Determination of Ultra Low Content of Carbon in Iron by Ion-Chromatography[†]

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A study on the determination of ultra low content of carbon was made by using ion-chromatography, coupled with the combustion method in oxygen gas stream. The considerable increase in the variation of conductivity with the content of carbonate ion was observed because of the high ionic conductivity of OH^- in the NaOH eluent. The Na^+ (OH^-) ion could be removed by a cation exchange column according to the reaction: $\text{R-H}^+ + \text{NaOH} \rightarrow \text{R-Na}^+ + \text{H}_2\text{O}$. Therefore, carbonate ions in NaOH absorbent, which absorbed CO_2 gas produced by the reaction of carbon in metal with oxygen gas, could be concentrated on the concentration column. It was found that 1.67 mass ppm of carbon in pure iron sample was determined within the accuracy of 0.24 mass ppm of standard deviation.

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I. Introduction

In recent years, the quantitative analysis for the impurity elements with ultra low content has been increasingly important in producing high quality materials. The content of carbon in metals is determined by the infrared absorptiometry, the coulometric titration⁽¹⁾, and the spectrophotometry⁽²⁾⁽³⁾, coupled with the combustion method in oxygen gas stream. In these methods, however, the sensitivity of detector and the fluctuation of carbon content in standard samples used for the calibration have the direct influence on the accuracy of analytical value. The ion-chromatography with a conductmetric detector is characterized by the selective separation of an objective ion from solution containing various ions.

The present authors⁽⁴⁾ previously reported that 1 mass ppm of nitrogen in metal or slag could be accurately determined by using the ion-chromatography coupled with steam distillation method. In this investigation, the analytical method for the ultra low content of carbon in metals was studied using the ion-chromatography, in which the NaOH absorbent for CO_2 gas obtained by the combustion method in oxygen gas stream and the Na_2CO_3 standard solution for calibration were used. These results were compared with those obtained by oxygen gas fusion-infrared absorptiometry.

II. Experimental

1. Combustion apparatus

The schematic diagram of a heating furnace and flow-path of oxygen gas is shown in Fig. 1. The horizontal

resistance furnace with SiC heating elements was used for the reaction between carbon in metal sample and oxygen gas. The temperature was kept at 1573 ± 2 K by a PID controller. The CO and CO_2 in oxygen gas were removed by using Pt-Pd alloy (1023 K), soda-lime, and 10% NaOH solution, and moisture was trapped by silica-gel. An alumina boat, which was heated at 1573 K in air before measurements, contains 0.5 ~ 1 g of metal sample and 1 g of Sn flux. This boat was heated under the atmosphere of oxygen gas flowing. The exhaled CO_2 was moved to the absorption cell by oxygen carrier gas. Then, gas was dispersed by using a glass filter (G3, open pore size: 40 ~ 100 μm) and absorbed by NaOH absorbent. The oxygen gas was stopped after a desirable duration and immediately the absorbent was sucked into the ion-chromatography using a teflon tube.

2. Ion-chromatography

The flow diagram of the ion-chromatography system is illustrated in Fig. 2. The apparatus consist of an eluent pump (TOA electronics Ltd., ICA-3010), a column oven (ICA-3051), a conductmetric detector (ICA-3030), and an auto concentrator (ICA-5311). Data acquisition and peak integration were carried out by means of a personal computer equipped with a data processor (Nihon Chromato Industry, CDS-86).

Ion separation was made by using an anion-exchange resin in a separation column (TOA Electronics Ltd., PCI-201S ($\phi 4.6 \times 100$ mm, 5×10^{-5} eq. capacity)) and a guard column (PCI-201SG) which was made from a polyacrylate gel containing a NR_3^+ functional group. The later column (PCI-201SG) was also used for ion concentration.

The carbonate ion in the sample solution flowed by a pump was adsorbed on the concentration column. The volume of the "concentrated" sample solution was controlled by the pumping duration. However, the OH^- ion

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Fig. 1 Flow Sheet of the combustion system.

Fig. 2 Flow Sheet of the ion-chromatograph system.

in NaOH solution, which was used for a CO₂ absorbent, disturbed the adsorption of the carbonate ion on the concentration column. In this investigation, a cation exchange resin in a separation column (TOA Electronics Ltd., PCI-305SG) was inserted before the concentration column in order to remove the OH⁻ ion according to the following reaction given:

The flowing path of valve was changed automatically after a given duration. Then, the carbonate ion adsorbed on the concentration column was carried to the separation column (315 ± 0.1 K), followed by the separation

from the other anions. The variation of conductivity with time was measured by a conductmetric cell controlled at 318 ± 0.1 K. The amount of carbonate ion was calculated by integrating the value for the conductivity using a data processor.

The CO₂ absorption into the eluent from the atmosphere was prevented by using the bottle with a soda-lime tube. Furthermore, the uniform composition of the eluent was obtained by a magnetic stirrer. The analytical reagent grade Na₂CO₃ (99.9 mass%) was dissolved in an ultra pure H₂O (>17.8 MΩ·cm) degassed by an ultra sonic vibrator and aspirator, and the solution was diluted for making the carbonate standard solution.

III. Results and Discussion

1. Selection of eluent

Hironaka *et al.*⁽⁵⁾ measured the content of carbonate ion in river water by ion-chromatography using the eluent containing 4×10^{-4} mol of trimellitic acid (benzene-1,2,4-tricarboxylic acid). However, the detection limit in their method is not acceptable for the present analysis of carbon content. It should be noted that in the analysis using ion-chromatography the selection of eluent component is of crucial importance for the determination of ultra low content of carbon.

The limiting equivalent conductivity of trimellitic and p-hydroxybenzoic acids, which were used for the analysis of carbonate ion by ion-chromatography, was reported as 54.6 and 32.4 S·cm²·mol⁻¹⁽⁶⁾, respectively. The sensitivity of the signal detected by the conductmetric cell using those eluents is too low to determine the ultra low content of carbon because of the small difference in limiting equivalent conductivity between those eluent components and carbonate ions (CO₃²⁻: 69.3 S·cm²·mol⁻¹, HCO₃⁻: 44.5 S·cm²·mol⁻¹).

Fig. 3 Chromatograms of carbonate ion in the solution containing various amounts of NaOH.

Therefore, NaOH having high limiting equivalent conductivity ($198.3 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) was adopted for the eluent component. Five vol pct of methanol was added to maintain the ability of anion-exchange resins.

The effect of NaOH content in the eluent on the conductivity was studied by use of the standard solution containing 0.50 ppm of carbon. The difference in conductivity, $\Delta\kappa$, is plotted against time in Fig. 3, in which the higher value for $\Delta\kappa$ implies the lower conductivity. The area corresponding to the amount of carbonate ion was calculated by a data processor. With increasing NaOH content in the eluent, the peak of carbonate ion is shifted to a shorter retention time, and overlapped to the peak obtained by the other ion at 0.002 mol NaOH. This

Fig. 4 Calibration line of carbon.

results in the inaccuracy of the analysis for the carbonate ion. Thus, the content of NaOH was chosen to be 0.0016 mol from the result shown in Fig. 3.

A calibration line obtained by using the Na_2CO_3 standard solution is shown in Fig. 4. These results were obtained at the concentrated volume of 1 cm^3 . The area at $C=0$ ppm, which corresponds to the blank in this method, was $0.213 \pm 0.004 \text{ V} \cdot \text{s}$. The results obtained by using the eluents containing 0.0015 mol of p-hydroxybenzoic acid (+0.0015 mol of N, N-Diethylethanolamine) and 4×10^{-4} mol of trimellitic acid are also shown in Fig. 4. It can be seen that the sensitivity using NaOH is higher than those using the other eluent components.

2. Effect of cation exchange column

The CO_2 gas produced by the combustion of carbon in a sample with O_2 gas stream was absorbed to the NaOH absorbent solution. A cation exchange column was inserted to the flowing path of sample solution between the concentration column and the pump in order to remove Na^+ ion in absorbent according to eq. (1). The effect of the cation exchange column on the relation between the area obtained by ion-chromatography and the NaOH content in the absorbent was studied by using the solution containing a constant amount of the carbonate ion and various amounts of NaOH. These results are shown in Fig. 5, where the value for the area, ΔArea , indicates the difference in the peak area obtained by sample from that by the solution without carbonate ion. In the measurements without a cation exchange column (+ mark) and with that of low exchange capacity (PCI-301 SG) (Δ mark), the OH^- ion remained in the solution by the presence of the Na^+ ion was found to disturb the adsorption of carbonate ion on the concentration column. In the measurements using a cation exchange column with high exchange capacity (PCI-305SG) ($\circ$ $\bullet$ marks), the Na^+ ion (OH^- ion) in the solution containing up to

Fig. 5 Relation between area and NaOH content in absorbent using different cation exchange column.

0.005 mol of NaOH can be removed at the flow rate of 2 cm³/min. It can be concluded, therefore, that the desirable NaOH content in the absorbent is 0.005 mol at the flow rate of 2.0 cm³/min.

3. Efficiency of concentration

The volume of sample solution carried to the concentration column can be controlled by the duration from the beginning to the valve change and by the flow rate of the auto concentrator as shown in Fig. 2. An increase in the volume of the concentrated sample solution can be expected to have the same effect on the ultra micro analysis as is observed in an increase of the sample weight. The value for the area obtained using 0.005 mol NaOH solution with 1.0 ppm C is plotted against the volume of the concentrated solution at 2.0 cm³/min of flow rate in Fig. 6. A good linear relation is observed up to 3 cm³ of the concentrated solution.

4. Stability of absorbent

The result for the absorption of CO₂ from atmosphere into 10 cm³ of the NaOH absorbent is shown in Fig. 7. Although the absorbent with the higher NaOH content can absorb a larger amount of CO₂, it is easily affected by atmosphere, as is clear from Fig. 7. The results shown in Figs. 5 and 7 suggest that the absorbent containing 0.005 mol NaOH is effective in analyzing the ultra low content of carbon.

5. Effect of flow rate of oxygen gas

In the combustion system shown in Fig. 1, oxygen gas was flowed at 100~200 cm³/min without a sample. The amount of carbonate ion, which was absorbed to 39.6 cm³ of 0.005 mol NaOH absorbent in the cell, increased linearly to the total oxygen gas volume regardless of the oxygen gas flow rate. This indicates that the total volume of oxygen gas, that is, the constant values for the oxygen flow rate as well as the flowing time should be

Fig. 6 Relation between area and volume of concentrated solution.

Fig. 7 Variation of CO₂ absorption from atmosphere with time.

Fig. 8 Effect of flow rate of oxygen gas on carbon content.

maintained.

The variation of measured carbon content with oxygen gas flow rate was studied by using the standard reference material of steel (The Iron and Steel Institute of Japan, JSS 200-9). The results are shown in Fig. 8. These results are obtained under the conditions of 39.6 cm³ of the absorbent volume, 20 min of the duration of oxygen gas flowing, and 1.0 cm³ of the volume of the concentrated sample solution. Since the bubbles in the absorption cell became large at a high flow rate of oxygen gas, CO₂ gas cannot be absorbed completely, thus leading to the lower carbon content. At low flow rate of oxygen gas, the replacement of exhaled CO₂ gas by oxygen carrier gas is so slow that the analyzed values for carbon content are scattered. The certified carbon content (83.5 ± 3.0 mass ppm) is indicated by an arrow. It can be seen from Fig. 8 that the proper range of oxygen gas flow rate is 100~200

Fig. 9 Effect of absorbent volume on carbon content.

cm³/min. Two or more glass filters are considered to be useful for the prevention of the coagulation of gas bubbles, which result in the decrease of the combustion time, that is, the duration of oxygen gas flowing.

6. Effect of absorbent volume

The relationship between the absorbent volume and the analyzed carbon content obtained by using two standard reference materials (The Iron and Steel Institute of Japan, JSS 200-9 and JSS 003-3 (11.2 ± 1.2 mass ppm)) is shown in Fig. 9. The sample weight and the concentrated volume were 0.5 g and 1.0 cm³, respectively, for the former standard reference material, and were 1.0 g and 2.0 cm³, respectively, for the latter one. The oxygen gas was flowed at 150~160 cm³/min for 20 min. The constant values for the analyzed carbon content were obtained by using more than 39.6 cm³ of absorbent. The effect of absorbent volume on CO₂ absorption is considered to be due to the depth of absorbent, which is related to the time for flotation of CO₂ bubbles in absorbent. The minimum depth of absorbent was calculated to be 220 mm under the inner diameter of an absorption cell (16 mm) and the volume of glass filter. In order to increase the time for flotation of bubbles in an absorbent, the absorbent was stirred at 50~300 r.p.m. using a magnetic stirrer. However, the analyzed carbon content was not affected by stirring. On the contrary, it decreased at high stirring speed due to the coagulation of bubbles.

7. Analysis of standard reference materials

The results for the carbon analysis of the standard reference materials of steels supplied by the Iron and Steel Institute of Japan and LECO Corporation, a pure iron, and tin are summarized in Table 1, along with those

Table 1 Comparison of carbon content in metal by ion-chromatography with that by oxygen gas fusion-infrared absorptiometry.

	Certified value	Infrared absorptiometry			This work		
		n	R	Average	n	R	Average
JSS 003-3	11	9	2.8	11.4 ± 0.8	4	0.59	9.91 ± 0.24
JSS 200-9	84	5	3.8	84.1 ± 1.4	9	1.37	82.00 ± 0.48
LECO 501-673	12	5	1.8	14.2 ± 0.6	3	0.50	12.16 ± 0.21
pure Fe	—				4	0.49	1.67 ± 0.24
Sn	—				4	0.32	4.35 ± 0.11

obtained by the oxygen gas fusion-infrared absorptiometry (HORIBA EMIA-520) using 0.5~0.7 g of sample and fluxes (W 1.0 g, Sn 0.3 g). The range of analytical values (R-value) and the standard deviation for all standard samples obtained by the present method are superior to those obtained by the conventional combustion method. The lowest value for the analyzed carbon content was 1.67 ± 0.24 mass ppm under the conditions of using 1.0 g of pure iron and 3.0 cm³ of the concentrated volume. The lower limit of detection in the present analytical method was considered to be 0.4 mass ppm in the case of 1.0 g sample weight and 3.0 cm³ concentrated volume, judging from the standard deviation of the carbon content in Sn flux (3σ). However, this was not confirmed analytically because a pure iron sample containing sufficiently enough low carbon could not be available.

IV. Conclusions

Quantitative analysis of ultra low contents of carbon in metals was made by using ion-chromatography coupled with the combustion method in an oxygen stream. The results obtained are summarized as follows:

- (1) The considerable increase in the variation of conductivity with the amount of carbonate ion was observed in the use of the NaOH eluent.
- (2) The appropriate content of NaOH in CO₂ absorbent was found to be 0.005 mol.
- (3) The carbonate ion could be concentrated by using a cation exchange column which removed the Na⁺ ion in an absorbent.
- (4) The amount of CO₂ absorbed in the NaOH absorbent depended on the size of bubbles and the time for flotation of them in the solution.
- (5) The precision of analyzed carbon content was determined to be 1.67 ± 0.24 mass ppm in the analysis of pure iron.

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