Rapid Analysis of Steels by ICP-AES Combined with Electrolytic Sample Dissolution

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Abstract:

A system was developed that rapidly electrolyzes a block steel sample, continuously introduces the resultant electrolyte into the apparatus of radio-frequency inductively coupled plasma atomic emission spectroscopy (ICP-AES), and quantitatively determines the trace elements in the sample. The analytical time per sample is about 60 s, and the analytical accuracy is approximately the same as that of the conventional manual ICP-AES method. When applied to the process control analysis of BOF steelmaking and secondary refining, among other processes, the new ICP-AES method can control the composition of steel with higher accuracy. The new ICP-AES method was found to be capable of determining a high silicon concentration of about 3% and detecting sulfur with high sensitivity (standard deviation of 0.80 μg/g for 25 μg/g). The electrolytic conditions of difficult-to-dissolve precipitates such as TiC and TiN were studied, and the feasibility of analyzing such precipitates was ascertained.

1. Introduction

Advancement of refining control technology by improved process control analysis capability is essential for achieving drastic cost savings in steelmaking processes. Rapid analytical techniques with higher than ever accuracy are demanded for such purposes as reducing the quality variability of general-purpose steels by aiming at the lower specification limits of valuable elements and manufac-

turing high-grade steels by controlling their chemical composition within narrow ranges.

Steelmaking process control analysis of BOF steelmaking and secondary refining, among other processes, is currently performed by spark emission spectrometry. The improving cleanliness of steels in recent years has made it necessary to analyze steel samples for elements present in very low quantities. It is becoming difficult to analyze production steels for such elements as carbon, sulfur, aluminum, calcium, and boron at the lower limits of their composition ranges[1].

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Inductively coupled plasma atomic emission spectrometry (ICP-AES) has may advantages, including the following:

(1) ICP-AES is generally superior to spark emission spectrometry in determining sensitivity and accuracy.

(2) While spark emission spectrometry is often affected by the microstructure of the sample due to discharge to the grain boundaries, ICP-AES is free from this problem because it uses solution samples.

(3) ICP-AES can accurately determine components in solution.

(4) ICP-AES is a wet analytical method, so that its analytical values can be traced to standard solutions.

For these advantages, ICP-AES is frequently used in analytical laboratories for quality inspection. It is unfit for process control analysis that calls for rapidity, however, for it requires complicated and long manual steps to take a block sample from a molten steel, pulverized and dissolved, and obtain a sample solution. That is, chips are machined from the sample, accurately weighed and dissolved in acid, and the resultant solution is accurately measured to a required volume.

To significantly shorten the time required to prepare a sample solution for wet analysis, the technique of rapidly dissolving a block sample taken from a molten steel becomes necessary.

Several reports have been published about rapid ICP-AES techniques that use the electrolysis of block metal samples. Yuan et al.[2] determined zinc, silicon, iron, manganese, chromium, magnesium, and copper in an aluminum alloy in ranges of 0.001 to 10 mass% with an accuracy equivalent to a relative standard deviation of 4% or less. For steel samples, Souza et al.[3] determined chromium, nickel, manganese, silicon, and iron in a stainless steel. These elements are 0.3 mass% or more in concentration, and their trace levels are not reported. Flock et al.[4] found good linearity between the emission intensity and the concentration of aluminum, manganese, nickel, and chromium in ranges of 0.001 to 30 mass%. They did not investigate in depth the accuracy of their determinations, however.

Some steels contain precipitates and inclusions that are not readily acid soluble at room temperature. The studies reported in the literature applied only the constant-current electrolytic technique to electrolyze samples and did not investigate the electrolytic conditions from the standpoint of quantitatively determining elements comprising difficult-to-dissolve compounds.

A rapid block steel sample electrolyzer was originally fabricated and combined with ICP-AES to build a new analytical system. The new system was used to analyze steel samples and to study applicability as a process control analytical method from the viewpoints of improved trace element determination accuracy and shortened analytical time[5]. As examples of use of this method in determining particular elements, the optimum conditions to electrolyze and analyze difficult-to-dissolve titanium compounds for titanium were investigated, and its application to the high-sensitivity determination of sulfur was studied.

2. Description of Rapid Steel Sample Electrolyzer

To determine a trace element with high accuracy, it is necessary to prepare a sample solution in which the analyte element is dissolved in a high enough concentration. To eliminate the physical, chemical, and optical interference effects of the matrix element iron, it is also important to match the matrix element concentration of the sample solution with that of the standard solution (this operation is termed matrix matching).

The trial fabrication of the rapid steel sample electrolyzer aimed at achieving the functions of not only rapidly dissolving a sample, but also preparing with good reproducibility sample solutions of concentration high enough for determining the trace elements with high accuracy.

The prototype rapid steel sample electrolyzer is schematically depicted in **Fig. 1**. The functions of the specific parts are explained according to the operating procedure.

(1) Setting of sample

The sample is set with its polished surface facing upward in the electrolytic cell. The air cylinder is lowered to fix the sample. A platinum wire contacts the sample to ensure the electrical continuity between the sample and the electrolyzer.

(2) Feeding of electrolyte

The electrolyte is fed at a constant rate by the constant-flow rate pump into the electrolytic cell.

(3) Electrolyzing

The sample is electrolyzed by taking it as the working electrode and the graphite built into the cell as counterelectrode. The potential is measured as potential difference with respect to the reference electrode.

(4) Analyzing

The solution obtained by the electrolysis of the sample has the undissolved residue removed by the line filter (made of Teflon with 10 μm pore size) and flows into the sampling tube. The excess solution overflows as drainage. The tube is continuously filled with the fresh electrolyte. This fresh electrolyte is drawn by the ICP-AES nebulizer and analyzed. The part of the sampling tube where the electrolyte collects measures 5 mm in inside diameter, 25 mm in depth, and 0.5 mL in inner volume.

(5) Cleaning

Cleaning water is fed by the constant-flow rate pump into the electrolytic cell and piping. The piping is entirely constructed of Teflon tube (1 mm in inner diameter and 2 mm in outer diameter). Joints are also made of Teflon.

The series of operations after the setting of the sample is automatically controlled by a personal computer system.

The electrolytic cell is the most important part of the electrolyzer and is designed with the following considerations taken into account:
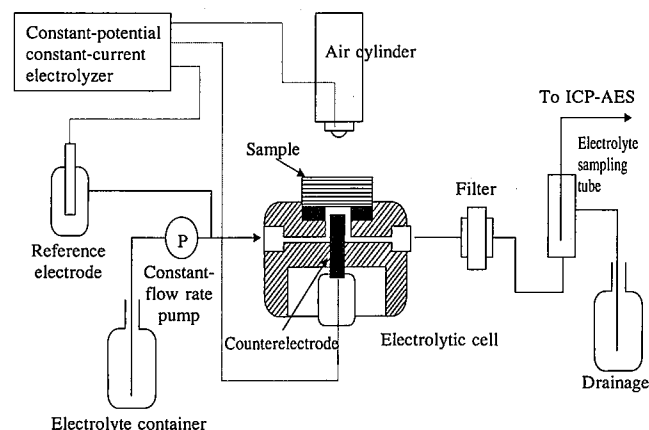

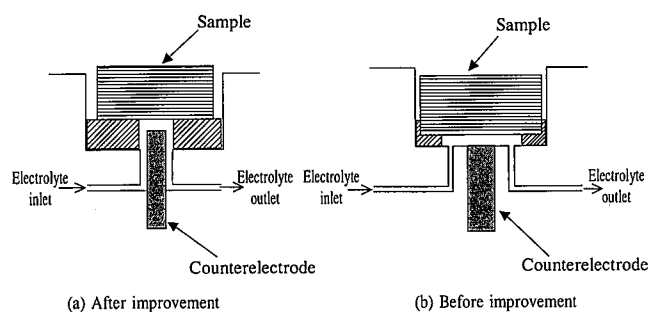Fig. 1 Schematic illustration of rapid steel sample electrolyzer

(a) After improvement   (b) Before improvement

Fig. 2 Schematic illustration of electrolytic cell

Table 1 ICP emission analysis conditions

Radio frequency output (kW)	1.2
Coolant gas flow rate (L/min)	10.5
Plasma gas flow rate (L/min)	1.5
Carrier gas flow rate (L/min)	1.0
Purge gas flow rate (L/min)	4.0
Integration time (s)	15

Table 2 Analytical line wavelengths (nm)

	Simultaneous multielement spectrometer	Sequential type spectrometer
Fe	259.94	438.36
Si	251.61	251.61
Mn	257.61	257.61
Ni	231.60	231.60
Cu	327.40	327.40
Al	396.15	396.15
Ti	334.94	334.94
Cr	367.72	267.72

(1) Stable control of electrolysis

(2) Rapid replacement of electrolyte

The cell shown in **Fig. 2**(b) was first fabricated and used in electrolytic experiments. It was found to be unable to control electrolysis. This problem was attributed to the insulation provided by the hydrogen gas generated by electrolysis in the cell. Change to the structure shown in **Fig. 2**(a) solved the problem. In the cell of **Fig. 2**(a), the incoming electrolyte is supplied in contact with the counterelectrode to the sample surface while sweeping out the bubbles formed in the cell. This condition is considered to ensure electrical continuity between the electrodes. The sample electrolysis area of the electrolytic cell shown in **Fig. 2**(a) is 10 mm in diameter, the electrode gap is 1 mm, and the inner volume is about 0.08 mL.

3. Analysis of Steel Samples

Cylindrically shaped steel samples, measuring about 30 mm in diameter and 10 to 30 mm in height, were used after polishing the bottom surface.

A 1:1 hydrochloric aid-water solution or 1:1:2 hydrochloric acid-nitric acid-water solution was used as the electrolyte. The electrolyte was supplied at a flow rate of 5 mL/min to the electrolytic cell, and electrolysis was conducted at constant current or potential. The temperature was room temperature for both the sample and the electrolyte.

A Shimadzu Model GVM-1000P simultaneous multielement vacuum-type spectrometer or Horiba Model PS-1000 sequential-type spectrometer was used as the ICP-AES spectrometer. The ICP-AES analytical conditions and analytical lines are listed in **Tables 1** and **2**, respectively.

Standard solutions were prepared by dissolving 0.3 or 0.5 g pure iron (99.99% Fe made by Johnson-Massay) in a 20 mL acid solution of the same composition as the electrolyte, adding standard solutions (made by Wako Pure Chemical Industries) for the atomic absorption spectroscopy of individual trace elements, and diluting to 100 mL with the acid solution. From analysis of two sets of standard solutions with different iron concentrations, analytical curves at the specific iron concentrations were prepared. These analytical curves were used to suit the electrolyte iron concentration that varies with the electrolytic conditions.

4. Experimental Results and Discussion

4.1 Sample electrolysis reproducibility and analytical time

One sample was analyzed five times to determine change with time in the iron emission intensity when it was electrolyzed at a constant current of 1.5 A (current density of 1.9 A/cm²) using the 1:1 hydrochloric acid-water solution as the electrolyte. The results are shown in **Fig. 3**. The simultaneous multielement spectrometer was used as the ICP-AES spectrometer, and the analysis was conducted in parallel with the electrolysis.

As can be seen from **Fig. 3**, the iron emission intensity stabilized about 30 s after the start of electrolysis. The iron concentration determined at this point of time was an average of 4.96 w/v% (relative standard deviation of 1.8%). Analytical values that agree well with the values calculated from the amount of coulomb counting were obtained with good reproducibility. Similar results were obtained for other trace elements.

Based on these results, the emission intensity 30 to 15 s after the start of electrolysis was integrated when the simultaneous multielement spectrometer was used. **Fig. 4** shows the processing flow of this analytical method. About 10 s were required to fill the electrolytic cell with the electrolyte. When the electrolytic cell was washed with water for about 20 s after the end of one analysis, the memory effect was prevented from working for the next analysis.
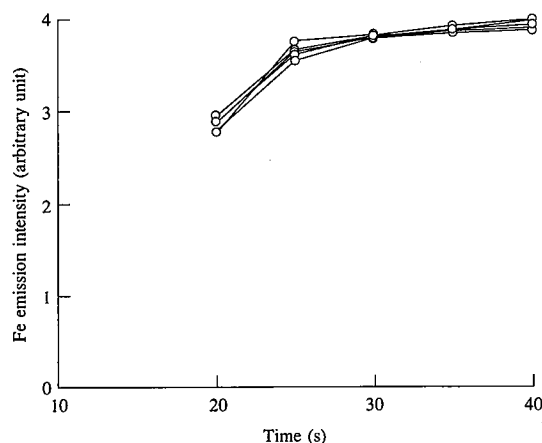

Fig. 3 Changes with time in iron emission intensity and reproducibility in constant-current electrolysis
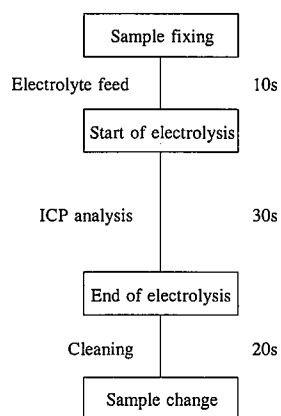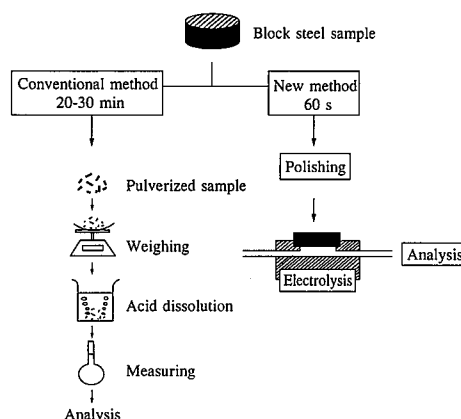
Fig. 4 Analytical processing flow

Fig. 5 Comparison of new and conventional ICP-AES methods for steel samples

The analytical time, including these operations, was about 60 s and was short enough to achieve rapidity as demanded for process control analysis. The new ICP-AES method is compared with the conventional manual ICP-AES method in **Fig. 5**. As is evident from **Fig. 5**, the new ICP-AES method is by far faster and simpler than the conventional manual ICP-AES method.

4.2 Analytical results

Table 3 lists the analytical results of Iron and Steel Institute of Japan certified reference materials (JSS). The samples were electrolyzed in the 1:1 hydrochloric acid-water solution flowing at a rate of 5 mL/min and at a constant current of 1.5 A (current density of 1.9 A/cm²).

As is evident from **Table 3**, the determined value of each element agreed relatively well with the certified value. Except for the high-content regions where some elements have somewhat large relative standard deviations, the new ICP-AES method provides repeatability equivalent to that of the conventional manual ICP-AES method, especially in the low-content regions.

Although not shown in **Table 3**, silicon was determined as successfully as the other metallic elements when its content was a high 3 mass%. As one example, a sample whose silicon content was determined to be 3.17% by gravimetry was analyzed to contain

3.22 mass% silicon by the new ICP-AES method with a relative standard deviation of 1.8%. When such a high-silicon sample is acid dissolved, it is hydrolyzed and precipitated, and is not directly amenable to ICP-AES. Its residues must be analyzed, or it must be separately analyzed by gravimetry. The new ICP-AES system did not have the precipitation of silicon probably because it electrolyzed the samples in hydrochloric acid at room temperature.

The titanium contents determined by the new ICP-AES method as given in **Table 3** are much lower than the certified values of the reference materials JSS 1003-1 and JSS 168-6. This is probably because titanium-bearing precipitates were not dissolved under the above-mentioned electrolytic conditions. For these materials, pulverized sample was taken from the block sample, dissolved in the 1:1 hydrochloric acid-water solution or 1:1:2 hydrochloric acid-nitric acid-water solution. The resultant sample solution was analyzed by the conventional manual ICP-AES method. The analyzed results are included in **Table 3**. The titanium in these samples is considered to exist as compounds like titanium carbide (TiC) or titanium nitride (TiN), which are not completely soluble in the 1:1 hydrochloric acid-water solution at room temperature and under heating.

Table 3 Analytical results of steel samples

Sample		Si	Mn	Ni	Cu	Al	Ti	Cr
JSS162-2	Certified value	0.50	0.098	0.31	0.042	0.015	-	0.30
	Result of new ICP-AES method	0.51	0.094	0.31	0.039	0.013	-	0.31
	Relative standard deviation (%)	1.6	4.1	4.1	2.1	10.2	-	5.8
JSS163-2	Certified value	0.21	0.57	0.11	0.10	0.026	-	0.10
	Result of new ICP-AES method	0.21	0.58	0.10	0.10	0.025	-	0.10
	Relative standard deviation (%)	1.9	2.2	1.9	3.8	4.9	-	3.0
JSS168-6	Certified value	0.21	0.41	0.015	-	0.044	0.078	0.011
	Result of new ICP-AES method	0.21	0.41	0.015	-	0.043	0.001	0.010
	Relative standard deviation (%)	1.6	1.8	1.8	—	2.8	16.4	5.3
Manual sample preparation ICP-AES method	HCl*1	0.22	0.42	0.016	-	0.043	0.006	0.004
	HCl+HNO3*2	0.22	0.42	0.016	-	0.046	0.077	0.010
JSS1003-1	Certified value	0.048	0.097	-	-	0.015	0.006	-
	Result of new ICP-AES method	0.044	0.096	-	-	0.012	0.001	-
	Relative standard deviation (%)	1.8	1.6	-	-	1.9	6.6	-
Manual sample preparation ICP-AES method	HCl*1	0.049	0.096	-	-	0.014	0.005	-
	HCl+HNO3*2	0.049	0.094	-	-	0.014	0.006	-

Electrolytic conditions: Constant-current electrolysis (1.9 A/cm²) ; Electrolyte: 1:1 hydrochloric acid-water solution
*1 : HCl (1+1), *2 : HCl+HNO₃+H₂O (1+1+2)

The new ICP-AES method basically analyzes only for what are called acid-soluble components. Some of the precipitates and inclusions contained in steels can be handled as acid-soluble components, depending on acid composition and heating conditions as noted above. The ability of the new ICP-AES method, characterized by rapid sample dissolution by electrolysis at room temperature, to determine elements comprising such difficult-to-dissolve compounds was studied as described below.

4.3 Study of electrolyte composition and electrolytic potential

In the above-mentioned constant-current electrolysis, the sample potential was about 0.2 V (vs a Ag/AgCl reference electrode). The dissolution of precipitates and inclusions in the sample are influenced by the electrolyte composition and the electrolytic potential.

First, constant-current electrolysis was performed by switching the electrolyte to the 1:1:2 hydrochloric acid-nitric acid-water solution. The changes with time in the sample potential (vs. the Ag/AgCl reference electrode) and in the iron and titanium emission intensities are shown in **Fig. 6**. As can be seen from **Fig. 6**, the sample potential rose from about 1.5 V to the neighborhood of 3 V during the electrolysis. Beyond this boundary, the titanium emission intensity temporarily increased, and the iron emission intensity diminished. This sudden potential rise may be attributed to the passivation of the sample surface in the electrolyte containing nitric acid. The titanium compounds left undissolved on the sample surface were presumably electrolyzed instantaneously as the potential rose. Since the electrolysis of the sample itself stopped after the passivation of the sample surface, it was difficult to accurately determine each element in the sample. This experimental result was thought to indicate the need for controlling the electrolytic potential at an optimum level.

Next, constant-potential electrolysis was conducted by using both the 1:1 hydrochloric acid-water solution and the 1:1:2 hydrochloric acid-nitric acid-water solution as the electrolytes and changing the potential, and ICP-AES analysis was then performed. The samples were the reference materials JSS 165 to 170. This experiment used the sequential type spectrometer, sampled the electrolyte after electrolysis for a certain time, introduced the electrolyte into the spectrometer, and analyzed it.

The titanium contents thus determined are given in **Table 4**. As indicated by the results, an electrolytic potential of 0.5 V or less

yielded lower values. As the electrolytic potential was raised, the analyzed titanium content of the samples that had exhibited lower values approached the certified value. In each electrolyte, the titanium content determined for each sample was almost satisfactory when the electrolytic potential ranged from 0.8 to 1 V. The average of the relative error with respect to the certified value was 13.9% and 8.6% for the electrolyte containing only hydrochloric acid and the electrolyte containing both hydrochloric acid and nitric acid, respectively. This suggests that the electrolyte containing both hydrochloric acid and nitric acid favors the more complete dissolution of titanium-bearing compounds as compared with the electrolyte containing only hydrochloric acid. The correlation coefficient between the determined value and the certified value was the best, 0.9986, at the electrolytic potential of 1 V when the electrolyte was the 1:1:2 hydrochloric acid-nitric acid-water solution (refer to **Fig. 7**).

4.4 High-sensitivity determination of sulfur in steel

Sulfur in a steel usually exists in the form of the nonmetallic inclusion MnS and adversely affects the properties of the steel, as exemplified by drops in ductility and toughness, deterioration of hot workability, and degradation of corrosion resistance. For this reason, the sulfur content is reduced to a very low level of 10 μg/g for some steel grades. These ultralow-sulfur steels are analyzed for sulfur by hydrogen sulfide vaporization, separation and absorption spectrophotometry and combustion-infrared absorption spectroscopy, but not usually by ICP-AES.

Table 4 Titanium determinations (mass%) when constant-potential electrolysis was applied*

Sample potential (V vs. Ag/AgCl)	JSS sample No. (certified value)					
	165-2 (0.013)	166-2 (0.089)	167-2 (0.26)	168-6 (0.078)	169-6 (0.012)	170-6 (0.103)
0.1	0.004	0.080	0.29	0.010	0.002	0.002
	-	-	-	-	-	-
0.5	0.006	0.085	0.29	0.069	0.009	0.079
	0.005	0.083	0.30	0.064	0.002	0.034
0.8	0.009	0.087	0.28	0.070	0.010	0.087
	0.010	0.089	0.29	0.072	0.011	0.104
1.0	-	-	-	-	-	-
	0.008	0.088	0.28	0.076	0.010	0.101

*Upper and lower rows present determined values when 1:1 HCl-H₂O solution and 1:1:2 HCl-HNO₃-H₂O solution were used as electrolytes, respectively.
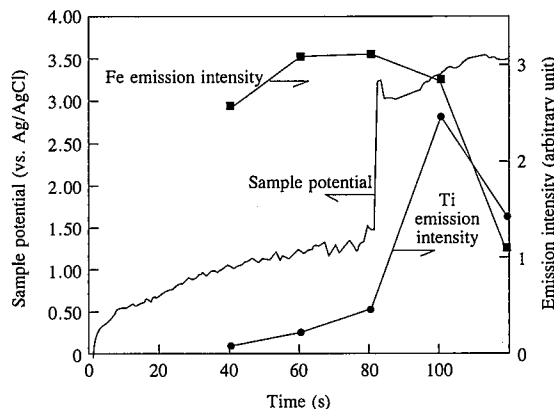

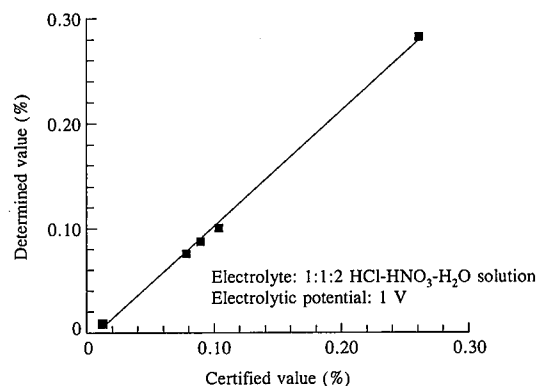Fig. 6 Changes with time in sample potential and iron and titanium emission intensities

Fig. 7 Titanium determined by using constant-potential electrolysis

ICP-AES is generally very sensitive to metallic elements, but not always highly sensitive to nonmetallic elements. Arsenic, selenium, and antimony are reduction reacted in an aqueous solution to form hydrides, which are introduced into the plasma to enhance their detection sensitivity (this method is called the gas-phase sample introduction method)[6,7]. As far as sulfur is concerned, it is reported that when the sulfur in the sample is oxidized to sulfonic ions during the dissolution of the sample and when hydrogen sulfide is generated in a reducing solution and introduced into the plasma, the sample introduction efficiency is enhanced and the analytical sensitivity is sharply increased[8].

The new ICP-AES method performs the entire process from the electrolysis of the sample to the introduction of the electrolyte into the plasma in a closed system. If it directly analyzes the hydrogen sulfide generated under the action of hydrochloric acid, it is considered to be capable of determining the sulfur in steel with high speed and sensitivity. Based on this, the determination of steel sulfur by the new ICP-AES method and the effect of elements coexisting in the sample were studied.

The ICP-AES analytical conditions were the same as described in Chapter 3. The analytical lines used were 259.94 nm for iron and 180.73 nm for sulfur. The 1:1 hydrochloric acid-water solution was mainly used as the electrolyte. For the purpose of comparison, some experimental runs were performed using a 1:2:3 hydrochloric acid-nitric acid-water solution as the electrolyte. The electrolyte was fed at a rate of 3.3 to 5 mL/min and was galvanostatically electrolyzed at room temperature and at a current of 1 A (current density of 1.3 A/cm²). The electrolyte was not introduced into the plasma in the form of the gas phase alone after separation into the gas and liquid phases, but the sample was electrolyzed and filtered, and the electrolyte flowing into the sampling tube was then drawn by the nebulizer, atomized and analyzed.

4.4.1 Relationship between sulfur content and sulfur/iron emission intensity ratio I (S/Fe)

When the 1:1 hydrochloric acid-water solution was used as the electrolyte, a good linear relationship was observed between the sulfur/iron emission intensity ratio I(S/Fe) and the sulfur concentration of the sample as shown in **Fig. 8**. Some samples yielded very low values. This will be discussed in the next section. **Fig. 8** also shows the analytical results obtained when a standard solution containing sulfur as sulfonic ions was diluted to match the sulfur concentration with the sulfur concentration of the steel sample. Comparison of the slope of the analytical curve of the new ICP-AES method with that of the sulfonic ion analytical curve shows that the new ICP-AES method can detect sulfur with very high sensitivity.

When the 1:2:3 hydrochloric acid-nitric acid-water solution was used as the electrolyte, the sulfur detection sensitivity was not as high as noted above, but dropped to almost the same level as indicated by the sulfonic ion analytical curve.

The sulfur determinations made by the new ICP-AES method are given in **Table 5**. From **Table 5**, it is evident that high accuracy is obtained in such low sulfur concentrations as 25 μg/g.

Sulfur in steels is considered to exist as manganese sulfide (MnS) and ferrous sulfide (FeS). These sulfur compounds easily produce hydrogen sulfide (H_2S) when dissolved in hydrochloric acid. Hydrogen sulfide is a gas, but is dissolved in water to 0.1 mol (M) to form hydrogen sulfide water. Hydrogen sulfide is weakly acidic and easily absorbed in alkaline solutions, but its solubility is thought to be low in strongly acidic solutions like the 1:1

hydrochloric acid-water solution. If a steel sample with a sulfur concentration of 1,000 μg/g is electrolyzed under the conditions of this experimental work, the hydrogen sulfide concentration of the electrolyte is of the order of 10^{-4} M at most. It is thus presumed to be very likely that the hydrogen sulfide evolved from the sample is entirely dissolvable in the 1:1 hydrochloric acid-water solution.

In this experimental study, hydrogen gas is produced at the counterelectrode during electrolysis, transported in contact with the electrolyte into the sampling tube, and separated from the electrolyte in the sampling tube. Here the hydrogen gas was removed out of the system, and the electrolyte alone was introduced into the plasma. At this point of time, the hydrogen sulfide generated from the sample was dissolved in the electrolyte. This hydrogen sulfide is presumed to have gasified the instant the electrolyte was injected into the spray chamber and to have been introduced into the plasma with high efficiency. Of the solution sample introduced into the spray chamber, only a few percent reaches the plasma.

The determination of sulfur by the new ICP-AES method has many outstanding characteristics as compared with the conventional hydride-generating ICP-AES method. Among such features are: (1) the new ICP-AES method uses no reducing agents and involves no complicated reduction reaction steps; (2) it introduces the sample not in the gaseous form, but sprays the sample in the solution form, so that it can determine sulfur with high sensitivity at the same time as metallic elements; and (3) it is free from the unstabilization of the plasma by the hydrogen gas. From the standpoint of analytical time, the new ICP-AES method can analyze samples in the block form, so that it has rapidity and simplicity comparable to those of spark emission spectroscopy.
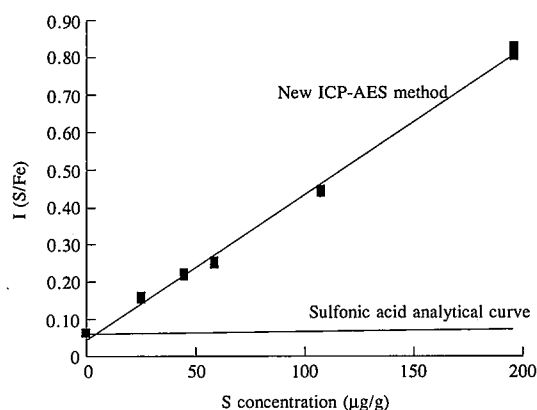

Fig. 8 Steel sulfur determined by new ICP-AES method

Table 5 Sulfur determined by new ICP-AES method* (μg/g, n = 3)

Sample	Certified value	Average value	Standard deviation
JSS1001-1	25	25.8	0.80
JSS1003-1	58	56.3	0.81
Sample "f"	195	207.0	3.82

*Electrolyte: 1:1 HCl-H₂O solution

4.4.2　Effects of coexisting elements

As described in 4.4.1, some samples exhibited abnormally low values. This problem was considered to be attributable to the effects of the coexisting elements in the samples.

One such effect is the sulfide ions that react with metal ions to form metal sulfides, which in turn reduces the generation of hydrogen sulfide. If the metal M exists with the oxidation number 2 in hydrochloric acid, the possible reactions in which the metal ions and sulfide ions are involved may be expressed as follows:

$$M^{2+} + S^{2-} = MS \downarrow \qquad \cdots\cdots(1)$$
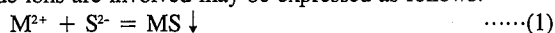
where the solubility product $S = [M^{2+}][S^{2-}]$.

Side reactions of M^{2+}

$$M^{2+} + Cl^- = MCl^+ \qquad \cdots\cdots(2)$$
$$MCl^+ + Cl^- = MCl_2 \qquad \cdots\cdots(3)$$

Side reactions of S^{2-}

$$S^{2-} + H^+ = HS^- \qquad \cdots\cdots(4)$$
$$HS^- + H^+ = H_2S \qquad \cdots\cdots(5)$$

Of the metal sulfides, copper sulfide (CuS) has a very small solubility product of $10^{-34.4}$ M^2. If copper is present in excess of a particular concentration, it may precipitate as CuS in hydrochloric acid. For the analytical samples in this experimental work, the copper and sulfur concentration product p[Cu][S] ($= -\log[Cu][S]$) in the electrolyte under the analytical conditions were calculated. The results are listed in **Table 6**. In **Table 6**, the samples are arranged in decreasing order of p[Cu][S]. The sulfur detection intensity was abnormally low for the three samples below the dotted line. This shows that when attention is focused on the copper concentration, a sample exhibits an abnormal value when its copper and sulfur concentration product is p[Cu][S] <10.

From the side reactions (2) to (5), increasing the hydrochloric acid concentration is predicted to inhibit the formation of metal sulfides. When the sample JSS 1002-1 and the sample "g" that exhibited normal values and the sample "e" that exhibited an abnormal value were analyzed by using 12N hydrochloric acid as the electrolyte, the sample "e" was confirmed to lie on the same straight line as the other two samples as shown in **Fig. 9**.

The experiments reported here were all run at room temperature. Since the solubility product is also affected by temperature, the formation of copper sulfide may be preventable by raising the temperature. This possibility will be studied in the future.
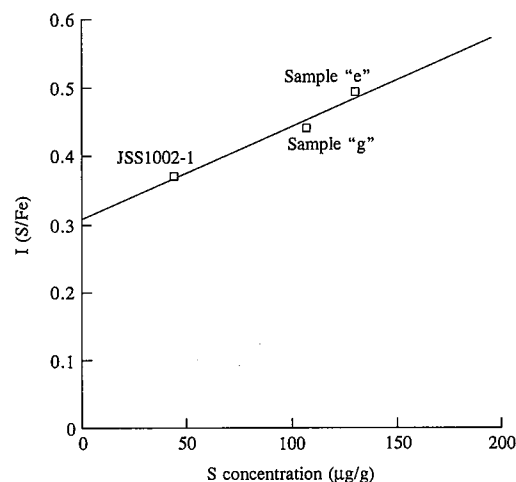

Fig. 9 Analytical results obtained when 12N hydrochloric acid was used as electrolyte

5. Conclusions

An ICP-AES system was built for the electrolysis of samples and applied to the analysis of block steel samples. The following findings were obtained:

(1) The analytical time is about 60 s and short enough for the new ICP-AES method to be applied to the process control analysis of steelmaking processes.

(2) The new ICP-AES method is as accurate as the conventional manual sample preparation ICP-AES method.

(3) Elements like titanium that may exist as difficult-to-dissolve compounds in samples can be determined by judicious selection of the electrolyte composition and electrolytic potential.

(4) Sulfur can be determined with high sensitivity.

If the electrolytic conditions are selected to suit specific steel grades and purposes, the new ICP-AES system is considered to be applicable to a wide spectrum of steels, including carbon steels.

Regarding titanium and aluminum contained as oxides in samples, the possibility of electrolyzing and analyzing such oxides by the new ICP-AES system will be studied in the future.

Table 6 Copper and sulfur concentration product p[Cu][S]

Sample	Concentration in steel (µg/g)		Concentration in electrolyte (µM)		$-\log[Cu][S]$
	Cu	S	[Cu]	[S]	
JSS1001-1	20	25	1.1	2.7	11.5
JSS1002-1	20	44	1.1	4.8	11.3
JSS1004-1	10	88	0.6	9.6	11.3
JSS1003-1	20	58	1.1	6.3	11.2
Sample "a"	50	50	2.8	5.5	10.8
Sample "g"	40	107	2.2	11	10.6
Sample "b"	110	50	6.1	5.5	10.5
Sample "f"	60	195	3.3	21	10.2
Sample "c"	510	50	28	5.5	9.8
Sample "d"	1,040	50	57	5.5	9.5
Sample "e"	3,010	130	166	14	8.6

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