Advanced Automatic Emission Spectrochemical Analyzer*

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Synopsis

Optical emission spectrometry is superior to other analytical methods in its rapidity. Therefore, it plays an important role in the field of elemental analysis at the steel making plants. However, further speedup and labor saving of the analysis by automation are required to progress of continuous steel making process. An apparatus has been developed to meet this need, and the following results were obtained.

(1) Analytical procedure was fully automated, from the receipt of samples to the transmission of analytical results. The time required for the analysis of a sample is 50 sec.

(2) Automatic standardization and automatic selection of working curves were also provided.

(3) Better precision results were obtained than by the conventional integration method in the analysis of routine steel samples taken from a converter by employing the pulse height distribution analysis method.

I. Introduction

The method of emission spectrochemical analysis has the characteristics of sufficient sensitivity, high precision, simultaneous analyzing, and rapidity.¹⁾ It is employed in the elemental analysis in steel making plants and steel products.²⁾ The advances in the optical emission spectrometric analysis of steel during the past dozen or so years have included the development of the high repetition rate excitation discharge source, the adoption of electronic computer,³⁾ etc.⁴⁾ They brought about a considerable reduction in analysis time.

However, a further speedup and labor saving of the analysis by automation are required for the progress of the continuous steel making process.⁵⁾ An automatic emission spectrochemical analyzer for making steel has been developed to meet this demand.

Its analytical procedures are fully automated, from the reception of samples being analyzed at the laboratory to the transmission of analytical results. This analyzer permits hot steel samples to be prepared, set on the excitation stand, analyzed, and reported, automatically. The standardization procedure to correct the drift of the analyzer is also done, automatically. The total laboratory time is 50 sec/sample for five element analysis.

II. Configuration

Figure 1 shows the configuration of the apparatus. It consists primarily of the automatic sample preparator and the analytical unit.

1. Automatic Sample Preparator

This preparator is composed of a sample cutter and grinder, a sample setting machine (robot), and a standard sample grinder. A steel sample arrives at the laboratory and is cut and ground by the sample preparation machine. The sample surface is polished on a circular belt sander. The swing-arm of the sample preparation machine transfers the sample to the sample transfer stage and the robot sets the sample on the excitation stand of the spectrometer. Photograph 1 shows this setting appearance. The hand of the robot rotates in every 90-deg arc. The maximum analyzing points of a sample are four. The robot takes away the sample after analyzing.

Standardization is periodically accomplished by the instructions from the central processing unit (SPQ-810). Photograph 2 shows the standardization process. The rotating disk of the standard sample grinder turns round and stops when the standard sample arrives at the position of the arm. The arm chucks the sample (Photo. 2(a)), and it is ground by the circular belt sander (Photo. 2(b)). The arm puts the sample back on the rotating disk. The rotating disk turns round again, and the robot holds the sample (Photo. 2(c)). The robot sets the sample on the ex-

Fig. 1. Configuration of advanced automatic emission spectrochemical analyzer.

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citation stand and the sample is analyzed. The drift correction constants are calculated⁶⁾ and the standardization is done. In the two point standardization, the above treatment is done twice with two kinds of samples.

2. Analytical Unit

The spectrometer is a vacuum type quantorecorder, Shimadzu GVM-100. The excitation source unit is the low-voltage spark type with the high repetition rate discharge, SG-400II. The readout console is REM-1000S with the PDA method (Pulse Height Distribution Analyzer), which can analyze a sample even with pinholes on the surface accurately to a certain extent.⁷⁾ Table 1 shows the analytical lines used for this analyzer.⁸⁾ For the internal standard line, the line Fe I 2 872.3 Å is used.⁹⁾ The precision of analysis with the line Fe I 2 872.3 Å was superior to that with the line Fe II 2 714.4 Å in our experiments.

For carbon analysis, two lines were used. The line C I 1 658.2 Å was used in the content range be-

low 0.1 % C.¹⁰⁾ Its line has high sensitivity and does not have an interfering line which overlaps the analytical line.

In the content range of 0.1 % C or above, the line C I 1 930.9 Å was used. For Si or Al analysis also different two lines were used in the high or low content range, respectively. Table 2 shows the analytical conditions used.

Photo. 1. Sample setting on excitation stand.

Table 2. Analytical conditions.

Excitation	Secondary voltage	400 V
	C-L-R	7 μ F-3 μ H-1.5 Ω
Discharge frequency		670 Hz
Counter electrode		Ag ϕ 6.2 mm, Cone 60 deg
Analytical gap		5.5 mm
Ar gas flow rate		10 l/min
Exposure	Preburn	1 000 pulses
	Analysis	1 000 pulses
PDA (Pulse Height Distribution Analysis)		Fe level, 70% Ratio method

- (a) Sample chacking by the arm of the standard sample grinder
- (b) Sample surface grinding by the standard sample grinder
- (c) Before sample holding by the analytical robot

Photo. 2. Automatic preparation of standard sample.

Table 1. Analytical lines.

Elements	C		Si		Mn	P	S	Al		Fe
	Low	High	Low	High				Low	High	
Wavelength (Å)	1 658.2 (I)	1 930.9 (I)	2 124.2 (I)	2 516.1 (I)	2 933.1 (II)	1 782.9 (I)	1 807.3 (I)	3 961.5 (I)	3 082.2 (I)	2 872.3 (I)

Note. Low : low content range, High : high content range

The selection of the working curve group²⁾ can be automatically done. The working curves are different for the varieties of steel and their history. A suitable analytical line is used for each content range analyzed. The working curve group is automatically selected by the central processing unit (SPQ-810). Table 3 shows an example. A sample group is selected from the intensities of each analytical line for the analyzed sample and is analyzed with the working curve of the sample group. In the case of carbon analysis, Fig. 2 shows that the working curves C-1

and C-2 are used in the intensity range (≤ 500) of the line C I 1 658.2 Å and the intensity range (≥ 150) of the line C I 1 930.9 Å, respectively.

III. Performance of Analyzer and Experimental

1. Analysis Time

The shortening of the sample transfer time by the robot and the analysis and data readout time was examined. Figure 3 shows the cycle time of analysis. The total laboratory time was 50 sec for one burn,

Table 3. Group of working curves.

Analytical lines (Å) Sample group				C		Si		Mn 2 933.1	P 1 782.9	S 1 807.3	Al	
				Low 1 658.2	High 1 930.9	Low 2 124.2	High 2 516.1				Low 3 961.5	High 3 082.2
1	Converter	Low C	①	C-1	—	Si-1	—	Mn-1	P-1	S-1	—	Al-3
			②	≤500	—	≤100	—	≤500	≤1 000	≤1 000	—	≥200
High C		①	—	C-2	Si-1	—	Mn-1	P-1	S-1	—	Al-3	
		②	—	≥150	≤100	—	≤500	≤1 000	≤1 000	—	≥200	
3	Ladle	Low C	①	C-1	—	Si-1	—	Mn-1	P-1	S-2	Al-1	—
			②	≤500	—	≥111	—	≥10	≤800	≤400	≥1 000	—
High C		①	—	C-2	Si-1	—	Mn-1	P-1	S-2	Al-1	—	
		②	—	≥150	≥111	—	≥10	≤800	≤400	≥1 000	—	
Low Si		①	C-1	—	—	Si-2	Mn-1	P-1	S-2	Al-1	—	
		②	≤500	—	—	≤500	≥10	≤800	≤400	≥1 000	—	
High Si		①	—	C-2	—	Si-2	Mn-2	P-1	S-3	Al-2	—	
		②	—	≥150	—	≥500	≤700	≤800	≤400	≥1 000	—	

Note, ①: Working curve number
②: Readout value
Low: low content range
High: high content range

(a.u.): arbitrary unit
Fig. 2. Working curve for C.

Fig. 3. Cycle time of analysis.

which were 32 sec for sample preparation, 8 sec for sample setting, 5 sec for analysis, 3 sec for data treatment and 2 sec for data transmission, from the reception of samples being analyzed at the laboratory to the transmission of the result.

In order to shorten the analysis time, the apparatus has the following operation. (a) When a sample arrives at the position ① of the sample preparation machine, the arm of the robot is at the position ③. After the finishing of sample preparation the swing arm of the sample preparation machine transfers the sample from the position ① to ②.

Before the swing-arm arrival at the position ② the arm of the robot starts to move from the position ③ to ②. The robot takes away the previous analyzing sample on the way between ③ and ②. (b) Ar gas flush begins at the point of time when a sample arrives at the position ②, and emission analysis starts at the same time with the sample setting on the excitation stand. (c) In the case that a sample is analyzed two times the robot lifts the sample immediately after the first analysis and rotates it in 90-deg arc and sets new analysis point on the excitation stand. The second emission analysis starts before the finishing of the first data treatment. In the same way a sample can be analyzed four times. Either the value of one measurement or the arithmetical mean value of number n of measurement data can be chosen as the analytical result by programing the computer.

2. Precision

The shortening of analysis time generally tends to lower precision of analysis. For example the expanding of the discrimination window level of the PDA method makes analyzing time shorten, but lower the precision. In the PDA method an internal standard method is employed, in which the intensities of analytical elements are measured only when the condition of emission is stable. Figure 4 shows the method. A pulse distribution of internal standard line is measured. The upper-reference I_H and the lower reference I_L are calculated by multiplying a coefficient K by I_M (M : the initial letter of median). The spectrum intensities of analytical element lines are measured when the spectrum intensities of the internal standard line are from I_L to I_H .

Here, I_H and I_L are entitled discrimination level. All the spectrum intensities in spark discharge are measured at the discrimination level 0 % ($I_H, I_L = 0$ %), and no intensity is measured at 100 % ($I_H, I_L = 100$ %). At a low discrimination level, the number of data samplings increases and the analysis time decreases as shown in Fig. 5. But repeatability of analysis lowers as shown in Fig. 6. In addition high repetition rate discharge cycle, and a small number of preburn and sampling discharge shorten analysis time but lower repeatability in general, however, there are some cases where a large number of discharge lowers repeatability.^{7,11)}

Three conditions which were capable of shortening analysis time were examined. They were (i) discharge cycle, (ii) preburn and sampling discharge

Fig. 4. Illustration of internal standard method in PDA method.

Fig. 5. Relation between discrimination level and sampling time.

number, and (iii) Fe discrimination level. The conditions were selected in which analysis time decreased and precision did not lower. Moreover four conditions were also examined which did not directly influence analysis time, but precision. They were (iv) values of $C-L-R$, (v) analytical gap, (vi) internal standard line, and (vii) measuring method.

The above seven conditions were examined and Table 2 shows the conditions chosen. As to the condition of (vii), two measuring methods were com-

pared.

One is the *R* method (Ratio method, in which the analytical line intensity/the internal standard line in-

Fig. 6. Relation between reproducibility and Fe discrimination level ($n=5$ times).

(A) *R* method

(B) *I* method

R method: ratio method for each spark pulse
I method: absolute intensity method

Fig. 7. Comparison of *R* method and *I* method for frequency distribution patterns.

tensity ratio is measured for each spark pulse and the median of the frequency distribution pattern is the measured intensity), and the other is the *I* method (Intensity method, in which the frequency distribution patterns of the analytical line intensity and of the internal standard line are respectively measured, and the ratio of their intensity medians is the measured intensity). The precision in the *R* method is generally higher than in the *I* method. This is because the frequency distribution of the *R* method varies less widely on the abscissa and has a sharper peak than the *I* method as shown in Fig. 7.

The reproducibility of this analyzer was compared with that of the integration method in Table 4. Substance samples from a converter were used and each sample was analyzed 5 times. Figure 8 shows a representative result of *C* analysis. The reproducibility of this analyzer using the PDA method was higher than the integration method. In the case that there are pinholes, cracks, *etc.* on the sample surface, oxygen gas leaves from the sample during discharge. The oxygen gas lowers the purity of argon gas near the spark column and it causes diffused discharge. For this reason the rate of vaporization of a sample varies and the reproducibility lowers.¹²⁾ In the integration method this phenomenon causes a large lowering of the reproducibility. However, in the PDA method in which the spectrum intensity is measured only when spark discharge is stable the reproducibility is higher than the integration method.

Table 4. Analytical conditions of integration method.

Apparatus	Excitation source	Shimadzu SG-400
	Vacuum spectrometer	Shimadzu GVM-100
	Measuring unit	241 000
Secondary voltage		400 V
C-L-R		5 μ F-5 μ H-1 Ω
Discharge frequency		400 Hz
Counter electrode		W ϕ 6.2, Cone 45 deg
Analytical gap		5 mm
Ar gas flow rate		10 l/min
Exposure		Preburn 4 sec Integration 3 sec
Analytical lines		C: 1 930.9 Å (I) Fe: 2 714.4 Å (II)

Fig. 8. Comparison of reproducibility for PDA and integration methods ($n=5$ times, sample temperature: room temperature).

3. Influence of Sample Temperature on Analytical Value

Some reports have been published on the influence of sample temperature on analytical value.^{12,15)} Kashima and Kubota¹²⁾ claimed that sample temperature increase generally results in a rise of spectrum intensity because of increase of evaporation from sample and increase of concentration of atoms in discharge column. Each analytical line has its own relationship between the intensity of analytical line and the sample temperature. For example the spectrum intensity of the line Fe 2 714.4 Å decreases¹⁵⁾ and that of the lines Fe 2 518 Å and Fe 2 926 Å increase¹²⁾ with increase of sample temperature. In analytical lines of C, Si, Mn, *etc.*, the intensities generally increase with increase of sample temperature, but the intensities of some lines decrease.¹³⁾ The analytical error can occur when the sample of a temperature of about 160 to 180 °C is analyzed by the analytical curve using the standard samples of room temperature. For this reason the relationship between analytical value and sample temperature was tested by the PDA method using sub-lance samples from a converter. Figure 9 shows the result of C analysis as a representative example. The analytical

Table 5. Accuracy for steel samples taken from a converter.

	C	Mn	P	S
σ_d (%)	0.012	0.011	0.0022	0.0020
Concentration range (%)	0.04 1.78	0.06 0.42	0.009 0.090	0.008 0.038

(Samples, $n=52$)

Fig. 9. Influence of sampe temperature on spectroscopic analytical result. Q_{180} and Q_{20} are spectroscopic analytical results at the temperature of 180 °C and 20 °C, respectively.

values were determined from the median of intensity ratios at room temperature and 180 °C, respectively by the analytical curve made using room temperature standard sample. The analytical values at the temperature of 180 °C, Q_{180} were about 0.02 % higher than at room temperature, Q_{20} . In the analysis of Mn and S, the analytical values at 180 °C were about 0.01 % and 0.002 %, respectively, higher than at room temperature. In the analysis of P, the difference in analytical values between at 180 °C and at room temperature was very small. In the analysis of sub-lance samples from a converter these differences were corrected.

4. Accuracy

The accuracies of analysis for sub-lance samples from a converter were examined. Each sample was analyzed twice. Table 5 shows the accuracies

$$\sigma_d = \sqrt{\sum d^2 / (n-1)}$$

where, d : difference of determinations from the chemically determined value
 n : number of samples.

The accuracies were good.

IV. Application

This analyzer is an apparatus which has been developed for shorter analysis time and analysis automation in order to handle the continuous steel making process.

On the other hand, a sampling technique from sublance without tilting the BOF vessel has been developed in BOF steelmaking process.^{16,17)} An application of this sampling technique to the previous portion of this automatic analyzer system makes automatic analysis from sampling to analyzing possible as shown in Fig. 10.

Fig. 10. Analytical system for converter operation.

V. Conclusion

A fully automatic emission spectrochemical analyzer has been developed, and the following results were obtained.

(1) Automatic analysis can be done from the reception of steel sample at the laboratory to the transmission of analytical results. The total laboratory time—from sample arrival to transmitting of the one time analytical data of five elements—is 50 sec/sample.

(2) Standardization is periodically accomplished by the instructions from the central processing unit with standard samples ground and set on the spark stand by the robot.

(3) The working curve group is automatically selected by the central processing unit.

(4) The precision and accuracy of analysis using the PDA method were good for sub-lance samples.

(5) This analyzer system makes automatic analy-

sis in BOF steelmaking process from sampling to analyzing possible.

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