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A Simplified Determination of Microquantity of Carbon in Iron, Steel and Ferro-Alloy*

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Synopsis

In order to determine rapidly and accurately microquantity (below 0.1 per cent) of carbon in iron, steel and ferro-alloys, 0.5~1 g of the sample was taken, carbon dioxide gas generated by its combustion was solidified by passing through a trap chilled in liquid air, and the solid carbon dioxide was vaporized and allowed to permeate a definite vacuum, the volume being read on the manometer.

The analytical results by this method agreed well with those by gravimetric method within a mean standard deviation of 0.0005 per cent in low-carbon steel, and well agreeing results were also obtained with chromium metal and manganese metal. The time required for the analysis by this method was 24~26 minutes.

I. Introduction

In these days, iron, steel and ferro-alloys containing very minute amount of carbon are in demand, and the method of determining such microquantity of carbon is studying.

The existing method includes the alkalimetry, in which the carbon dioxide gas generated by the combustion of a sample is led into a spiralled tube containing known concentration of sodium hydroxide and the excess of sodium hydroxide is titrated with standard hydrochloric acid; and in the other method of collecting the carbon dioxide gas generated from the sample into a trap chilled in liquid oxygen, this collected solid in a known vacuum is vaporized, and the pressure is read on a McLeod vacuum gauge.

The former method is difficult to find the end point of the titration, and the procedure must be carried out with great caution. The latter method requires expensive apparatus, such as mercury diffusion pump, rotary pump and McLeod vacuum gauge with high degree of vacuum technique.

In order to remove these defects and to determine microamount of carbon accurately and rapidly with a simple apparatus, the present authors examined some improvement of the method of Smiley⁽¹⁾ and of Holt⁽²⁾ reported recently, and found a method that could be applied with a good result to the analysis of low-carbon steel, chromium metal and manganese metal.

* The 902nd report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Japan Analyst, **6** (1957), 650.

(1) W.G. Smiley, Anal. Chem., **27** (1955), 1098.

(2) B.D. Holt, *ibid.*, **27** (1955), 1500.

II. Experimental method

1. Experimental apparatus

The apparatus used in the present method is briefly outlined in Fig. 1. The apparatus consists of oxygen purification, sample combustion and gas collection and determination parts.

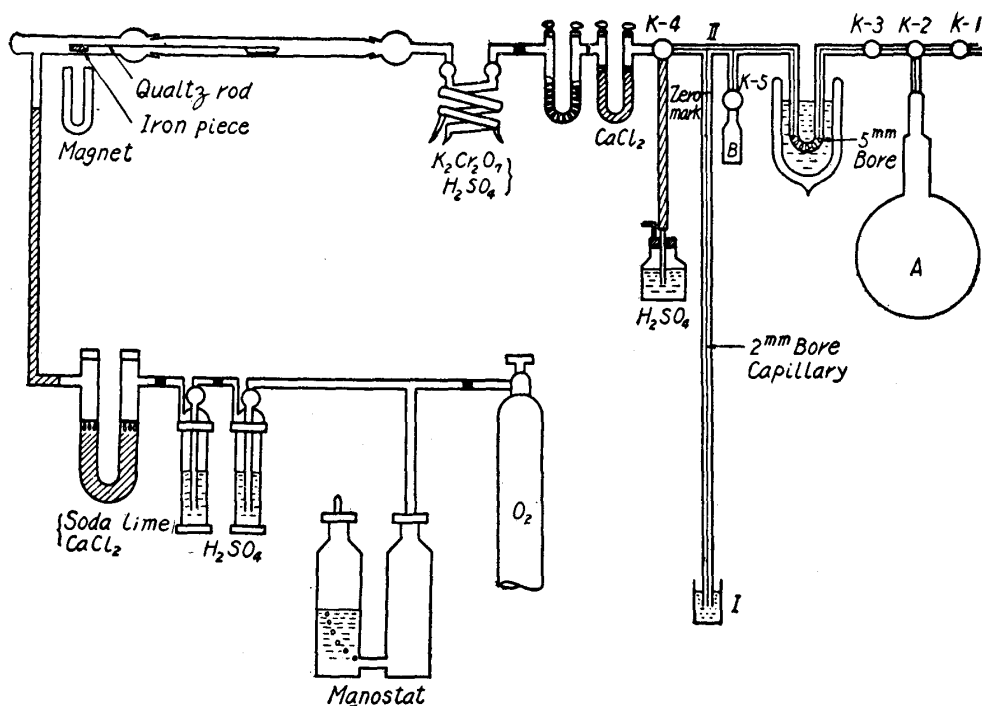


Fig. 1. Apparatus for microdetermination of carbon in iron, steel and ferro-alloys.

(i) Oxygen purification part

This part consists of gas washers containing concentrated sulfuric acid, soda lime and calcium chloride. A manostat is attached here to facilitate the adjustment of flow velocity.

(ii) Sample combustion part

Ordinary silicon carbide rod furnace and a combustion tube with copper oxide, as a catalyst, are used. Either end of the combustion tube is ground and connected with tapered hard glass so as to make the tube air-tight. After putting the boat in the combustion tube, a quartz rod is inserted into the heating portion of the tube, and the end of this rod is combined with an iron piece, which is moved by a magnet from outside of the combustion tube to push the boat into the heating portion. In order to remove sulfur dioxide gas from the gas generated by combustion of the sample, a series of tubes containing sulfuric acid saturated with chromic acid and calcium chloride are attached to the other end of the combustion tube.

(iii) Gas collection and determination part

This part consists of a capillary tube, 2 mm in inside diameter, with four cocks,

of which K_2 , K_3 and K_4 are three-way cocks. Gas collecting U-tube is also of 2 mm in diameter but the bent portion is 5 mm in diameter and filled with glass wool to make the collection of gas perfect.

The determination portion also consists of a capillary tube, 2 mm in diameter. The zero point position of the capillary tube is about 760 mm above the surface of mercury pool and about 40~50 mm above the zero point is taken as a dead space. A beaker containing mercury is placed below the manometer and the correction of the zero point for the change in atmospheric pressure is made by adjusting capillary surface of mercury. The manometer also serves as a flow meter during combustion of the sample and a reading of 40 mm corresponds to the flow rate of 120 ml/min in this apparatus.

In the diagram shown as Fig. 1, A is a vacuum trap and B is a gas collector of about 7.5 ml capacity large enough for the determination of a large amount of carbon.

The volume into which the carbon dioxide gas is to be dispersed must be determined beforehand. The volume of the space into which the gas is dispersed, i. e. the volume between K-4 and K-3 in this apparatus is determined as follows: A leveling tube with mercury is connected by rubber just below the manometer, the apparatus is placed in atmospheric pressure, and the mercury is brought up to zero point. The cock is then closed, the leveling tube is brought down below the manometer, and the reading X_1 is taken. Then the cock is opened and the manometer reading X_2 is taken. If the atmospheric pressure is h and the volume is V , then from the Boyle's law

$$Vh = (V + SX_1)(h - X_2 + X_1)$$

$$\therefore V = SX_1(h - X_2 + X_1)/(X_2 - X_1)$$

In the present apparatus, this volume is 3.72 ml and that of B is 7.53 ml. The cross-sectional area of the manometer, S , is obtained from the weight and the length of mercury column.

2. Analytical procedure

All the air in the back portion of the cock K-4 in the apparatus is evacuated and the adjustment of the zero point for the change in atmospheric pressure is made by mercury. The burning portion is maintained at 1200°C, the boat containing a sample is placed in a low-temperature portion of the combustion tube, the quartz rod is placed in position, and the glass tube is set in place. The rotary pump is already in motion by this time. Oxygen is let in gently through K-4 and when the manometer reading reaches 40 mmHg, the flow velocity will be 120 ml/min. After letting oxygen in for 3~5 minutes, the air in the whole apparatus is exchanged with oxygen, the trap is chilled in a Dewar bottle containing liquid nitrogen, and the sample boat is pushed into the heating portion of the combustion tube. The sample is burnt for 15 minutes, while adjusting the amount of oxygen, then the cock K-4 is closed, and oxygen in the trap is expelled to return to zero point.

After expulsion of oxygen, the cock K-3 is closed, the Dewar bottle is taken away, and the trap is warmed in a slightly warm water. The collected carbon dioxide gas is thereby vaporized and the pressure is read on the manometer. When the manometer reading has been taken, the cock K-3 is again closed and the apparatus is maintained in vacuum.

The amount of carbon determined by this method is calculated by the following equation:

$$W = 0.000,00064 \left(V \cdot x + S \left(\frac{x}{10} \right)^2 \right) \text{ (taking the room temperature to be } 27^\circ\text{C)}$$

$$C\% = \frac{(\text{Sample } W - \text{Blank } W) \times 100}{\text{Sample (g)}}$$

where S is the cross-sectional area of the manometer in cm^2 , V the volume of the trap in ml, x the manometer reading in mm, and W the amount of carbon in g.

III. Experimental results

The results obtained on several kinds of low-carbon steel by the present and usual gravimetric methods are compared in Tables 1~3.

As can be seen in these tables, there is no significant difference between them, and the precision of the present method is far better than that of the gravimetry.

Table 4 shows the result on a low-carbon steel.

The blank value in the present apparatus, when a boat is inserted, is 8 mmHg on the manometer, or 0.0019 per cent/g, and when the boat is absent in the apparatus, it is 4 mmHg or 0.0009 per cent/g.

Results obtained on chromium metal, ferrochromium and manganese metal are shown in Table 5.

The time required for the determination by the present method is 24~26 minutes, as shown in Table 6.

Table 1. Results on determination of low-carbon steel by the present and gravimetric method (1).

Method	Sample	Amt. used (g)	Manometer reading(mm)	Carbon (%) mean(%)	Standard deviation		
Present	Carbon steel 13278	1.0	50.5	0.0102	0.0005		
			48.0				
			53.7				
			50.0				
			52.0				
Gravimetry	Ditto	3.0	0.0091	0.0103	0.0010		
			0.0091				
			0.0099				
			0.0118				
			0.0118				
Method	N	df	Mean	$\sum(x_1 - \bar{x})^2$	w^2	w	t
Present	5	4	0.0102	21×10^{-8}			
Gravimetry	5	4	0.0103	148×10^{-8}	21×10^{-8}	46×10^{-5}	$0.85 < 2.306$ (5% $df=8$)
		8	0.0001	169×10^{-8}			

Table 2. Results on determination of low-carbon steel by the present and gravimetric method (2).

Method	Sample	Amt. used (g)	Manometer reading(mm)	Carbon (%)	Carbon mean (%)	Standard deviation	
Present	Carbon steel 13269	0.5	159.0	0.0731	0.0738	0.0010	
			163.0	0.0753			
			157.2	0.0726			
			160.0	0.0737			
			161.6	0.0744			
Gravimetry	Ditto	2.0		0.0736	0.0753	0.0020	
				0.0763			
				0.0736			
				0.0736			
				0.0777			
Method	N	df	Mean	$\sum(x_i - \bar{x})^2$	w^2	w	t
Present	5	4	0.0738	114×10^{-8}			
Gravimetry	4	3	0.0753	418×10^{-8}	76×10^{-8}	87×10^{-5}	$1.7 < 2.365$ (5% df = 7)
		7	0.0015	532×10^{-8}			

Table 3. Results on determination of low-carbon steel by the present and gravimetric method.

Method	Sample	Amt. used (g)	Manometer reading(mm)	Carbon (%)	Carbon mean (%)	Standard deviation	
Present	Carbon steel 14402	1.0	59.5	0.0123	0.0124	0.0007	
			56.3	0.0116			
			59.9	0.0124			
			62.7	0.0131			
			61.8	0.0128			
Gravimetry	Ditto	2.0		0.0122	0.0126	0.0008	
				0.0136			
				0.0118			
				0.0130			
				0.0130			
Method	N	df	Mean	$(x - \bar{x})$	w	w	t
Present	5	4	0.0124	32×10^{-8}			
Gravimetry	4	3	0.0126	65×10^{-8}	14×10^{-8}	37×10^{-5}	$0.9 < 2.365$ (5% df = 7)
		7	0.0002	97×10^{-8}			

Table 4. Analysis of various low-carbon steel.

Sample	Amt. used	C detd. (%)	mean (%)	Standard (%)	Error (%)	Standard deviation
Yawata 5656	1.0	0.0207	0.021	0.021	± 0	0.0003
		0.0209				
		0.0210				
		0.0214				
		0.0208				
Yawata 465	1.0	0.0101	0.010	0.010	± 0	0.0003
		0.0104				
		0.0105				
		0.0098				
		0.0100				
14339	1.0	0.0204	0.020	0.020	± 0	0.0003
		0.0200				
		0.0198				
		0.0199				
		0.0200				
Standard sample 1(a)	0.5	0.108	0.106	0.11	-0.004	0.0021
		0.105				
		0.104				

Table 5. Determination of carbon in chromium metal, ferrochrome and manganese metal.

Sample	Amt. used (g)	Carbon (%)	Mean (%)
Chromium metal	1.0	0.0190	0.0198
		0.0201	
		0.0204	
Ferrochrome	1.0	0.0254	0.0256
		0.0250	
		0.0263	
Manganese metal	1.0	0.0076	0.0074
		0.0080	
		0.0067	
		0.0068	
		0.0080	

Table 6. Time Required for each Step of Analysis.

Weighing of sample	1 min
Expelling of air	3~5
Combustion of sample and collection of CO ₂	15
Vacuum	1
Vaporization of CO ₂	2
Reading	1
Vacuum	1
Total	24~26 min.

Summary

In order to determine the microquantity of carbon in iron and steel rapidly and accurately, some improvement was made on the method of Smiley and others, and experiments were made with this apparatus on low-carbon steel, chromium metal and manganese metal. It was thereby seen that the present method had precision comparable with that of the gravimetric method, and that the determination could be completed in 24~26 minutes.