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A New Spectrophotometric Determination of Small Amounts of Titanium in Steel and Ferroalloys. I

Determination of Titanium in Steel and Cast Iron*

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Synopsis

A new spectrophotometric method of using sodium alizarin-sulfonate⁽¹⁾ was applied to the determination of a small amount of titanium in steel and cast iron. Such a separation of iron as in the case of hydrogen peroxide method was unnecessary, and 0.2~0.002 per cent of titanium in some steels and cast iron was determined without any separation of iron. When sample contained much chromium as in high chromium steel, it was separated briefly with mercury cathode electrolysis.

I. Introduction

In order to determine a small amount of titanium in iron and steel, the hydrogen peroxide method has been usually applied after titanium had been separated as phosphate or cupferronate. A new spectrophotometric method of titanium of using sodium alizarin sulfonate and stannous chloride has been investigated in the present authors' laboratory, some results of which were already reported⁽¹⁾. By this method a small amount of titanium could be determined without interference of large amount of iron, small amount of vanadium and so on. Therefore, it seems that titanium in some steels and cast irons should be determined simply and accurately without separation of iron. Then, this method was applied to the determination of titanium in some steels and cast irons, and satisfactory results were obtained.

II. Reagents and apparatus

1. Reagents

Hydrochloric acid: 6N and 12N of hydrochloric acid were used.

Ammonium oxalate solution: saturated solution was used.

Sodium alizarin sulfonate solution: 0.2 per cent of aqueous solution was used. (AS will be used as the abbreviated expression of sodium alizarin sulfonate in the following.)

Stannous chloride solution: 20 per cent of 6N hydrochloric acid solution was used.

* The 916th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Journal of the Chemical Society of Japan, **78** (1957), 1337.

(1) Gotô, Kakita and Namiki: Sci. Rep. RITU, **A9** (1957), 245.

Titanium standard solution: This was prepared to dissolve titanium dioxide (analytical grade) in 1N sulphuric acid after fusing with potassium pyrosulfate. The concentration of this solution was determined volumetrically after reducing with liquid zinc amalgam method. Then, the solution was diluted accurately to the definite volume with 1N sulfuric acid.

2. Apparatus

Hitachi photoelectric spectrophotometer (EPU-2 type) with cells of 1 cm was used.

III. Calibration curve and sensitivity

The solutions containing 5~40 μg of titanium were put in several beakers and gradually evaporated to about 1 ml with gentle heating. 2 ml of 12N hydrochloric acid was added to each beaker and salts were dissolved. These solutions were transferred to graduated cylinder with ground glass stopper, and remaining solutions in beakers were washed away into graduated cylinder with 2 ml of 12 N hydrochloric acid and 2 ml of ammonium oxalate solution. Then, 0.7 ml of AS solution and 2 ml of stannous chloride solution were added, and these solutions were diluted to 10 ml with water. After complete mixing and standing about half an hour at about 15°C, the absorbances of these solutions were measured at the wave length of 760 $\text{m}\mu$ and the calibration curve as shown in Fig. 1 was obtained. As the blank test solution the same solution as the practical sample solution was treated without adding of AS solution, because the absorption of AS solution was negligibly small at the wave length of 760 $\text{m}\mu$ as shown in Fig. 2, and because the effect of AS solution could be negligible by adding constant amount of AS solution with pipet.

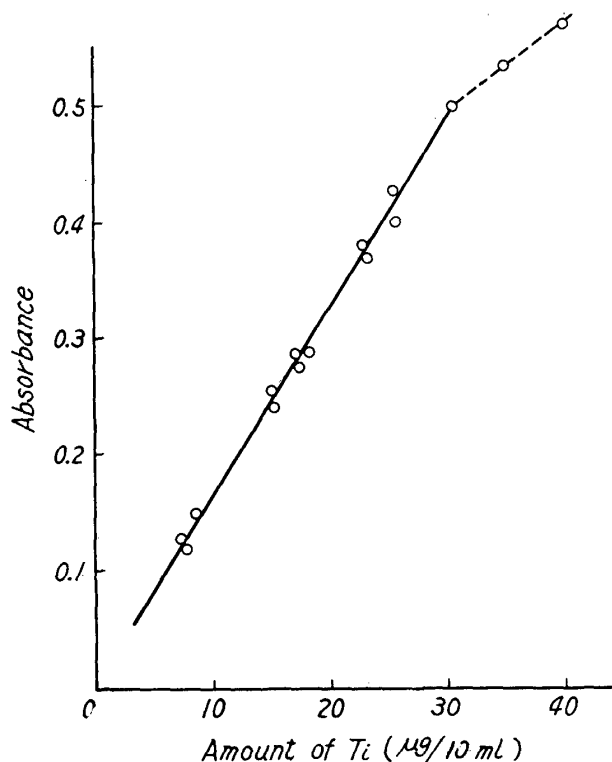


Fig. 1. Calibration curve at 760 $\text{m}\mu$, and at about 15°C.

In order to investigate the sensitivity of this method, the molecular absorption coefficient was obtained and compared with that of hydrogen peroxide method. The result is shown in Table 1, from which it will be seen that the sensitivity of this method is about ten times as large as that of hydrogen peroxide method.

Table 1. Molecular absorption coefficient of alizarin sulfonate method and hydrogenperoxide method.

Method	Wave length (m μ)	Molecular absorption coefficient
Alizarin sulfonate method	760	8170
Hydrogen peroxide method	410	730
	425	690

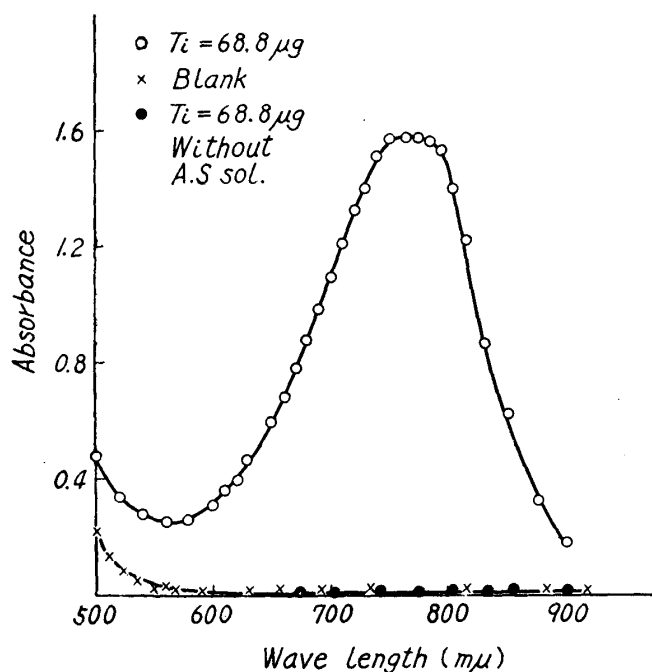


Fig. 2. Absorption curve of Ti-A·S solution.

IV. Analytical procedure

It was investigated already that the coexistence of iron had no effect up to 300 mg on this method. The time required to develop the color, however, was prolonged over 45 minutes, when iron coexists with titanium, as stannous chloride also reduces Fe^{3+} to Fe^{2+} . The more the iron exists in the sample solution, the more the addition of stannous chloride is required. On the other hand, manganese, nickel, chromium, cobalt, molybdenum, tungsten, vanadium, zirconium, niobium, tantalum, copper and germanium gave no influence to this reaction up to 0.2 mg of those elements. Aluminium and zinc also had no effect up to 100 mg. From these results, the analytical procedure for titanium in steel and cast iron was proposed as follows:

Dissolve 0.1~0.2 g** of sample in 40~50 ml of 6N hydrochloric acid with heating. Filter the insoluble residue, transfer it to platinum crucible and ignite.

** Containing titanium below 300 μg .

After ignition, add 1~2 ml of sulfuric acid and hydrofluoric acid heat to remove silica and continue heating to white fume of sulfuric acid. Then, fuse the residue with 1~2 g of potassium pyrosulfate or potassium bisulfate. After a little cooling, dissolve the melt with 20~30 ml of hydrochloric acid (1 + 5) and combine with the above filtrate. After cooling, transfer the solution to 100 ml calibrated flask, and adjust the mark with water. Put 10 ml of the solution into two beakers with pipet from the calibrated flask. One is the sample solution and the other is blank test solution. Evaporate these solutions below 1 ml on the hot plate. After cooling, dissolve the salts with 2 ml of hydrochloric acid and transfer it to 10 ml graduated cylinder with ground glass stopper. Wash the each beaker with 2 ml of hydrochloric acid and 2 ml of ammonium oxalate solution and combine washings with main solution. After adding 0.7 ml of AS solution to the solution which will be treated as sample solution, add 2 ml of stannous chloride solution to both solutions. Dilute to 10 ml with water and mix them well. After standing the solution for 50~60 minutes at about 15°C***, measure the absorbance at 760 m μ by using the solution which does not contain AS solution as the reference solution, and determine the titanium content.

V. Experimental results

1. After adding the standard titanium solution to electrolytic iron, titanium in it was determined by the above procedure. Satisfactory results were obtained as shown in Table 2.

Table 2. Determination of titanium added to iron.

Fe used (g)	Ti added (μ g)	Absorbance	Ti found (μ g)	Error (μ g)
0.10	11.5	0.186	11.4	-0.1
0.10	11.5	0.186	11.4	-0.1
0.20	11.5	0.190	11.6	+0.1
0.20	11.5	0.186	11.4	-0.1
0.10	22.9	0.367	22.7	-0.2
0.10	22.9	0.374	23.0	+0.1
0.20	22.9	0.374	23.0	+0.1
0.20	22.9	0.375	23.2	+0.3

Then the procedure of this method was applied after adding titanium to various steels. The results are shown in Table 3.

2. This method was applied to some samples containing titanium, and the results are shown in Table 4. In this table the results obtained with hydrogen peroxide

*** Maximum absorption is obtained at the standing for 45~90 minutes at about 15°C after solution was colored. When the temperature of the solution becomes high, both the velocity of color development and the decoloration become quick. In this case, these influences are negligible, if the procedure obeys the condition under which the calibration curve is made.

method are also shown, and these results are in good agreement with each other.

As previously mentioned, 0.002~0.2 per cent of titanium in steel and cast iron could be determined simply and accurately without separation of iron.

Table 3. Determination of titanium added to some steels.

Steel	Steel used (g)	Ti added (μg)	Absorbance	Ti found (μg)	Error (g)
Low carbon steel	0.10	7.7	0.129	7.9	+0.2
	0.10	7.7	0.120	7.4	-0.3
Vanadium steel (0.3% V)	0.10	22.9	0.366	22.6	-0.3
	0.10	22.9	0.374	23.0	+0.1
Chromium steel* (45% Cr)	0.10	22.9	0.367	22.7	-0.2
	0.10	22.9	0.360	22.2	-0.7
Cr-W steel (0.9% Cr 0.7% W)	0.10	22.9	0.370	22.8	-0.1
	0.10	22.9	0.370	22.8	-0.1

* Cr was briefly separated with mercury cathode method (ca. 1N HCl sol., electrolytic current: 15A, magnetic current: 5, for ca. 1hr.)

Table 4. Determination of titanium in steels and cast irons.

Sample	Sample taken (g)	Absorbance	Ti found (%)	Results with H_2O_2 method (%)
Low carbon steel	0.10	0.422	0.026	0.028
	0.10	0.423	0.026	
Ni-Cr steel (0.9% Cr, 2.9% Ni)	0.02	0.292	0.090	0.088
	0.02	0.288	0.088	
Cast iron (1)	0.05	0.089	0.0109	0.011
	0.05	0.103	0.0126	
Cast iron (2)	0.02	0.195	0.061	0.055
Cast iron (3)	0.02	0.288	0.088	0.082
NBS 170 B. O. H.	0.01	0.375	0.231	0.232*
	0.01	0.369	0.227	

* NBS standard value.

Summary

(1) A small amount of titanium in steel and cast iron was determined with a new spectrophotometric method by using alizarin sulfonate solution and stannous chloride.

(2) In this method the separation of titanium from iron was unnecessary, except special case such as high chromium steel ($\text{Cr} > 20\%$), and 0.2~0.002 per cent of titanium in steel and cast iron could be accurately determined.