurement sensitivity on the low absorbance side. At the manufacturing site, there is a demand for measurements on the high absorbance side. For example, for the quality control of the evaporation coating process for low-melting point metals, it is desirable to directly evaluate the generated state of a metal vapor. Atomic absorption spectrometry is suitable in this regard because quantification can be performed simply by directing light at the surface of molten steel. In a system with an excessive atomic vapor, the absorbance is saturated and the conventional atomic absorption spectrometry technique cannot be used directly.

An example of this is the direct analysis of components in molten steel being studied by the authors. Particularly, Mn is an element that significantly affects the properties of steel. Steel products containing more than 1% Mn have been available in recent years, resulting in a high demand for analysis in the steel manufacturing process. In the steel manufacturing process in which Mn is added to adjust steel composition, the accuracy and promptness of analysis directly affect the production costs, including specific consumption and productivity. Therefore, studies on on-line analysis has been conducted to directly quantify Mn concentration in molten steel.^{3,4)} To allow on-line analysis, we have studied direct quantification of a Mn vapor present on the surface

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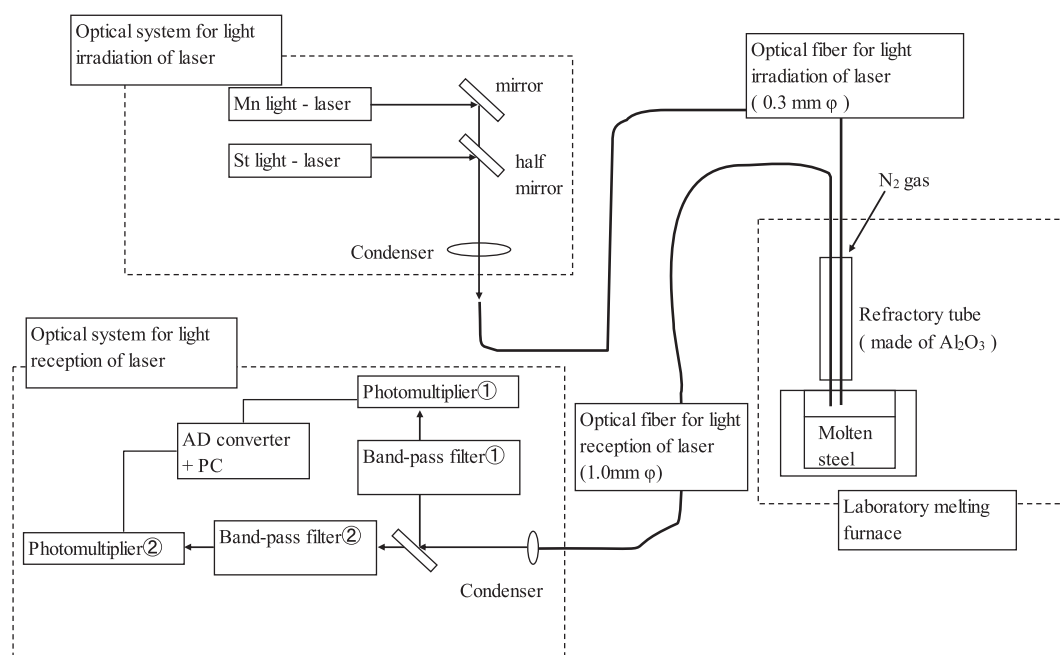


Fig. 1. Setup of the experiment using a laboratory melting furnace.

of molten steel by atomic absorption spectrometry.^{5,6)}

Our study has confirmed that the use of a wavelength-variable laser as the light source allows the dynamic range to be extended approximately more than 100 times.⁷⁾ To apply this technique to the measurement of Mn concentration in molten steel, we have attempted to quantify Mn concentration in molten steel using a laboratory melting furnace by directing laser light at the surface of molten steel through an optical fiber. In addition, to obtain appropriate absorption sensitivity, we have investigated the relationship between the laser emission wavelength and absorbance using an atomic absorption burner. The results are presented in this paper.

2. Experiment

Figure 1 shows the setup of the experiment using a laboratory melting furnace. **Figure 2** shows the setup of the experiment using an atomic absorption spectrometer.

2.1. Measurement of Mn Concentration in Molten Steel Using a Laboratory Melting Furnace⁶⁾

2.1.1. Melting Furnace

5 kg of pure iron containing less than 0.005% Mn was melted in the air atmosphere in a high-frequency induction furnace. Metal Mn was gradually added to adjust the Mn concentration in the molten steel. Sampling was performed during the adjustment of the Mn concentration and the given time interval. After the experiment, chemical analysis was performed to measure an accurate Mn concentration. When, during the experiment, slag was suspended and blocked the light from being emitted or received, it was removed with a tool to keep the surface of the molten steel clean.

2.1.2. Light Source and Optical Measurement System

The laser light source used as the light source for the analysis of the Mn concentration (hereinafter, the “Mn light”) is

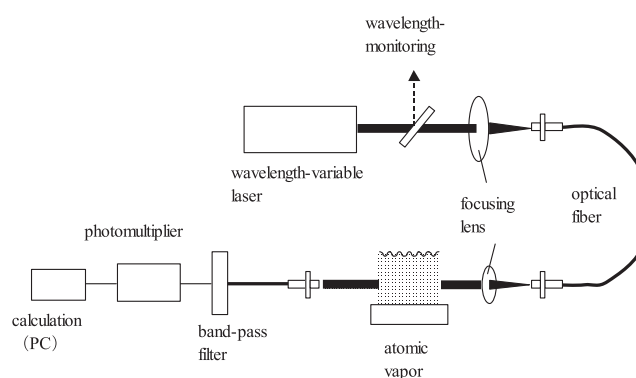


Fig. 2. Setup of the experiment using an atomic absorption spectrometer (AAS).

a custom-made light source that has a second harmonic generator built in Showa Optronics’ wavelength-variable laser light source LUDORA. It is a system that is composed of a continuum YAG laser second harmonic (532 nm) generator/Ti-sapphire wavelength-variable laser/LBO harmonic generator to emit laser light with a wavelength near 400 nm. About 50 mW laser light with a full width at half maximum (FWHM) of about 1 pm was continuously emitted. The center wavelength of the laser irradiation was changed between 403.41 and 403.43 nm. The wavelength and the FWHM were measured with ADVANTEST’s spectrum analyzer (Model Q8347). Hitachi Metals’ blue SHG laser source (Model ICD-430) was used as the standard light source (hereinafter, the “St light”) for reflectance correction.⁶⁾ The wavelength of this laser was around 430 nm and not involved in Mn absorption. The absorbance $A = -\log(I/I_0)$ was calculated from the light intensity ratio $I_{0Mn}/I_{0St} = I_0$ at which light absorption does not occur and the light intensity ratio $I_{Mn}/I_{St} = I$ at which light absorption occurs. Part of each laser beam was sampled and the output intensity was monitored and corrected. The laser beams emitted from the two

laser light sources were superimposed with a half mirror on the same optical path and introduced into the end of a single-core optical fiber with a core diameter of 0.3 mm. A chopper to block the light at a duty ratio of 0.5 was placed at the entrance end of the optical fiber, and the intensity of the radiant light as the background light was evaluated. The other end of the optical fiber was guided to the furnace side and placed 20 to 30 mm above the molten steel to direct the beam at the surface of the molten steel. The reflected light from the surface of the molten steel was directly received at the end of a single-core optical fiber with a core diameter of 1.0 mm. The Mn light from the other end of the optical fiber was measured through a band-pass filter with a band-pass width of about 1 nm, and the St light was measured through a band-pass filter with a band-pass width of about 2 nm. The light intensity was measured with a photomultiplier. The two optical fibers for directing and receiving light were held in place in a refractory tube. Nitrogen gas was introduced into the tube at a rate of about 10 L/min mainly for cooling purposes.

2.2. Investigation of Absorption Sensitivity with an Atomic Absorption Spectrometer

2.2.1. Optical Measurement System

As shown in Fig. 2, the basic configuration of the experimental system is as described in the previous report.⁷⁾ The wavelength-variable laser and the photometric system for the measurement of Mn absorbance described in Section 2.1.2 were used. The light from the laser light source was introduced into the end of a 0.8 mm diameter single-core optical fiber. The other end was placed on the extension of the slit of the atomizing burner in the atomic absorption spectrometer. The light from the optical fiber was focused with a condenser lens. The system was set up to allow the light to pass parallel to the slit 10 mm above it. The light was introduced through the 0.8 mm diameter single-core optical fiber on the extension of the slit of the atomizing burner into the spectrometry/light receiving unit. **Table 1** shows the main apparatus and analytical conditions.

Table 1. Apparatus and analytical conditions of the developed Laser AAS system.

○ Laser	
· Laser	YAG - Ti sapphire - LBO
· Wavelength	403.41 nm
· Average power	50 mW
○ Transmission optical fiber	
· Material	quartz glass
· Diameter	0.8 mm ϕ (single core)
○ Spectroscopic condition	
· Grating	1 200 lines/mm
· Detector	photodiode array
○ AAS	
· Slit length	100 mm
· Flame	air - acetylene

2.2.2. Atomic Vapor Generation Unit

A solution with dissolved metal Mn was drawn and vaporized using the atomizing unit of Nippon Jarrell Ash's atomic absorption spectrophotometer AA1. The burner has a 100 mm slit. The solution was heated and vaporized with an air acetylene flame.

2.2.3. Sample Solution

10 g of Kanto Chemical's metal Mn was dissolved with 20 ml of (1+1) nitric acid and diluted into 20 $\mu\text{g/ml}$ Mn.

3. Results and Discussions

3.1. Time-Resolved Measurement of the Reflected Light from the Surface of Molten Steel

Figure 3 shows an example of a measurement of the reflected light from the surface of molten steel with no Mn added. Due to the oscillation of the surface of the molten steel, the light is not always reflected in the same direction. The accuracy of measurement degrades due to the decrease in the signal-background (S/B) ratio unless an appropriate time-resolved measurement is performed. Figure 3 shows the results of data sampling performed at 2 msec intervals with an AD converter. The figure shows that intermittent reflected light was properly measured. A comparison between the waveform of the Mn light and that of the St light in the figure shows that they are very similar, except for the background intensity. If the light is improperly introduced into the end of the optical fiber on the incident side, the shape of the outgoing light beam is different for the Mn light and the St light, preventing a proper correction of reflectance. An accurate adjustment requires a beam profiler. However, the wavelengths of the laser light used in the experiment were in the visible range. This was confirmed by projecting the light on paper or other surfaces. The cause of the higher background level for the St light than for the Mn light can be explained as follows. The difference in brightness of radiant light due to the wavelength difference between 403 nm and 430 nm estimated by Planck's distribution equation is 2.4 times at most. The difference is more than 10 times in the measurements made, indicating the effect of the difference in the resolution of the band-pass filter used. The measurement needs improvement. The measurements of the St light at 2 msec intervals were sorted by

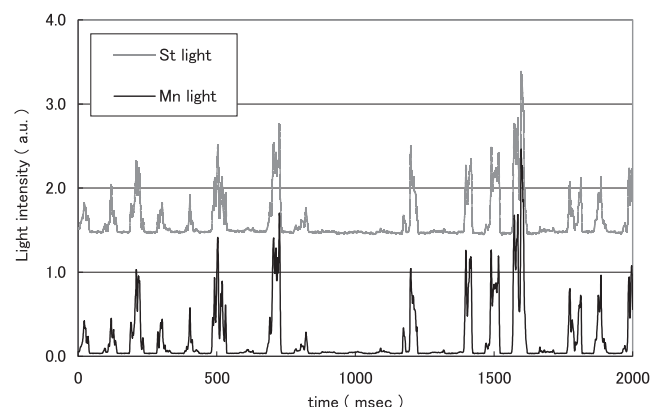


Fig. 3. Example of a time-resolved measurement of the reflected light from the surface of molten steel.

intensity. Highest 10% was defined as signal intensity and the average for 50% and less was defined as background intensity. Net reflected light intensity was obtained for the Mn light and the St light.

3.2. Measurement of Mn Concentration in Molten Steel Using Wavelength-Variable Laser Light

With the laser emission wavelength set to the atomic absorption center wavelength (a wavemeter reading: 403.410 nm), a laser beam was directed at the surface of the molten steel, and the relationship between the Mn concentration in the molten steel and absorbance was investigated. The absorbance for each measurement was obtained by calculating $-\log(I/I_0)$ from the reflected light intensity I_0 ($= I_{0Mn}/I_{0St}$) for the molten steel with no Mn added and the reflected light intensity I ($= I_{Mn}/I_{St}$) for the molten steel with different Mn concentrations. **Figure 4** shows the results of three repeated measurements made at 2 sec intervals for the molten steel with different Mn concentrations. The laser light intensity is very high compared to a hollow cathode lamp (HCL). As the photometric conditions, such as the integration time, were changed, the absorbance increased without being saturated at Mn concentrations of up to 1.0% in the molten steel. However, in the experiment using an atomic absorption spectrometer, measurements were made for an absorbance of up to 4.⁷⁾ In the current experiment, an absorbance of 2.5 was the upper limit and the accuracy of repeated measurements was low. The possible causes are: (1) that the change in the thickness of the atom-absorbing layer could not be corrected⁶⁾ (2) that the wavelength and FWHM of the laser beam were not stable; and (3) that weak light needed to be measured in a high-absorbance concentration range but the radiant light from the surface of the molten steel interfered with the measurement. For the issue in (1), a wavelength-variable laser light source for the measurement of Fe absorbance is being prepared. The instability of the laser beam in (2) was determined to be due to the effect of the slight temperature change around the housing of the wavelength-variable laser used in the experiment,

which is a type that does not have a laser emission wavelength correction mechanism. Accurate control of the atmosphere temperature around the housing was considered to be difficult. To ensure the stability of the wavelength and FWHM of the laser beam, a Tygon tube was wrapped around the housing and cooling water was circulated. The water temperature was controlled to around $\pm 0.05^\circ\text{C}$ with a chiller. **Figure 5** shows the effect of the ambient temperature control. The stability of both the wavelength and the FWHM significantly increased compared to that before the improvements were made.

For the issue in (3), the S/B ratio for the Mn light intensity is less than or equal to 1 for the molten steel with a 1.0% Mn concentration due to light absorption by the Mn vapor. Probably, the decrease in measurement precision of weak light intensity affected the narrowing of the dynamic range. The measurement range of Mn concentration required in the steel manufacturing processes is in the order of 0.05 to 2.0%, and a dynamic range of two orders of magnitude should be sufficient. Changing the laser emission wavelength of the wavelength-variable laser light used as the light source was considered to reduce the absorption sensitivity, and the wavelength-dependence of the absorption sensitivity was investigated using an atomic absorption spectrometer.

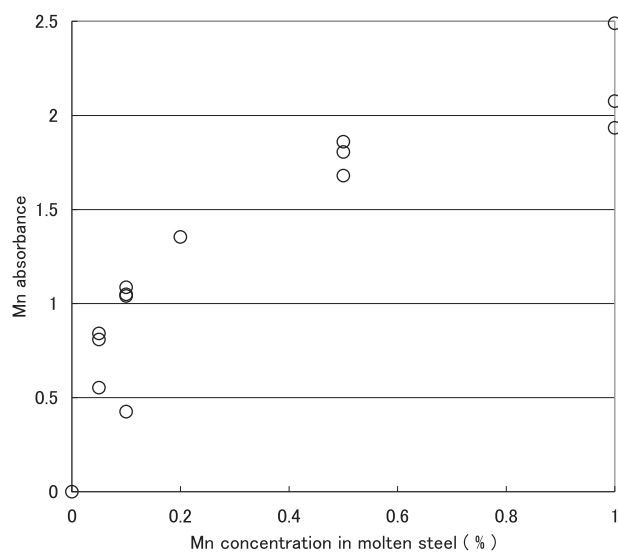


Fig. 4. Relationship between Mn concentration in molten steel and absorbance (with the laser emission wavelength set to the Mn absorption center wavelength).

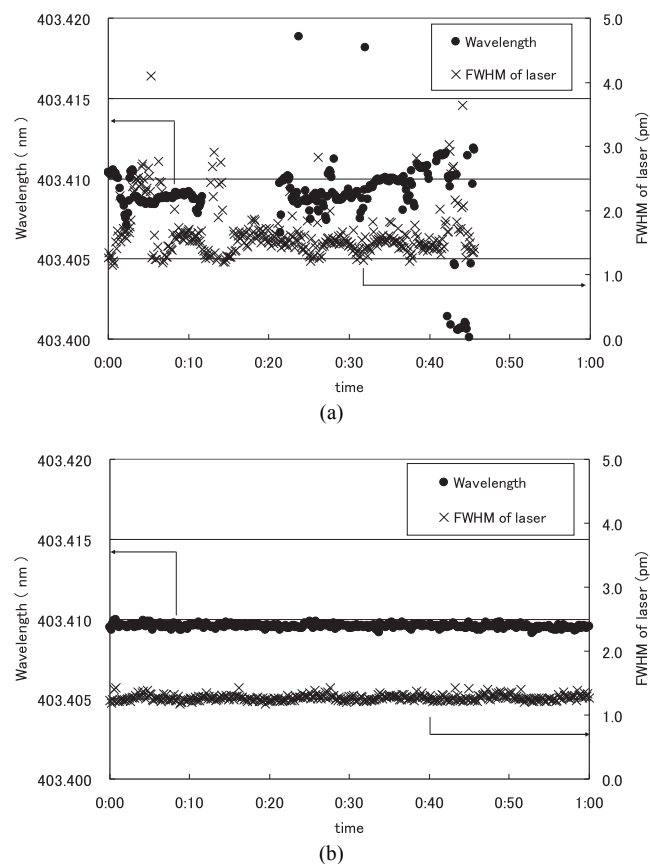


Fig. 5. (a) Example of a temporal measurement of the laser emission wavelength and FWHM of the laser light used for Mn concentration measurements (before wavelength stabilization). (b) Example of a temporal measurement of the laser emission wavelength and FWHM of the laser light used for Mn concentration measurements (after wavelength stabilization).

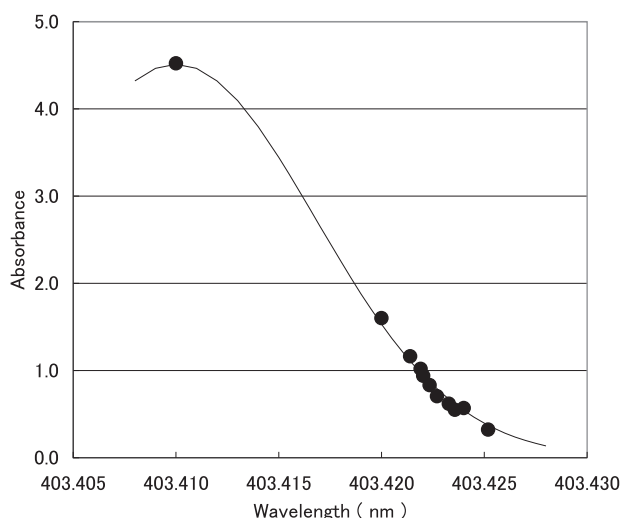


Fig. 6. Relationship between the laser emission wavelength of the laser light and absorbance.

3.3. Laser Emission Wavelength and Absorbance

Figure 6 shows the relationship between the wavelength and absorbance when a 20 $\mu\text{g}/\text{ml}$ Mn solution was introduced into the atomic absorption burner. The absorption sensitivity is lower near the wavelength of 403.420 to 403.425 nm at the base of the absorption peak than at the Mn absorption center wavelength of 403.410 nm, indicating that the absorption sensitivity can be adjusted by changing the laser emission wavelength. The FWHM of the absorption peak was estimated to be in the order of 0.016 nm by approximating the obtained results by a normal distribution. This is in good agreement with the value of around 0.01 nm reported in the literature. This means that using a wavelength-variable laser as the light source in atomic absorption spectrometry allows measurements with appropriate absorption sensitivity for the amount of vapor on the manufacturing floor. Similarly, the sensitivity could have been reduced by shifting the laser emission wavelength to the shorter wavelength side. This investigation, however, was not conducted, taking into account the efficiency of the experiment.

Based on the results of the laboratory experiment shown in Fig. 4, it was considered appropriate to adjust the sensitivity in the measurement of Mn concentration in molten steel to about 1/10 for the absorption center wavelength. An experiment using the melting furnace was performed again with the laser emission wavelength set to 403.4245 nm.

3.4. Reduction of the Absorption Sensitivity

Figure 7 shows the relationship between Mn concentration and absorbance for the laser emission wavelength set to 403.4245 nm. There is a nearly linear relationship between them for Mn concentrations of up to 1.5%. The variation in the absorbance and the slight deviation from the linear relationship in the absorbance for a 1.5% Mn concentration are probably due to the significant effect of the change in the thickness of the atom-absorbing layer. This variation could

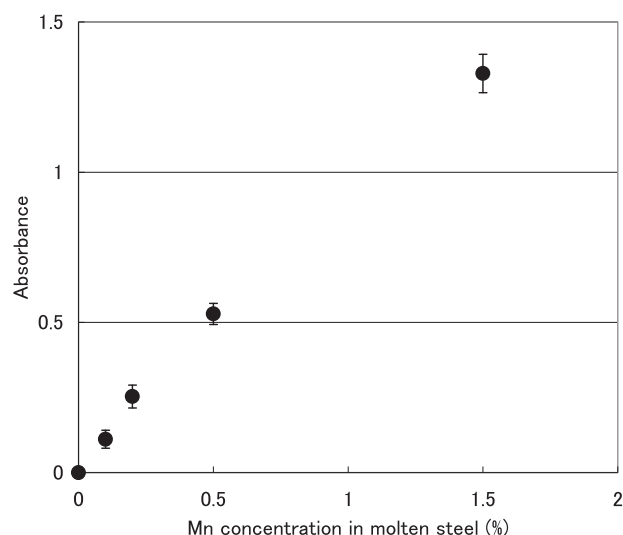


Fig. 7. Relationship between Mn concentration in molten steel and measured absorbance (with the laser emission wavelength shifted from the Mn absorption center to the longer wavelength side).

be adequately corrected by evaluating the atom-absorption of Fe.⁶⁾

The light intensity after absorption is relatively higher when the absorption sensitivity is reduced than when the laser wavelength for the Mn light is in the absorption center, making it possible to keep the S/B ratio high for the radiant light. This allows quantification of Mn concentrations of 1.5% or higher and increases the gradient of the change in absorbance in a high concentration range, which are advantageous in terms of the accuracy of quantification of Mn concentration.

5. Conclusions

Atomic absorption spectrometry using a wavelength-variable laser as the light source was performed, and the results are:

- (1) We have found that appropriate absorption sensitivity can be obtained by changing the laser emission wavelength.
- (2) We have demonstrated the possibility of directly quantifying Mn concentrations of up to 1.5% in molten steel from a Mn vapor present on its surface.

REFERENCES

- 1) C. Schnuerer-Patschan, A. Zybin, H. Groll and K. Niemax: *J. Anal. at Spectrom.*, **8** (1993), 1103.
- 2) A. V. Zybin, V. V. Liger and Yu A. Kuritsyn: *Spectrochim. Acta B*, **54** (1999), 613.
- 3) H. Ozaki, T. Takahashi, Y. Iwai, Y. Gunji and E. Sudo: *Tetsu-to-Hagané*, **68** (1982), 872.
- 4) K. Chiba, A. Ono, M. Saeki and T. Ohno: *Bunseki Kagaku*, **37** (1988), 365.
- 5) T. Tsuji, T. Mochizuki, Y. Ishibashi, N. Gunji, T. Akiyoshi and Y. Muraki: *CAMP-ISIJ*, **3** (1990), 599.
- 6) T. Ishida, T. Akiyoshi, I. Sumi, R. Kawabata, A. Chino and S. Kinoshiro: *Tetsu-to-Hagané*, **95** (2009), 690.
- 7) T. Ishida and T. Akiyoshi: *Bunseki Kagaku*, **59** (2010), 911.