Rapid Determination of Chromium by Differential Spectrophotometry

Rapid Determination of Chromium by Differential Spectrophotometry*

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Synopsis

The differential spectrophotometric method was applied to the determination of chromium in ferrochromium and high chromium alloys. Chromium was analysed by reading the absorbance of chromium (VI) in 1N perchloric acid at 350 mμ against the reference solution containing 16.0 mg chromium per 100 ml. The common alloying elements, iron, nickel and manganese, did not interfere up to about 50 per cent concentration. However, when samples contained over 50 per cent iron, iron was removed by solvent extraction from hydrochloric acid solution. Similarly, titanium and cobalt did not interfere up to 20 per cent concentration.

I. Introduction

Following the differential spectrophotometric determination of copper in copper alloys,[1] chromium in chromium alloys was determined by differential spectrophotometry.

A few works[2] on the spectrophotometric determination of a large amount of chromium have been reported. In these cases the light absorption of chromic ion (Cr^{+3}) was utilized, so that the correction for nickel content was necessary, when a large amount of nickel coexisted. Then the light absorption of chromate ion (Cr^{6+}) was applied to the differential spectrophotometric method. Using this method a large quantity of chromium in 18–8 stainless steel or ferrochromium was determined.

II. Reagents and apparatus

1. Reagents

Chromium metal of 99.9 per cent was used to prepare the reference standard solution. Hydrochloric acid, nitric acid, hydrofluoric acid, phosphoric acid, sulfuric acid and perchloric acid of analytical grade reagents were used. Methyl iso-buthyl ketone or other organic solvents of analytical grade reagent were used for the separation of iron from chromic chloride.

2. Apparatus

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* The 1037th report of the Research Institute for Iron, Steel and Other Metls. Reported in Japan Institute of Metals, **23** (1959), 371.
(1) K. Hirokawa, J. Japan Inst. Metals, **22** (1958), 181.
(2) S. Mizoguchi, Japan Analyst, **5** (1956), 454.

Hitachi spectrophotometer of EPU-2 type having cell width of 1 cm was used.

III. Absorption curve

Zero point one five zero gram of metallic chromium, which was ground below 40 mesh, was dissolved in 20 ml of hydrochloric acid (1+1). After cooling this solution, 20 ml of perchloric acid was added to it and heated on the hot plate at 210～250°C. Fume of the perchloric acid came out and chromium ion was oxidized to chromate ion by heating. After it was cooled the salt was dissolved in water of 100 ml. 5 ml of the solution was transferred to the volumetric flask of 100 ml by pipet and each was diluted to the mark with perchloric acid of 1N, 2N, 3N and 6N. The relations between the absorption of these solutions and the concentration of the perchloric acid are shown in Fig. 1. Similarly, the absorptions of iron, nickel and manganese in 1N perchloric acid were measured, and the
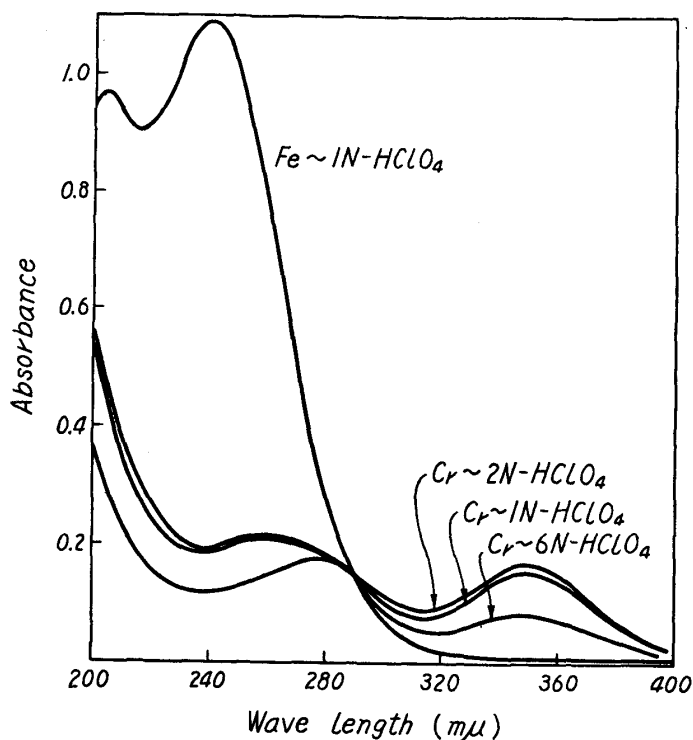

Fig. 1. Absorption curves.

absorption curve of iron was obtained as shown in Fig. 1, but the absorptions of nickel and manganese were negligibly small. A maximum absorption of chromium was obtained at 350 mμ. The difference of the absorbance between 1N perchloric acid and 2 N perchloric acid solution was very small, so that the concentration of the perchloric acid was kept at 1 N and the measurement was carried out at the the wave length of 350 mμ.

IV. Studies on the influence of diverse acids and decomposition of sample

In order to study the influence of diverse acid on the absorbance of the solution, the following experiments were carried out. From the solution treated like that used in the preparation of absorption curve, 15 mg of chromium in 1 N perchloric acid solution were transferred to a volumetric flask of 100 ml. After various amounts of hydrochloric acid, nitric acid, sulfuric acid, perchloric acid and phosphoric acid were added, each solution was diluted to the mark with 1 N perchloric acid. In Table 1 the absorbances of these solutions obtained by referr-

Table 1.   Effect of some acids on the absorbance.*

Sorts of acids \ Volume of acid	5.0 ml	10.0 ml	20.0 ml
6N-HCl	0.370 0.365	0.369 0.367	0.366 0.365
6N-HNO$_3$	0.399 0.398	0.400 0.398	0.392 0.388
6N-H$_2$SO$_4$	0.360 0.364	0.366 0.370	0.350 0.358
6N-H$_3$PO$_4$	0.367 0.370	0.355 0.356	0.350 0.350
6N-HClO$_4$	0.395 0.394	0.384 0.385	0.362 0.368

* Absorbance of reference solution containing 15.0 mg
Cr in 1N-HClO$_4$ of 100ml was set at 0.400.

ing to 1 N perchloric acid solution are shown. When the measurements were carried out at 350 mμ, with 0.3 mm of slit width and sensitivity of 10, the coexistence of hydrochloric acid, sulfuric acid and phosphoric acid resulted in the decrease in the absorbance. The influences of hydrochloric acid, nitric acid and hydrofluoric acid could be neglected by evaporating the sample solution to fume with perchloric acid, and by measuring the absorbance of it after diluting to the definite volume with water.   A little danger of the loss of chromium should be considered, when the solution was evaporated in the presence of perchloric acid and hydrochloric acid.   Therefore, next investigations were carried out.   Various known amounts of chromium in hydrochloric acid solution   (15.0 mg Cr) were taken in beaker.   Perchloric acid was added to these solutions and heated gradually at about 210 ~250°C on a hot plate.   When fume came out, beakers were covered with watch glass, and the temperature of them were kept at about 200~210°C in order to avoid violent boiling.   Chromium ion was oxidized to chromate ion with various heating time were shown in Fig. 2.   After cooling, the acidity of these solutions was controlled to 1 N perchloric acid solution, and the absorbances of these solutions measured are shown in Fig 2, and the decrease in the absorbance
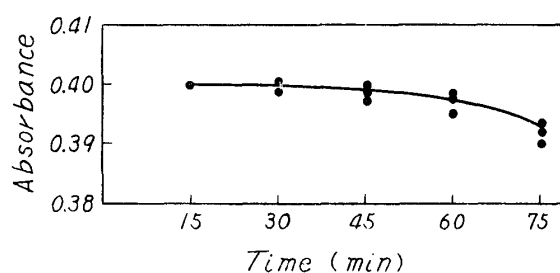
Fig. 2.   Relation between heating time and absorbance.

was negligibly small in the above procedure.

V. Selection of the concentration of reference solution

As described in the previous report[1] on the differential spectrophotometric determination of copper, to determine the suitable concentration of reference solution aC_1, in whicha C_1 is maximum in the equation of

$$dC_2/C_2 = 0.43d\,(I_2/I_1)\big/I_2/I_1\,\{\log(I_2/I_1) - a\,C_1\}\ ,$$

was investigated in the concentration range from 4.4 mg chromium per 100 ml to 20.1 mg chromium per 100 ml in 1 N perchloric acid solution.   In the above equation, C_2 is the concentration of the sample solution, C_1 the concentration of the reference solution I_2 and I_1 transmittances of the sample solution and the reference solution respectively, and $a=\mathrm{Ar}/C_2\text{-}C_1$, Ar being the absorbance of C_2 against C_1.

These results are shown in Table 2, and it seemed that chromium   in the

Table 2.   Computation of the best concentration for
reference solution..

C_1 mg/100ml	C_2 mg/100ml	Ar	Slit width (mm)	a	$a\ C_1$
8.10	12.50	0.398	0.05	88.5	0.71
8.10	16.10	0.930	0.11	117.5	0.94
8.10	20.10	2.000	0.11	167.0	1.34
12.50	16.10	0.580	0.11	166.0	2.04
12.50	20.10	1.500	0.16	198.0	2.48
16.10	20.10	1.040	0.30	260.0	4.19
16.10	24.10	1.450	0.30	182.0	2.94
16.10	28.20	1.500	0.30	125.0	2.01
20.10	24.10	0.345	0.90	86.5	1.74
20.10	58.20	0.426	0.90	52.5	1.05

concentration range from 16 mg per 100 ml to 20 mg per 100 ml was accurately estimated.

VI. Preparation of calibration curve

The calibration curve was prepared by the above investigation.   From 0.37 to 0.45 g of metallic chromium were dissolved in 20 ml of hydrochloric acid (1+1). After cooling, the acid solutions were diluted to 100 ml with water.   Then 10 ml of each of these solutions were taken in beakers respectively, which were marked at the level of 30 ml. 35 ml of perchloric acid was added to these solutions and

evaporated to fume on the heater of about 200~250°C. After fuming, beakers were covered with watch glass, and heated at about 200~250°C to oxidize Cr^{3+}.
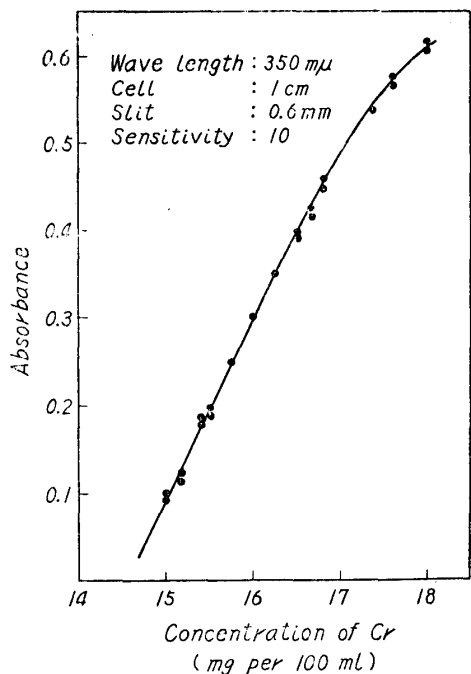

Fig. 3. Calibration curve

The solution was gradually evaporated to the mark in order to control the acidity. After cooling, the solution was accurately diluted with water to 250 ml and mixed well. The absorbance of the reference solution containing 40.0 mg chromium per 250 ml was adjusted at 0.300, and the absorbance of the above solution was measured against the reference solution. From these absorbances and their chromium content, the calibration curve was obtained as shown in Fig. 3. In this case, the absorbance showed little variation with the liquid temperature of 15~25°C.

VII. Interference by diverse ions

The influences of diverse elements accompanied commonly in chromium alloys, such as iron, nickel, manganese, titanium vanadium, molybdenum, cobalt and aluminium, were investigated. These results are shown in Table 3. In this

Table 3. Effect of other metals.

Cr used (mg/100ml)	Metals added (mg/100ml)	Cr found (mg/100ml)	Error (mg/100ml)	Relative error (%)
15.84	24.0 Fe	16.00	+0.16	+0.94
15.80	16.0 Fe	15.88	+0.08	+0.50
15.88	32.0 Ni	15.85	−0.03	−0.12
15.88	32.0 Mn	15.88	0.00	0.00
15.85	6.0 Ti	15.68	−0.23	−1.4
15.80	4.0 Ti	15.74	−0.06	−0.38
15.80	8.0 V	15.74	−0.06	−0.38
16.18	4.0 Mo	16.31	+0.13	+0.80
15.94	0.8 Mo	16.11	+0.02	+0.12
16.12	8.0 Co	16.04	−0.08	−0.5
16.18	3.6 Al	16.12	−0.06	−0.37

case ammonium molybdate for molybdenum and sodium tungstate for tungsten were used. From these results, it was recognized that the existence of iron as much as chromium, titanium up to the amount of one fifth of chromium, and nickel and manganese over the same amount of chromium could be allowed within 0.5 per cent of relative error in this analysis. Therefore, when iron was present above 50 per cent in the sample, iron had to be separated.

VIII. Analytical procedure

After the above investigation, the following procedure was proposed.

Sample containing chromium below 0.4 g and 0.4000 g of metallic chromium are simultaneously taken in different beakers. 20 ml of hydrochloric acid (1+1) are added and heated to dissolve them. Then 10 ml of nitric acid, if necessary a few drops of hydrofluoric acid, are added ; and samples are completely dissolved. After the dissolution is completed, the solutions are cooled and transferred to the volumetric flasks of 100 ml and diluted to the mark with water. 10 ml of each of these solutions are put into beakers of 100 ml which was graduated at the level of 30 ml. 35~40 ml of perchloric acid is added to each of these solutions and these are treated in the same way as the procedure for the preparation of calibration curve. Then the chromium in the sample solution is determined by using the reference solution of metallic chromium.

When the amount of iron in sample is over 50 per cent, the sample solution is diluted to 100 ml with hydrochloric acid (1+1) instead of water. From this flask, 10 ml of the solution is pipetted into the separatory funnel, and iron in this solution is extracted with 20 ml of organic solvent, while chromium remains in aqueous phase. After the extraction, organic phase is washed with 5 ml of hydrochloric acid (1+1). This washing solution is added to the original solution, and simultaneously perchloric acid is added and heated. Near the fuming of perchloric acid, nitric acid of 3~ 5 ml was added and heating is continued, and organic substance in the solution is destroyed. Then the procedure similar to the above-mentioned is followed.

In these cases, as chromium reference solution, the stock solution of known concentration may be used.

IX. Analytical results

The results applied to the determination of the chromium in some ferrochro-

Table 4. Determination of chromium in some alloys.

Sample	Sample taken (g)	Cr found by this method (%)	Cr found by standard method (%)
Ferrochromium (A)	0.6390 0.6397	63.00 62.97	62.96
Ferrochromium (B)	0.6413 0.6420	62.61 62.54	62.58
High chromium steel (45% Cr)	0.9048 0.8915	44.95 44.95	44.82
Nickel-chrommium steel (60% Ni, 20% Cr etc.)	2.0031 2.0004	19.92 19.96	20.05
18-8 Stainless Steel (A)	2.1880 2.1850	18.29 18.33	18.24
18-8 Stainless Steel (B)	2.1686 2.1613	18.93 18.98	18.84

mium and 18–8 stainless steels are shown in Table 5. Good agreements with the standard method were obtained. In the case of nickel-chromium steel, however, the negative errors were observed due to the presence of nickel.

Summary

A differential spectrophotometric determination of chromium in chromium alloys were investigated, after samples were dissolved with hydrochloric acid and nitric acid. When a large amount of iron was present, it was removed by solvent extraction ; the solution was evaporated to fuming of perchloric acid. The acid concentration in the sample solution was adjusted to about 1 N perchloric acid solution. The absorbance of the sample solution was measured against the reference solution of metallic chromium which was treated in the same way as the sample solution. With this procedure chromium of 10~80 per cent in a sample could be analyzed within 30~50 minutes.