Giant Pulse Laser Direct Spectrochemical Analysis of C, Si, and Mn in Liquid Iron*

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Synopsis

For the purpose of the process control in continuous steelmaking, a new method of G. P. (Giant Pulse) laser direct spectrochemical analysis of C, Si, and Mn in liquid iron has been developed. This method is characterized by coincidence of optical axes of laser and spectrometer. In this study, fundamental conditions for the analysis of C, Si, and Mn, especially taking a serious view of C, have been studied. The following results have been obtained:

(1) Influence of variations in the level of liquid iron surface on spectral intensities and intensity ratios has been evaluated. It has been shown that, for the purpose of minimization of these influences, intensity ratio should be used.

(2) Si and Mn analyses are possible with the use of cylinder type and cone type atmosphere controlling apparatus.

(3) In C analysis, it has been shown that CO gas generated in the surface of liquid iron has effects upon spectral intensity of CI 193.1 nm, and these effects can be eliminated by using cone type atmosphere controlling apparatus. C analysis is possible with the use of this apparatus.

I. Introduction

The method of direct analysis of the elements in liquid iron was a dream for metallurgists and analysts. Advantages of analysis in liquid state are given as follows:

- 1) an expectation of much time saving in analysis for the purpose of process control
- 2) a small analytical error by matrix effect which results from difference in the structure of samples caused by their composition and condition of solidification, in comparison with the case of analyzing solid samples with the method of spectrochemical analysis by spark discharge.

As concerning to the method of direct analysis which is the method of emission spectroscopic analysis by some excitation energy, various attempts¹⁻²¹⁾ have been made until now. But all these attempts have not been used in practical for direct analysis.

This study was made for examining the possibility in direct analysis of C, Si, and Mn in liquid iron in the process control of the NRIM continuous steelmaking process which was developed for all automatization in steelmaking process. The most suitable analytical means for this purpose was examined. As the result, the method of emission spectrochemical analysis was adopted from the point of view of its speed and its ability of analyzing multiple elements at the same time, and Giant Pulse (G. P.) laser was used as excitation energy. The method using G. P. laser

is most suitable for the above-mentioned purpose, because, in comparison with the method using electric discharge, this method has no contamination in electrode and has no inhomogeneity in energy supply in respect of using light.

As to this method, E. F. Runge *et al.*¹⁵⁾ analyzed Ni and Cr in liquid stainless steel with spectrograph by focussing G. P. laser to the surface of hot metal in air. But, in their report, analytical conditions were not examined precisely. Moreover, this method had a weakpoint in that errors by fluctuation in the level of hot metal were caused by no co-axiality in the optical systems of laser beam and spectrograph, and atmosphere was not controlled.

Therefore, authors have studied the possibility of direct spectrochemical analysis of C, Si, and Mn in liquid iron, especially taking a serious view of C, with the use of G. P. laser as excitation energy and the method of coincidence (co-axial) in the optical systems of laser beam and spectrometer.

II. Reasons for Maintaining Co-axiality in Optical Systems of Laser Beam and Spectrometer

In the case of direct spectrochemical analysis of liquid iron, to minimize the errors of analysis caused by fluctuation in the surface level of hot metal, is one of the important problems. When laser beam is focussed obliquely to the surface of hot metal, the position of laser plasma deviates to the direction of its surface caused by its fluctuation, and the smaller the angle from laser beam to this surface, the greater its degree is. On the other hand, in this case, the greater the optical axis in the system of spectrometer deviates from that of laser beam, the greater the analytical errors become. Accordingly, if co-axiality in the optical systems is maintained, it could be said that at least the position of laser plasma does not deviate from the optical axis of spectrometer. But, even in this case, energy density of laser beam in the surface of liquid iron varies by fluctuation of surface level, which causes analytical errors. So, if both optical axes are placed perpendicular to the surface, variations in energy density can be minimized for the same fluctuations. And, to make further smaller the variations in energy density, it is important to make focal length of laser beam condenser lens as long as possible. But this length has a limit because there is a possibility of atmospheric

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discharge before laser beam reaches the surface of hot metal, and efficiency in condensing spectra falls.

From the above investigation, it can be concluded that the best method to minimize analytical errors caused by fluctuation in the surface level of hot metal, is to maintain co-axiality in the optical systems of laser beam and spectrometer, to hold both optical axes perpendicular to the surface of hot metal, and to use the laser beam condenser lens which focal length is properly long.

III. Experimental Method

1. Experimental Apparatus

The experimental apparatus is fundamentally composed of a direct-reading spectrometer and a G. P. laser apparatus, which is replaced by parts of electric discharge. The construction of this apparatus, G. P. laser apparatus, and spectrometer is identical to that used by the foregoing report,²²⁾ in which the optical systems of laser beam and spectrometer are co-axial and perpendicular to the surface of hot metal.

Atmosphere control was made by setting a cylinder type atmosphere controlling apparatus, or a cone type atmosphere controlling apparatus in quartz between sample and condenser lens as shown in Fig. 1, and regulating Ar gas flow rate to ordinary 20 l/min. The cone type atmosphere controlling apparatus was used for the purpose of avoiding afterward-mentioned effects of CO gas, sample vapor, and slag in the case of liquid samples. A shutter was equipped between atmosphere controlling apparatus and condenser lens for avoiding metal vapor sticking to the surface of condenser lens. This shutter has a structure in which intermixing of air can be kept off in opening and shutting.

Laser energy was measured by the same procedure as the foregoing report.²²⁾ In the experiment of liquid samples, solid materials were melted by a high-frequency induction melting furnace (output: 15 kW, frequency: 400 kHz). Temperature was measured by optical pyrometer.

2. Experimental Method

Experimental method was the same as the foregoing report.²²⁾ But, in the case of liquid samples, Ar+3 %H₂ gas was passed into the surface with the use of cylinder type atmosphere controlling apparatus until melt down of samples, and after changing the atmosphere controlling apparatus to the cone type, Ar gas was passed for about 30 min. After that, experimental run was begun. Namely, after measurement of 2 or 3 units of spectral intensity, sample was taken by silica tube, and at the same time temperature of liquid iron was measured by optical pyrometer. Samples were analyzed by chemical method. Position of the surface of liquid iron was regulated to a constant level.

3. Samples and Analytical Lines

Solid samples used in this experiment were the same as the foregoing report.²²⁾ In liquid sample experiment, Fe-high C binary alloy (about 4 % C) and Fe-low C binary alloy, which were premelted from electrolytic iron, were used as melting materials. In the case of Mn and Si analysis, after the Fe-high C binary alloy was melted, its composition was adjusted by adding Mn and ferro-Si in order. In the case of C analysis, after the Fe-high C binary alloy or Fe-low C binary alloy was melted with addition of ferro-Si (0.5~2 %), its composition was adjusted by letting it stand. This procedure is a utilization of the phenomenon that decarburization proceeds as time goes.

Analytical lines used in this experiment are the same as the foregoing report.²²⁾

IV. Experimental Results and Discussion

1. Influence of Sample Position

For understanding the variations in spectral intensity with the variations in surface level of the samples, which is considered to be important in direct analysis of liquid samples, influence of sample position on spectral intensity was investigated as characteristics of this analytical apparatus. In this apparatus, as the optical systems of laser beam and spectrometer are

Fig. 1.
Atmosphere controlling apparatus.

co-axial, influence of sample position means that of displacement of sample position in the axes of both optical systems. Cylinder type atmosphere controlling apparatus was used for atmosphere control.

The relation between each spectral intensity and sample position is shown in Fig. 2. Here, negative sign on the abscissa means the direction to the condenser lens. The variations in each spectral intensity have convex curves having the maximum values in the different positions. Under the conditions of this apparatus, following three factors change according to the variations of sample position:

- 1) variations in average density of laser energy on the surface of the sample,
- 2) variations in spectral intensity caused by displacement of light source in the axis of optical system, which are controlled by the dependence of refractive index of quartz lens in the optical system of spectrometer on wavelength
- 3) variations in the condensing efficiency caused by the variations in the angle of light source to the surface of condenser lens.

The most effective factors are considered to be 1) and 2) among the above factors. The arrangement of the maximum in each curve of spectral line in the order of wavelength is mainly due to the factor of 2). The focal length in the condenser lens of laser beam is so long (254.2 mm) that variation of the average density of laser energy is not so great, consequently it is not considered that the influence of the factor of 1) is not explicitly shown.

The relation between the intensity ratio of each spectral line to FeII 271.4 nm and BG 220.5 nm, and sample position is given in Fig. 3. Compared with Fig. 2, it is observed that the influence of the variations in the sample position near the focus become clearly small.

The result of evaluated variations in each intensity ratio with variations in the level of hot metal at the focus is shown in Table 1. As concerning to the influence of the variations in the surface level of hot metal, it is smaller in taking intensity ratio except C. So, in respect of diminishing the influence of the varia-

tions in the surface level of hot metal on each spectral intensity, it is proper to take intensity ratio to FeII 271.4 nm (in the case of C, it is also proper to take intensity ratio to BG 220.5 nm), and to set the sample position in the vicinity of focus. In this apparatus, which uses quartz lens in the optical system of spectrometer, because its refractive index is dependent on wavelength, the maximum value of each spectral intensity is not in the same site. But, if condenser mirror is used instead of quartz lens, the maximum value is in the same site, so more flexible analysis to the variations in the surface level can be realized.

2. Direct Analysis of Liquid Samples

1. Liquid Sample Analysis with the Use of Cylinder Type Atmosphere Controlling Apparatus

In view of the effects of each factor which was understood in solid samples, experiments of liquid samples were made with the use of cylinder type atmosphere controlling apparatus. Atmosphere of the experiments is Ar 20 l/min, and the surface level of liquid sample is at the focus.

Table 1. Variations in intensity ratios (%) according to variations in surface level of sample.

Line pair	Variations in surface level of liquid iron (mm)			
	±10	±5	±2	±1
Mn II 293.3 nm Fe II 271.4 nm	±4.62	±2.31	±0.924	±0.462
Si I 212.4 nm Fe II 271.4 nm	±13.6	±6.82	±2.73	±1.36
C I 193.1 nm Fe II 271.4 nm	±19.5	±9.74	±3.90	±1.95
Mn II 293.3 nm BG 220.5 nm	±38.9	±19.4	±7.77	±3.89
Si I 212.4 nm BG 220.5 nm	±24.0	±12.0	±4.81	±2.40
C I 193.1 nm BG 220.5 nm	±18.8	±9.39	±3.76	±1.88

Fig. 2. Relation between relative intensity and distance from focus of laser beam.

Fig. 3. Relation between intensity ratio and distance from focus of laser beam.

(1) Si and Mn Analysis

Fe-high C binary alloy was melted in different charges, and in each charge, experiment was made by adding Si or Mn to the melt in order.

Experimental relation between Si % in liquid iron and SiI 212.4 nm/FeII 271.4 nm and that between Mn % in liquid iron and MnII 293.3 nm/FeII 271.4 nm are given in Fig. 4. Temperature range of these experiments is 1 430~1 510 °C and 1 440~1 600 °C, respectively. Influence of temperature seems to be small, and almost good result is obtained.

(2) C Analysis

Fe-C binary alloys of different level of C were melted three times, and the relation between C % in liquid iron and intensity ratio was examined.

Its result is given in Fig. 5. Under about 0.3 % C, the difference in intensity ratio is recognized, but above about 0.3 %, the amount of scatter is great, so if calibration curve can be drawn, the slope is almost zero.

As concerning to the cause of this phenomenon, it can be considered that existence of CO in the surface of liquid iron caused by decarburization of the melt relates to this phenomenon. So, average evolution

rate of CO gas is calculated from average decarburization rate in each sampling interval. As shown in Table 2, it is clear that there is a difference in the average evolution rate of CO gas. Accordingly, it is likely that CO gas concentration in the surface of the melt and the mixing condition of the gas are not constant in each charge and in each sampling time, which influences spectral intensity.

2. Examination of the Influence of CO₂ Gas

In order to examine the influence of CO gas existing on the surface of liquid iron on each spectral intensity, some simple model experiments were done with the use of solid samples. Considering the safety of experiment, CO₂ gas was used instead of CO gas. CO gas, which exists on the surface of liquid iron, is created by the reaction of C in the melt, and as this state can be reproduced, two methods of CO₂ gas introduction were adopted as shown in Fig. 6. In both cases, Ar gas flows from upper side at 20 l/min.

With respect to MnII 293.3 nm, SiI 212.4 nm, and FeII 271.4 nm, variations of each spectral intensity in the case of A type method is given in Fig. 7. Influence of CO₂ gas is hardly noticeable in this range of flow rate. But with respect to CI 193.1 nm, influence of CO₂ gas is clearly noticed. Namely, the spectral intensity increases rapidly, and after that decreases slowly. And also in B type method with the use of Fe-0.7 %C alloy as sample, CI 193.1 nm varies in the same manner. From these experimental results, it can be inferred that influence of CO₂ gas is small in

Fig. 4. Calibration curves of Mn and Si using cylinder type atmosphere controlling apparatus.

Fig. 5. Relation between CI 193.1 nm/FeII 271.4 nm and C content.

Table 2. Estimation of average rate of CO gas evolution.

C content		Duration (min)	Average rate of decarburization (%/min)	Average rate of CO gas evolution (Ncm ³ /min)
Start (%)	Final (%)			
1.47	1.14	80	0.0041	77
0.56	0.27	40	0.0072	134
0.28	0.10	55	0.0032	60
0.10	0.06	20	0.0020	37

Fig. 6. CO₂ gas introducing apparatus.

Fig. 7. Influence of CO₂ gas flow rate on relative intensity using cylinder type atmosphere controlling apparatus in the case of A type CO₂ gas introducing apparatus.

Fig. 8. Influence of CO₂ gas flow rate on intensity ratio to FeII 271.4 nm using cone type atmosphere controlling apparatus in the case of B type CO₂ gas introducing apparatus.

the process itself of plasma formation created by laser. It can be explained that CO₂ gas, which does not change the nature of plasma itself extensively, is introduced with C atoms of the sample into the plasma in the process of expansion and cooling in the plasma generated in the surface of the sample, and so that the spectral intensity of CI 913.1 nm increases.

3. Effectiveness of Cone Type Atmosphere Controlling Apparatus

Because it was confirmed that CO or CO₂ gas influenced the spectral intensity of CI 193.1 nm from the foregoing paragraph, means for minimizing this influence as possible was considered. As a result, a cone type atmosphere controlling apparatus, which aims to minimize CO or CO₂ gas concentration at the laser-irradiated part of the sample, was designed. This apparatus has a small diameter in the part of Ar gas flowing out, so that the linear speed of Ar is large at this part (cone type: linear speed of 271 cm/min at the diameter of this part of 9.7 mm, flow rate of 20 l/min, cylinder type: linear speed of 4.65 cm/min at the diameter of this part of 74 mm, flow rate of 20 l/min), and it was expected that the removal effect of CO or CO₂ gas at the surface of the sample was greater than in the cylinder type.

The same experiment as the foregoing paragraph was done with the use of this apparatus, and its effect was investigated. Its result is shown in Fig. 8. Sample is Fe-0.83 %C alloy in this case. The result in the case of cylinder type atmosphere controlling apparatus is also shown for comparison. Intensity ratio of CI 193.1 nm is almost constant in the cone type, as shown in Fig. 8, so the effect in removal of CO₂ gas is confirmed. In the same manner, it is clear that this apparatus is also effective in removal of CO gas.

4. Liquid Sample Analysis with the Use of Cone Type Atmosphere Controlling Apparatus

(1) Si and Mn Analysis

The possibility of Si and Mn analysis in liquid iron

Fig. 9. Calibration curves of Si and Mn using cone type atmosphere controlling apparatus.

was pursued with the use of cone type atmosphere controlling apparatus. In this case Si and Mn were added at the same time. Temperature was not measured.

The relations between Si % and Mn % and SiI 212.4 nm/FeII 271.4 nm, MnII 293.3 nm/FeII 271.4 nm, respectively, are shown in Fig. 9. In this figure, points with bars are data on the way to desiliconization and demanganization during adding no more Si and Mn, leaving hot metal as it is. Both Si and Mn have gentle slopes above 0.5 % or so. This may be due to a particularity in melt in addition to the self-absorption phenomenon. However, under 0.5 % or so, these relations are thought to be sufficiently applicable to analysis based on the inclination.

Also in the case of taking ratio to BG 220.5 nm, almost the same relation was obtained.

(2) C Analysis

The possibility of C analysis in liquid iron with the

use of cone type atmosphere controlling apparatus was examined.

The relations between $CI\ 193.1\text{ nm}/FeII\ 271.4\text{ nm}$ and $C\%$ in liquid iron, and the relations between $CI\ 193.1\text{ nm}/BG\ 220.5\text{ nm}$ and $C\%$ in liquid iron are given in Figs. 10 and 11, respectively. The experimental data in four melts are shown in these figures. In Fig. 11, though each position of the sample surface is different, each curve of three melted samples at laser energy 0.40 J and so falls on almost the same curve.

Figure 10 does not show close agreement as much as Fig. 11. This difference between Fig. 10 and Fig. 11 can be explained from the fact that intensity ratios to $FeII\ 271.4\text{ nm}$ vary greater than to $BG\ 220.5\text{ nm}$ in the vicinity of zero sample position, according to the relations between intensity ratio and distance from focus of laser beam shown in Fig. 3. The average rates of CO gas evolution in time intervals of each sampling, which is calculated from C analysis, are $82.0\sim 133$ (average: 104) Ncm^3/min in No. 1 melt, $76.5\sim 205$ (average: 125) Ncm^3/min in No. 2, $224\sim 355$ (average: 283) Ncm^3/min in No. 3, and $4.9\sim 140$ (average: 74.3) Ncm^3/min in No. 4. It is considered

Fig. 10. Calibration curve of C using cone type atmosphere controlling apparatus ($CI\ 193.1\text{ nm}/FeII\ 271.4\text{ nm}$ vs. C content).

Fig. 11. Calibration curve of C using cone type atmosphere controlling apparatus ($CI\ 193.1\text{ nm}/BG\ 220.5\text{ nm}$ vs. C content).

that relations in each melt are almost not affected by average rate of CO gas evolution varying greatly, which shows the effect of this cone type atmosphere controlling apparatus.

(3) Effect of Liquid Iron Temperature

Though the effect of temperature was not measured systematically, the effect of temperature on spectral intensity was not recognized.

An example of the relation between liquid iron temperature and spectral intensity is shown in Fig. 12. These data were measured in the course of the above-mentioned experiments. These spectral intensities ($BG\ 220.5\text{ nm}$ and $FeII\ 271.4\text{ nm}$) can be considered to be not affected by $C\%$ in liquid iron, so according to the above relations the effect of temperature can be estimated. In temperature region of about $1450\sim 1650\text{ }^\circ\text{C}$, each spectral intensity can be regarded as almost constant, so it can be considered that at least liquid iron temperature does not greatly influence analysis.

(4) Comparison of Solid Sample with Liquid Sample

Spectral intensity of solid sample was compared with that of liquid sample. This comparison is given in Fig. 13. The data of solid samples were measured at the same time of each melting. $FeII\ 271.4\text{ nm}$ and $CI\ 193.1\text{ nm}$ in liquid sample are both smaller than in solid sample, but $BG\ 220.5\text{ nm}$ is greater. This is thought to be caused by difference between solid sample and liquid sample in various properties. Accordingly, in liquid sample, because of increase in background, decrease in SN ratio is estimated, so it is handicapped in analysis. But, as confirmed about solid sample in the preceding report,²²⁾ if time resolution is also applied to liquid sample, improvement in SN ratio can be expected.

5. Examination of Analytical Errors

Analytical errors in the liquid sample analysis with the use of cone type atmosphere controlling apparatus are a little examined. A regression equation for the relation between intensity ratio and concentration is obtained per each melt, and then inversely individual intensity ratio and its average are substituted into the

Fig. 12. Influence of liquid iron temperature on spectral intensity.

regression equation to calculate concentration, so relative errors are obtained. Regression equations are two of the first order approximation and power approximation, that having higher decision factor γ^2 is adopted. These results are shown in Table 3.

On C analysis, there is a fair scattering in the average of relative errors at each melt (5.35~59.9 % in one unit, 3.54~39.7 % in 2~4 units), it can not be denied that even the best average of relative errors in

this analysis is inferior in comparison with ordinary spectrochemical analysis by spark discharge. But spark discharge analysis uses the integral value of 1 000 times at 20 sec of integral time in the case of 50 Hz, on the contrary in this case laser analysis used only 10~20 shots, and because relative errors decrease clearly in the case of laser shots of 2~4 units (10~20 shots) as compared with the case of laser shot of one unit (5 shots), if the number of laser shots is increased, it is considered to be able to approach the level of spark discharge. Mn and Si have also the same situation. There is almost no difference between intensity ratio to FeII 271.4 nm and that to BG 220.5 nm.

V. Future of the Method of Direct Analysis by G. P. Laser

As described above, the authors confirmed the possibility of C, Si, and Mn analysis in liquid iron as a laboratory step. In the case of analysis of another metallic elements such as Ni, Cr and so on, there may be considered to be no problem. And for P and S analysis, low concentration analysis is severe in point of SN ratio, but it may be possible if time resolution apparatus is applied.

For the purpose of further improving authors' method and apparatus of analysis, the following means must be considered.

(1) The authors' method of collecting spectrum uses lens system, and because of its wavelength-dependence of refractive index, in the case of multiple element analysis at the same time, the most suitable

Fig. 13. Comparison of solid sample with liquid sample in relative intensity. ①: No. 1 charge, ②: No. 2 charge, ③: No. 3 charge.

Table 3. Relative errors in values of analysis.

Charge No.	Line pair	Regression equation	Coefficient of decision, γ^2	Average value of relative errors (%)	
				1 unit	2~4 unit
1	C I 193.1 nm Fe II 271.4 nm	$y=1.312+0.266x$	0.894	54.7	5.24
2	C I 193.1 nm Fe II 271.4 nm	$y=1.385+0.202x$	0.914	8.75	6.91
3	C I 193.1 nm Fe II 271.4 nm	$y=1.446x^{0.182}$	0.935	20.0	17.4
4	C I 193.1 nm Fe II 271.4 nm	$y=1.018x^{0.0623}$	0.904	38.7	30.3
5	Mn II 293.3 nm Fe II 271.4 nm	$y=1.321x^{0.0727}$	0.870	70.3	59.0
5	Si I 212.4 nm Fe II 271.4 nm	$y=2.415x^{0.106}$	0.983	11.0	11.5
1	C I 193.1 nm BG 220.5 nm	$y=0.958+0.232x$	0.885	46.2	5.71
2	C I 193.1 nm BG 220.5 nm	$y=1.100x^{0.312}$	0.961	5.35	3.54
3	C I 193.1 nm BG 220.5 nm	$y=0.978+0.190x$	0.928	16.4	15.3
4	C I 193.1 nm BG 220.5 nm	$y=0.640x^{0.0548}$	0.863	59.9	39.7
5	Mn II 293.3 nm BG 220.5 nm	$y=1.368x^{0.0870}$	0.980	62.8	15.6
5	Si I 212.4 nm BG 220.5 nm	$y=2.465x^{0.114}$	0.979	13.8	12.4

condition of each analytical line is not constant. Accordingly, in order to remove this effect, use of mirror is desirable.

(2) In order to raise SN ratio, it is necessary to examine the method such as collecting spectrum at the part of high SN ratio in laser plasma (space resolution), in addition to time resolution.

(3) It is necessary to examine standard samples. The authors have an idea, which is the method of measuring and deciding the relation between standard solid samples and liquid samples in advance, and using these solid samples as calibration. But it is the problem to examine furthermore.

It can be speculated that this apparatus has many applications in the broad area of industrial uses. Application methods of this apparatus to industrial stage have a fundamental solution or a prospect, but for its practical use some consideration will be needed.

As concerning to time needed for analysis, which is one of the most important factors in the methods of analysis for process control, the analysis can be finished within 1 min, because now new Q-switching ruby or neodymium glass laser having output of 100 MW and high repeating rate of 1 Hz is in the market. But for analyzing more rapidly, it is desirable to develop a laser with a higher repeating rate, which is truly suitable for laser analysis.

VI. Conclusion

The possibility of direct spectrochemical analysis of C, Si, and Mn in liquid iron with the use of G. P. laser as excitation source has been investigated, especially taking a serious view of C. The following results have been obtained:

(1) In this analytical method, the best method to minimize analytical errors caused by fluctuation in the surface level of hot metal, is to maintain co-axiality in the optical systems of laser beam and spectrometer. For further minimizing analytical errors, intensity ratio to relative intensity of Fe should be used.

(2) In C analysis, it has been shown that CO gas generated in the surface of liquid iron has effects upon spectral intensity of C, and these effects can be eliminated by using cone type atmosphere controlling apparatus.

(3) Si and Mn analyses are almost not influenced by CO gas, and are possible with the use of cylinder type or cone type atmosphere controlling apparatus.

(4) With the use of cone type atmosphere controlling apparatus, C analysis is possible.

(5) Temperature in liquid iron seems to have little influence upon spectral intensity.

(6) With the comparison between spectral intensity in solid sample and liquid sample, it has been shown that SN ratio decreases in liquid sample. But, applying time resolution can improve SN ratio.

(7) As a result of examination of relative errors in

the analysis of liquid sample, it has become known that relative errors in liquid sample are greater than in solid sample. But it can be reduced by increasing the number of laser shots.

(8) About the future of this method of direct analysis, some points to improve and investigate have been indicated.

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