

THE DETERMINATION OF OXYGEN AND NITROGEN IN IRONS AND STEELS BY THE VACUUM FUSION METHOD

By H. C. Vacher and Louis Jordan

ABSTRACT

Results of an extended study of the vacuum-fusion method for the determination of gases in steels are presented. The apparatus consists of a vacuum furnace and an analytical train for determining carbon monoxide, hydrogen, and nitrogen at low pressures. Simplification of the analytical procedure, the use of a mercury diffusion pump, and the adoption of a sample loading device have improved the method. The method (in the absence of interferences) gives values reproducible to within 0.002 per cent for both oxygen and nitrogen. The accuracy of the oxygen determination is affected by the presence of certain oxides which are decomposed with difficulty, and by the presence of certain reactive metallic vapors during the evolution of carbon monoxide. The accuracy of the nitrogen determination is not affected by these factors.

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I. INTRODUCTION

The history of the development and summaries of methods for the determination of oxygen and other gases in iron and steel have been published by Meyer,¹ by Hessenbruch,² and by Meissner³ within the past few years. The experimental work described in this paper is a continuation of work initiated by Jordan and Eckman^{4,5} in developing methods for the determination of oxygen, hydrogen, and nitrogen in iron and steel. Since the publication of their work, papers have appeared describing certain improvements in procedure and giving data to show the precision and accuracy to be expected from these methods.

¹ O. Meyer, Über den heutigen Stand der Bestimmung von Sauerstoff in Stahl und Eisen, *Z. Angew. Chem.*, **41**, pp. 1273-1275, 1295-1298; 1928.

² W. Hessenbruch, Die Unterschung der Gase in den Metallen, *Z. Metallkunde*, **21**, pp. 46-55; 1929.

³ F. Meissner, Beitrag zur Bestimmung der Oxyde in Eisen und Stahl, *Mitt. Forschungs-inst. Ver. Stahlwerke Aktienges., Dortmund*, **1**, pp. 223-79; 1930.

⁴ Louis Jordan and J. R. Eckman, Gases in Metals. II. The Determination of Oxygen and Hydrogen in Metals by Fusion in Vacuum, *B. S. Sci. Paper No. 514*; 1925.

⁵ Louis Jordan and J. R. Eckman, Gases in Metals. III. The Determination of Nitrogen in Metals by Fusion in Vacuum, *B. S. Sci. Paper No. 563*; 1927.

Walker and Patrick⁶ showed that oxygen contained in iron probably could be recovered as carbon monoxide by a vacuum fusion in graphite, although the furnace conditions and technique employed by them made it difficult to obtain precise results. However, the promising possibility of complete conversion of oxides to a readily determinable form, together with the possibility of using carbon as a material for crucibles, made this method very attractive. Jordan and Eckman, after a survey of existing vacuum fusion methods, undertook to improve the furnace condition and technique of the Walker and Patrick method. By using a high-frequency induction furnace they showed that precise results could be obtained and that the oxygen of oxides usually encountered in steel could be recovered when contained in relatively pure iron, such as ingot iron. The method, as described by Jordan and Eckman has been modified by Hessenbruch and Oberhoffer,⁷ by adding (a) a sample loading device, whereby the crucible at the temperature of the analysis may be loaded with one or more samples of steel without opening the furnace to the atmosphere and (b) the use of a mercury diffusion pump in order to extract the gases more rapidly from the furnace. Von Seth⁸ further modified the apparatus by water cooling the walls of the evacuated furnace tube and by keeping all refractory oxides outside of the high temperature zone. Diergarten⁹ constructed a resistance type of furnace as a substitute for the high-frequency furnace. His results, obtained with this resistance furnace, were in good agreement with results obtained with a high-frequency furnace.

Hessenbruch and Oberhoffer pointed out the interference of manganese in analyses made according to the procedure used in the early part of their work, but their final conclusion was that such interference was not serious in their recommended procedure, namely, melting under lower pressures attained by means of a mercury diffusion pump. Von Seth concluded from his work, that methods for determining oxygen in metals by a vacuum fusion in graphite did not yield accurate results on account of gas reactions with condensed metals or metal vapors in the colder parts of the furnace.

Thanheiser and Müller,¹⁰ using essentially the improved method of Oberhoffer and Hessenbruch, concluded that, of the oxides possibly present in steel, only iron oxide and manganese oxide were completely reduced. The oxygen which was present in combination with silicon or aluminum was only partially recovered at a temperature of 1,500° C. If higher temperatures were used in order to reduce the oxides of aluminum and silicon more completely, the blank corrections became excessively large and the increased vaporization of manganese made the results inaccurate. Thanheiser and Müller also found that very considerable losses of oxygen often resulted when the fusion was made in a crucible containing residues from previous analyses.

⁶ W. M. Walker and W. A. Patrick, Determination of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace, Eighth Int. Cong. App. Chem., 21, pp. 139-148; 1912.

⁷ W. Hessenbruch and P. Oberhoffer, Ein verbessertes Schnellverfahren zur Bestimmung der Gase in Metallen, insbesondere des Sauerstoffs im Stahl, Archiv Eisenhüttenwesen, 1, pp. 583-600; 1928.

⁸ R. Von Seth, Jernk. Ann., 112, pp. 113-150; 1928; Stahl u. Eisen, 48, pp. 1374-1375; 1928.

⁹ Hans Diergarten, Zur Bestimmung der Gase in Metallen, usw., Archiv Eisenhüttenwesen, 2, pp. 813-828; 1929.

¹⁰ G. Thanheiser and C. A. Müller, Beitrag zur Bestimmung des Sauerstoffs im Stahl nach dem Heissextraktionsverfahren, Mitt. Kaiser Wilhelm Inst. Eisenforsch., II, pp. 87-94; 1929.

Recently Diergarten¹¹ has fully confirmed the earlier results of Walker and Patrick and of Jordan and Eckman to the effect that silica is completely reduced in the vacuum-fusion method and that recoveries of over 90 per cent of oxygen combined as alumina can be made. He also calls attention to errors caused by reactions between the vapors of manganese, or aluminum, and carbon monoxide. The analysis, in his opinion, becomes inaccurate when material in the crucible at the start of an analysis contains manganese or aluminum in excess of 0.7 and 0.3 per cent, respectively.

II. APPARATUS AND PROCEDURE

The apparatus for the vacuum-fusion method at present in use in the laboratories of the National Bureau of Standards differs in several respects from the earlier apparatus described by Jordan and Eckman. The analytical train has been simplified by eliminating two of the four absorption tubes. Provision has been made for the determination of nitrogen with oxygen and hydrogen, and the complete analysis (oxygen, hydrogen, and nitrogen) is carried out in a closed analytical train. The furnace is of new design and is provided with a sample loading device similar to that used by Hessenbruch and Oberhoffer. A mercury diffusion pump is used to allow melting the sample under lower pressures than in the earlier apparatus, and the same pump serves to circulate the gases in the closed analytical train.

1. IMPROVEMENTS IN THE GAS ANALYSIS TRAIN

Gravimetric methods for the determination of oxygen and hydrogen are employed in the improved apparatus. This method of analysis of gases at low pressure has the distinct advantage of eliminating a collecting pump (necessary if a volumetric method at atmospheric pressure is to be used) and of being easily adaptable to either large or small quantities of gas, as compared with the difficulties involved if a volumetric method of analysis at low pressures is to be used.

In the earlier apparatus a mechanical vacuum pump drew the gases, evolved in the vacuum furnace, through an evacuated absorbent train. Water, carbon dioxide, hydrogen, and carbon monoxide were determined by the increase in weight of four tubes filled with solid absorbents, 2 with phosphorus pentoxide and 2 with ascarite.

Jordan and Eckman¹² showed that nitrogen also could be recovered from iron and steel by a vacuum-fusion method. In their method the sample was fused in vacuo in a graphite crucible, and the gases evolved from the sample were absorbed in calcium vapor. The nitrogen of the calcium nitride thus formed, was determined by the ordinary acid solution and distillation method. The analysis of a ferrous material for oxygen, hydrogen, and nitrogen required two samples and two complete operations.

In the improved apparatus, where the gases are retained in a closed system, the residual gas, after the absorption of water and carbon dioxide, consists of nitrogen. The determination of the volume of this residual gas, therefore, permits the determination of oxygen,

¹¹ H. Diergarten, Zur Bestimmung der Gase in Metallen, usw., *Archiv Eisenhüttenwesen*, **3**, pp. 577-586; 1930.

¹² See footnote 5, p. 375.

hydrogen, and nitrogen on one sample and in one operation. This determination is possible in the improved train.

(a) GENERAL DESCRIPTION OF TRAIN

A drawing of the improved train is shown in Figure 1. The complete train, furnace, and absorbent tubes may be evacuated by a mechanical vacuum pump which is connected at *M* or they can be filled independently with dry, carbon dioxide-free air through *H*. The gases evolved from the metal sample are removed from the furnace (*A*) by means of a 2-stage mercury diffusion vacuum pump (*B*) which delivers the gases to the reservoirs (*R*₁ and *R*₂). Subsequently, the gases are circulated over hot copper oxide (*C*) and through absorbent tubes containing phosphorus pentoxide (*T*₁) and ascarite (*T*₂).

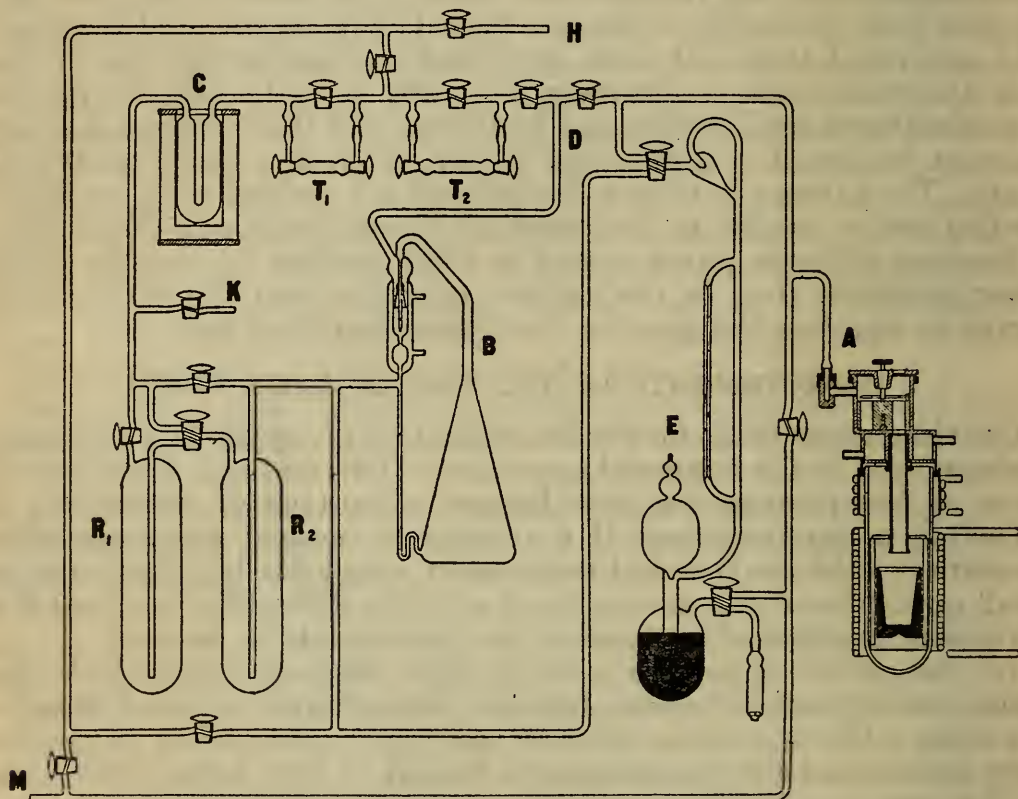


FIGURE 1.—Diagram of apparatus for the determination of gases in metals by the vacuum-fusion method

Any unoxidized or unabsorbed gas is returned to the low-pressure side of the diffusion pump (*D*). The pressure at the furnace inlet (*A*) and the pressure in the reservoirs can be measured by means of the McLeod gage (*E*). In order to reoxidize the copper oxide, air is drawn into the train at *H* and removed by the laboratory vacuum at *K*.

(b) ELIMINATION OF FIRST TWO TUBES FROM EARLIER APPARATUS

In the 4-tube train the first two tubes absorbed water vapor and carbon dioxide, respectively, if these gases were present in the gases evolved in the furnace. After passing through the first two tubes the gases were passed over hot copper oxide, to oxidize hydrogen and carbon monoxide to water vapor and carbon dioxide, respectively.

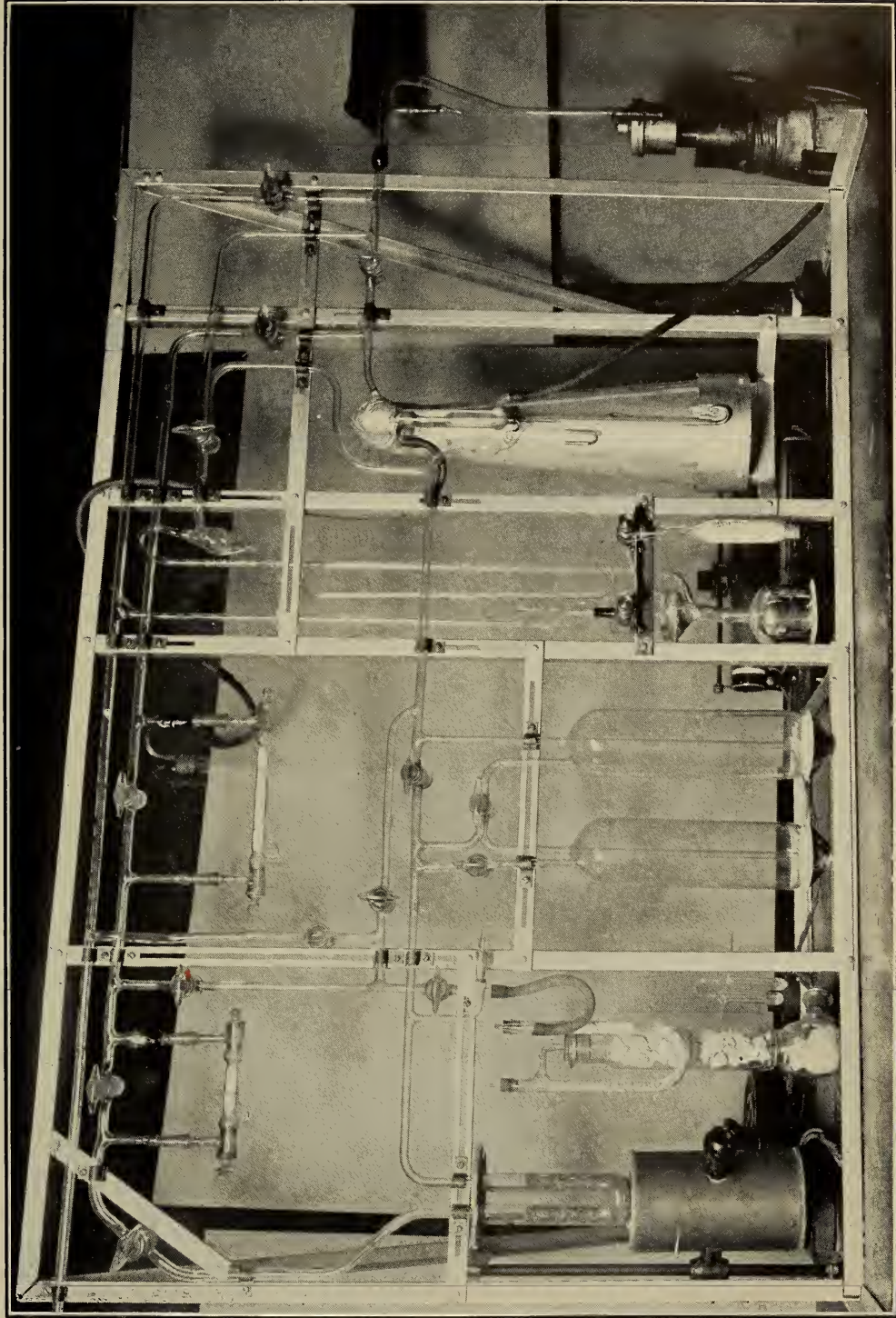


FIGURE 2.—Assembled apparatus

This water vapor and carbon dioxide were recovered in a second pair of absorption tubes. A review of the data obtained showed that the increase in weight of the first two tubes during a run seldom exceeded the blank correction. In other words, the amounts of water vapor and of carbon dioxide evolved from the sample were negligible, and consequently the first two absorption tubes might just as well be eliminated. The data in Table 1 show that the amounts of oxygen recovered in a 4-tube train, corrected for the blank determination, and the amount of oxygen recovered in a 2-tube train, corrected for the blank determination, are identical within the limits of experimental error. Similar data are available for the determination of hydrogen, which is present only in minute amounts in ordinary ferrous materials. The absence of appreciable amounts of carbon dioxide and of water vapor in the furnace gases, therefore, is established and the simplification of the train by the elimination of two absorption tubes is justified.

TABLE 1.—Comparison of analyses made with four tubes and with two tubes in the absorption trains

4-tube train oxygen	2-tube train oxygen
<i>Per cent</i>	<i>Per cent</i>
0.020	0.021
.008	.007
.012	.011
.013	.013
.003	.002
.003	.002
.133	.132
.143	.143

(c) CONSTRUCTION AND OPERATION OF ANALYTICAL TRAIN

The train is mounted on a 31 by 45 inch frame made from $\frac{3}{4}$ -inch angle iron. (Fig. 2.) The uprights and cross pieces within the frame are slotted so that the clamps holding the glass tubes of the train are movable. This facilitates the construction of the train and also repairs and changes in design.

The mercury diffusion pump is a 2-stage Stimson¹³ pump, modified so that one condenser will serve both stages. This type of pump is capable of working against a fore pressure of 15 to 20 mm of mercury. The same pump is used to extract gases from the furnace, to collect them in one or two 600 to 700 ml reservoirs, and to circulate the gases through the copper oxide furnace and the absorbent tubes. It has been found advisable to use only one reservoir when making analyses of samples of 20 g of iron or steel. If the volume of the train is increased the time for clean-up of oxidized gases is correspondingly increased.

The vacuum gage is of the McLeod type with multiple compression volumes to allow use over a range of pressures from 20 to 0.001 mm of mercury. This gage is connected to the train to permit reading pressures on both the high pressure and low pressure sides of the diffusion pump.

¹³ H. F. Stimson, A Two-stage Diffusion and Jet Pump, J. Washington Acad. Sci., 7, p. 477; 1917.

The extracted gases are passed over copper oxide in order to oxidize any hydrogen or carbon monoxide present. The copper oxide is contained in a U tube of 1.8 cm diameter Pyrex glass tubing, and fills each side of the U to a height of 15 cm. The tube is heated in a vertically adjustable resistance furnace. It is advisable to reduce the commercial copper oxide "wire" with hydrogen or with carbon monoxide at a low temperature (150° to 200° C.) and then to reoxidize at 300° C. This treatment increases the rate of oxidation of gases in the analytical procedure. The copper oxide is kept at approximately 300° C. during the analyses.

The construction of the weighed absorption tubes (T_1 and T_2 , fig. 1) is shown in detail in Figure 3. These tubes are connected to

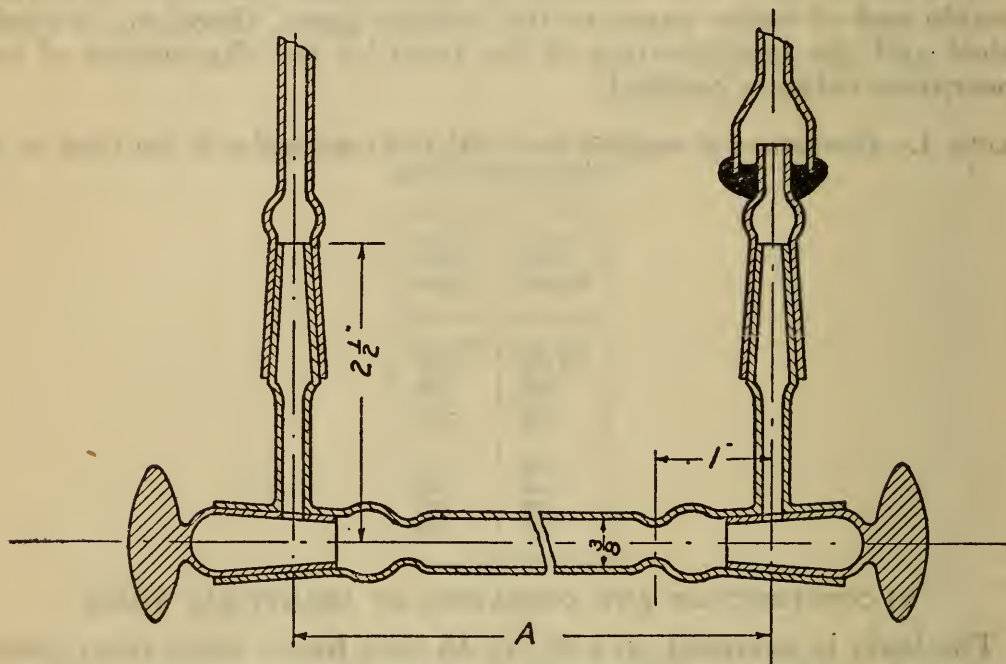


FIGURE 3.—Details of construction of absorption tube

the train by lubricated ground glass joints. The lubricant used in these joints and in the stopcocks throughout the train is the high vacuum lubricant described by Shepard and Ledig.¹⁴ The ground joints of the absorption tubes are made interchangeable, and one of the connections to the train for each tube is made through a wax seal as shown in Figure 3. This provides for greater ease in adjusting the train to receive tubes of slightly different lengths or tubes whose connecting arms may not be exactly parallel.

Two sizes of tubes are used. The phosphorus pentoxide tube (T_1) is 4 inches long (dimension A , fig. 3) and the ascarite tube (T_2) is 6 inches long. These tubes are filled with the absorbents by clamping the tube vertically in a ring stand and packing a small plug of glass wool against the end of a fixed rod entering the tubes from the lower end. A short piece of rubber tubing, about three-eighths inch long is fitted over a funnel stem in such a position that the rubber will fit tightly in the barrel of the stopcock at the opening of the side arm of the tube and thus prevent fine particles of the absorbents from

¹⁴ G. M. Shepard and P. G. Ledig, Rubber Stopcock Lubricants for High Vacuum and Other Uses, *Ind. Eng. Chem.*, **19**, p. 1059; 1927.

collecting in this arm. The absorbent is then poured in through the short-stem glass funnel and the tube is gently tapped to distribute the absorbent evenly. Another small plug of glass wool is then gently pressed on top of the absorbent material. Tight packing of absorbents is to be avoided as it retards the circulation of gases through the analytical train. In filling the ascarite tube, phosphorus pentoxide is placed on both sides of the ascarite to guard against the escape from the tube of the water liberated when the tubes are evacuated. The ascarite, which is about 8 mesh as received, is crushed to about 20 mesh just before loading in the tube. A 2-inch column of ascarite thus prepared will absorb at least 0.2 g carbon dioxide (100 ml at N. T. P.). The arms of the tubes are carefully wiped with ether, to remove the lubricant from the ground glass joints before weighing. The weighings are made against a similar tube used as a counterpoise.

After the oxidized gases have been absorbed, the residual gas is pumped from the copper oxide tube and absorbent tubes and collected in the reservoirs. The pressure of the residual gas is read on the McLeod gage and this pressure reading is converted to grams of nitrogen by means of a previously determined factor.

This train has been discussed as a gravimetric train, but it is equally adaptable to volumetric analysis, if desired. In the volumetric procedure the gases to be analyzed are collected in the reservoir system and the pressure recorded. The gases are then circulated through the copper oxide furnace and the phosphorus pentoxide tube until there is no further decrease in pressure in five minutes while the gases are still circulating. The gases are again collected in the reservoir system and the pressure recorded, the remaining gases are again circulated through the copper oxide, and this time through the ascarite tube (T_2) until there is again no decrease in pressure in five minutes. The residual gas is again collected and the pressure recorded. Since there is no change in volume when hydrogen and carbon monoxide are oxidized, the differences in the pressure readings before and after each of the two periods of circulation are the respective partial pressures of the hydrogen and carbon monoxide. These changes in pressures are then converted to grams hydrogen, oxygen, and nitrogen by means of factors previously determined.

The calculation of these volumetric factors may be illustrated as follows:

	mm	
In the determination of carbon dioxide in a gas mixture, the pressure in the reservoir system, before absorption of CO ₂	= 8	
The pressure after absorption of CO ₂	= 2	
	<hr style="width: 100%;"/>	
The change in pressure, due to removal of CO ₂ by absorption.....	= 6	
	<hr style="width: 100%;"/>	

	g
The weight of this volume of CO ₂ absorbed in an ascarite tube.....	= 0.006

Therefore, for this reservoir system at room temperature, a change in pressure of 6 mm is equivalent to 0.006 g of CO₂, or 1 mm pressure is equivalent to 0.001 g of CO₂.

From this relation the weight of any other gas, equivalent to a change in pressure of 1 mm, in this reservoir system can be computed from the respective molecular weights of the gas in question and of the carbon dioxide. For instance, the equivalent weight of hydrogen would be 2/44 that of carbon dioxide, and the equivalent weight of

nitrogen would be 28/44 that of carbon dioxide. The factor for carbon monoxide would be the same as for nitrogen, 28/44. Therefore, in this reservoir system, a change in pressure of 1 mm is equivalent to 0.001 g CO₂; or to 0.000045 g H₂; or to 0.00064 g N₂; or to 0.00064 g CO.

In the gravimetric procedure the gases to be analyzed usually are allowed to accumulate in the reservoirs and absorption train until the gas evolution in the furnace is complete; that is, until the gas pressure in the furnace drops to the pressure shown before the sample was dropped into the crucible. After the evolution of gas is complete, the furnace is cut off from the analytical train and the gases which have been accumulated in the reservoir are circulated through the complete analytical train until there is no further decrease in pressure as shown by the McLeod gage. The residual gas is then collected in the reservoir system and its pressure determined. This pressure is converted to weight of nitrogen by means of a factor, as previously described in the volumetric procedure. The hydrogen and oxygen are determined from the increase in weight of absorption tubes T_1 and T_2 , which contain, respectively, water and carbon dioxide formed by oxidation of the original hydrogen and carbon monoxide of the gas mixture.

In cases where the gas evolution is unusually large, it has been found advisable to vary the above procedure slightly. If the pressure in the train exceeds 10 to 15 mm of mercury, the gases are circulated through the absorbents for short intervals of time without waiting to complete the extraction of the gases from the furnace. This absorption of gas reduces the pressure in the system and is advisable as the diffusion pump ceases to function efficiently when the fore pressure becomes too great.

The volumetric and gravimetric procedures yield the same results and require about the same time for an analysis. The gravimetric procedure has been used in the National Bureau of Standards laboratories, mainly because it requires less time when only oxygen is desired. Results obtained by these two procedures in analyses of a series of samples of the same steels are given in Table 2.

TABLE 2.—Comparison of results obtained by gravimetric and volumetric procedures of gas analyses

	Gravimetric			Volumetric		
	O ₂	H ₂	N ₂	O ₂	H ₂	N ₂
	¹ Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Open-hearth iron No. 3.....	-----	0.0002 ----- .0002 ----- .0001 -----	0.002 ----- .001 ----- .001 -----	-----	0.0001 ----- .0001 ----- .0001 ----- .0003 -----	0.002 ----- .002 ----- .002 ----- .001 -----
Welding rod.....	0.044	-----	.003	0.043	.0000	.004
Open-hearth iron No. 2D.....	{ .065 ----- .064 -----	-----	.002 ----- .002 -----	.060 ----- .062 ----- .064 -----	-----	.002 ----- .003 ----- .003 -----

2. IMPROVEMENTS IN FURNACE CONDITIONS AND TECHNIQUE

The furnace procedure for the earlier apparatus in the vacuum-fusion method called for a preliminary outgassing of the crucible and

furnace at $1,600^{\circ}\text{C}$., usually for a period of from one-half to one hour. The furnace was then allowed to cool to room temperature, opened, and the crucible removed, charged with the sample, and returned to the furnace as soon as possible. The furnace cap was then replaced, sealed, the furnace tube evacuated, and the apparatus was then ready for heating, melting of the sample, and analysis of the evolved gases. The three latter operations required a total of about one hour. A similar analysis, without a sample, determined the gases evolved from the furnace and crucible and the values so obtained for oxygen and hydrogen were used as a blank correction. Hessenbruch and Oberhoffer have improved this procedure as already indicated, by adopting a sample loading device, similar to that used by Oberhoffer and Shenck,¹⁵ to introduce the sample into the crucible. A similar sample loading device has been adopted for the present furnace.

The present furnace procedure consists essentially in outgassing at a high temperature, $1,700^{\circ}$ to $1,750^{\circ}\text{C}$., then cooling to the analysis temperature, usually about $1,600^{\circ}\text{C}$., dropping the sample at once from the sample loading device into the crucible, and analyzing the gases evolved. The amount of gases coming from the furnace and crucible—that is, the “blank” correction—is determined by analyzing the gases pumped from the furnace for approximately the same length of time as that used in making a sample analysis.

(a) DESIGN AND CONSTRUCTION OF FURNACE

A drawing of the assembled furnace is shown in Figure 4. It consists of three major units—a sample loading device and water-cooled furnace cap (*A*), a furnace tube and water-cooled collar (*B*), a crucible, radiation screen, and crucible rest (*C*). The sample chamber of the sample loading device and the water-cooled furnace cap are constructed as a single unit. The furnace cap is sealed to the water-cooled collar and furnace tube with a picein wax. The cover of the sample chamber contains a window to permit observation of the melt and temperature measurements. This cover is sealed to the sample loading device with picein wax in a small channel provided for the purpose. A tapered metal plug for turning the revolving cylinder which contains the samples projects through the cover. The plug is lubricated with high vacuum lubricant. The whole cap unit is made of brass, the entire outer wall of the combined unit being machined from a single piece of wrought brass. This avoids all soldered joints except for attaching the brass disk forming the bottom of the water chamber of the cap.

A five-eighths-inch diameter fused silica tube which acts as a guide for the falling metal samples is suspended from two brass hooks which are soldered to the underside of the furnace cap. A small brass collar, carrying two pins (shown in detail at *D*, fig. 4) is clamped tightly about this silica tube to provide means for its support from the water-cooled cap. The lower end of the silica tube projects through a quartz disk, which serves as a screen against upward radiation from the crucible. The disk rests on the walls of the radiation screen. The lower end of the tube is flanged to facilitate removal of the disk from the furnace. If spattering of metal from the crucible is troublesome, it has been

¹⁵ P. Oberhoffer and H. Shenck, Theoretische und experimentelle Untersuchungen über die Desoxydation des Eisens mit Mangan, Stahl, u. Eisen, 47, pp. 1526-1536; 1927.

found advantageous to use a silica guide tube with a straight lower end. A thin walled graphite tube is slipped over the end of the silica tube and extends downward to the level of the top of the graphite crucible. The lower end of this graphite sleeve is split to prevent excessive heating by high-frequency induction. A graphite disk is

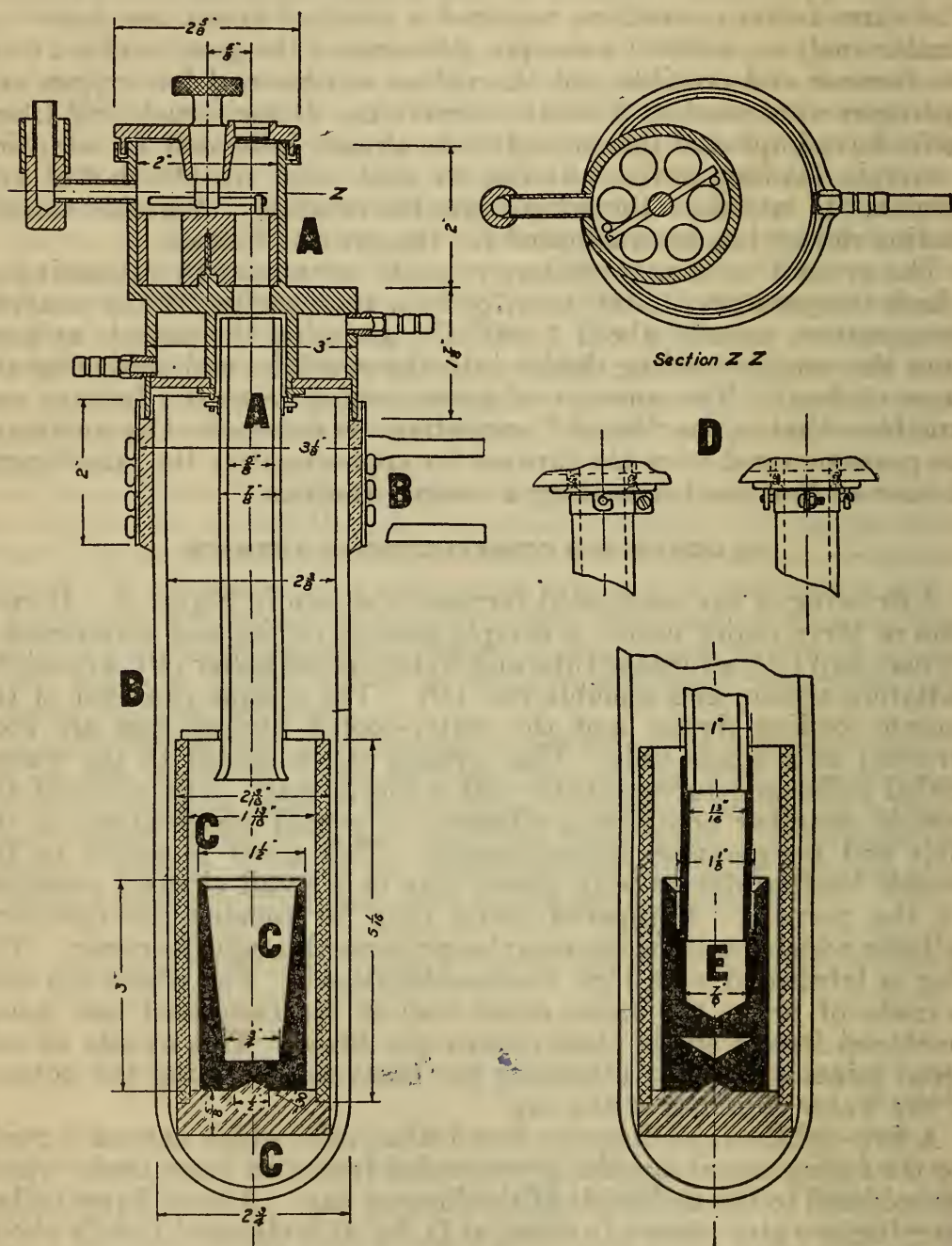


FIGURE 4.—Details of vacuum furnace and sample loading device

fitted over the end of the graphite extension tube and rests on the top of the graphite crucible. For analysis where it is desired to use a new crucible for each determination, the graphite extension tube and silica tube rest on a small graphite crucible which is contained within a graphite shell as shown in Figure 4, *E*. The fused silica furnace tube has a drawn-down closure at its lower end and a water-cooled

collar at its top. This water-cooled collar is fastened to the silica tube with a zinc powder-sodium silicate cement¹⁶ in such a way that there is provided a channel for retaining in place the wax which makes the vacuum tight seal to the furnace cap. The furnace cap should rest upon the open end of the silica tube rather than on the wax or zinc cement.

The crucibles in which the metal samples are melted are machined from Acheson graphite. The base of each crucible is recessed to fit over a small cone in the center of the magnesia block upon which both the crucible and the cylindrical radiation screen rest. This construction serves to keep the crucible and radiation screen properly centered. The radiation screen may be made from sintered magnesia or more conveniently of mullite or sillimanite porcelain.

The magnesia block for supporting the crucible and radiation screen is made by tamping electrically sintered and ground magnesia, moistened with a 2 per cent magnesium chloride solution, into a machined graphite form, drying and calcining at about 1,700° C. It is important that this magnesia support should rest in the bottom of the silica furnace tube as shown in Figure 4; that is, fitting loosely with only approximately line contact with the silica, or, that it be supported on a short section of a small silica tube ($\frac{5}{8}$ or 1 inch bore) so that it never becomes tightly wedged in the larger silica tube. If the magnesia block fits the larger tube too tightly thermal expansion during heating of the graphite crucible may break the silica tube.

The assembled furnace is connected to the analytical train by a picein wax seal as shown in Figure 1.

(b) OPERATION OF FURNACE

In preparing the furnace for an analysis, the crucible is maintained at 1,700° to 1,750° C., with the diffusion pump in operation, until the pressure in the furnace drops to about 0.1 mm. Hg. Experience has shown that, if the preheating is carried to this point, subsequent gas evolution during an actual analysis at about 1,600° C. will not cause an excessively large blank. The above-mentioned pressure is arbitrary and depends upon the assembly of the furnace and the capacity of the diffusion pump. It represents a pressure that decreases but slightly during three or four hours' heating. After the preliminary heating at 1,700° to 1,750° C., the temperature is maintained at about 1,600° C. while the blank run and actual determinations are made. The pressure of the gases within the furnace during a blank analysis will be referred to as the base pressure. For a given apparatus this base pressure should be closely approximated for all blanks and at the beginning and end of all sample analyses. The precision of the blank analyses to a large extent determines the over-all precision of a sample analysis.

The data in Table 3 demonstrate the uniformity of the blank corrections for oxygen, hydrogen, and nitrogen when the same temperature and base pressure are used. In the absence of conditions which would obviously cause errors, oxygen determinations on commercial

¹⁶ The zinc powder-sodium silicate cement is made by mixing 2 volumes of 20-mesh zinc powder and 1 volume of zinc dust. This mixture is moistened with sufficient dilute sodium silicate to form a plastic cement. Technical sodium silicate is diluted with an equal volume of water. When the cement has been packed in place it is first air dried and then further dried and hardened by heating in the flame of a hand torch.

steels are reproducible to within 0.002 per cent. If larger amounts of oxygen are present, to the extent of 0.03 to 0.06 per cent, the agreement between individual determinations usually is within 0.004 per cent.

TABLE 3.—*Magnitude of blank corrections*

	O ₂	H ₂	N ₂
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
Blank No. 1.....	0.0031	0.00028	0.0011
Blank No. 2.....	.0034	.00000	.0010
Blank No. 3.....	.0024	.00005	.0015
Blank No. 4.....	.0022	.00005	.0015

NOTE.—These blanks represent the gases evolved during a 30-minute heating following the preliminary heating of the furnace. Temperature 1,550° to 1,600° C.; base pressure 0.04 to 0.03 mm. Weights of gases evolved are calculated to equivalent per cent by weight of a 20 g. metal sample.

The preceding discussion of the amount of the blank correction assumes a furnace temperature of about 1,600° C. Experience has shown that this is the optimum temperature of operation for this apparatus. Higher temperatures invariably result in larger and more irregular blanks. These factors are of greater importance than the possibility of more complete recovery of oxygen from difficultly reducible oxides at a higher temperature.

III. ACCURACY OF THE VACUUM FUSION ANALYSIS

It is common practice in determining the accuracy of analytical methods to prepare synthetic samples containing known amounts of the constituents to be determined. This was done by Jordan and Eckman¹⁷ and the conclusion reached was that the oxygen and nitrogen of the oxides and nitrides usually encountered in commercial ferrous materials can be determined by the vacuum-fusion method. A condition was made, however, that manganese if present in sufficient quantity might affect the recovery of oxygen. In the analysis of many samples of ferrous materials, irregularities were encountered which indicated clearly that, when manganese and carbon monoxide were evolved simultaneously from the fused sample, variable amounts of oxygen would remain in the furnace. Such a condition made it impossible to assume that synthetic samples of known oxygen and manganese contents would indicate correctly the loss of oxygen to be expected for commercial steels of the same manganese content. A close study of these analyses, considering inaccuracies caused by segregation, the conditions under which the oxides were decomposed, the manganese content of the material, and the probable composition of the oxides as indicated by residue analyses, has made it possible to define more clearly the limitations of the vacuum-fusion method.

1. SAMPLING

Iron or steel when crushed or cut to small pieces in contact with atmospheric oxygen may absorb or react with variable amounts of oxygen often sufficient to make oxygen analyses inaccurate. This

¹⁷ See footnotes 4 and 5, p. 375.

has been previously discussed by numerous investigators^{18 19 20 21} who have encountered this error in studying methods for determining oxygen in various kinds of ferrous materials. In order to avoid this difficulty, a procedure for securing and preserving samples milled under oil has been described by Cain and Pettijohn.²² Such procedures are not commonly used with the vacuum fusion method as it is much simpler to select a few relatively large pieces, preferably only one, from the material to be analyzed and clean the samples by grinding off the surface.

The uneven distribution of oxygen in the ingot and, consequently, in finished steel has made sampling a difficult matter and the difficulty is greatly increased if the samples consist of only one or two pieces. It has been shown by Diergarten²³ that as the center of an ingot is approached from the sides, the material becomes richer in oxygen. This is also true for a short distance from the bottom of the ingot. Under these conditions the selection of one or two small pieces to represent the entire specimen, is a difficult matter. Much better agreement in results is obtained between duplicate samples taken from the same longitudinal plane than is obtained from duplicate samples in the same horizontal plane. The magnitude of these transverse segregations of oxygen will depend on the size of the original ingot and the conditions under which it was cast. As an illustration of the segregation which may be encountered, Grossman²⁴ cites an ingot of rimming steel which contained 0.02 per cent oxygen in the outer portions and 0.07 per cent oxygen in the core.

TABLE 4.—Oxygen values from different portions of a commercial ingot iron plate

Plate No.	Location of samples	
	Center portion, a, b, c, d, oxygen	Outer portion, e, f, g, h, oxygen
	<i>Per cent</i>	<i>Per cent</i>
812404.....	0.070	0.062
80496T.....	.081	.057
812406.....	.067	.059

¹⁸ J. R. Cain and E. Pettijohn, A Critical Study of the Ledebur Method for Determining Oxygen in Iron and Steel, B. S. Tech. Paper No. 118; 1919.

¹⁹ J. R. Eckman, Louis Jordan, and W. E. Jominy, The Oxygen Content of Coke and Charcoal Cast Irons, Trans. Am. Foundrymen's Assoc., **33**, p. 431; 1926.

²⁰ P. Oberhoffer and E. Piwowarsky, Ueber den Sauerstoff im Roh und Gusseisen, Stahl u. Eisen, **47**, pp. 521-533; 1927.

²¹ Bengt Kjerrman and Louis Jordan, A Study of the Hydrogen, Antimony, Tin Method for the Determination of Oxygen in Cast Irons, B. S. Jour. Research, **1**, pp. 701-721; 1928.

²² See footnote 18.

²³ See footnote 11, p. 377.

²⁴ M. A. Grossman, Oxygen in Steel, Trans. Am. Soc. Steel Treat., **18**, pp. 601-631; 1930.

TABLE 5.—Variation of oxygen values with type of sample and with location in original ingot

Sample No.	Type of sampling	
	I, oxygen	II, oxygen
17M.....	Per cent 0.011 .012	Per cent 0.013
17B.....		
19M.....	Per cent .009 .010	Per cent .018 .017
19B.....		
21M.....	Per cent .007 .007	Per cent .017 .009
21B.....		

Table 4 presents the results obtained from a series of analyses of three pieces of commercial ingot iron. Each piece was one-half of a

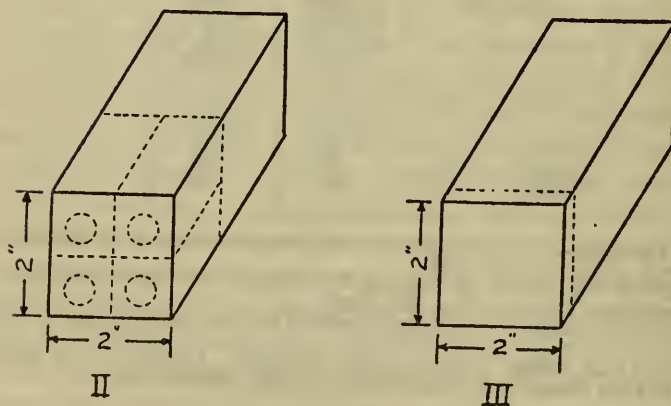
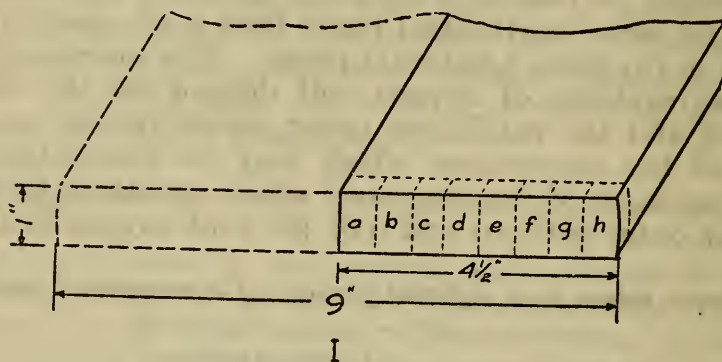


FIGURE 5.—Types of sampling

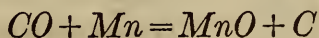
section cut transversely from a 1-inch thick by 9-inch wide plate of ingot iron. The pieces were sampled as indicated in Figure 5, I. Two groups of four pieces, *a, b, c, d* and *e, f, g, h*, were each analyzed as one sample. The analyses of the center portion of the plate, *a, b, c, d*, representing the center portion of the ingot, gave higher values for the oxygen content than did the outer portions of the plate. The importance of the location of check samples in the material to be analyzed is again emphasized by the results given in Table 5. Pieces were cut for sampling from 2-inch square bars of carburizing steel. Each of the

bars represented material which was initially the middle or bottom portions of the original ingot. Two types of samples were used for the oxygen determinations: First, one-half inch cylinders were machined from quarter sections of the bar (fig. 5, *II*); second, thin slices, one-eighth to three-sixteenths inch thick were cut from the bars (fig. 5, *III*). It was possible to obtain good agreement between check samples when the same type of sample was used, but it was not always possible to obtain good agreement between the two types of samples. The analyses of bars 17M from middle of ingot 17 and 17B from bottom of ingot 17 show that differences in oxygen content from bars taken from the same ingot may be encountered.

It is evident, therefore, that commercial steel which has been worked from ingots may vary considerably in oxygen content and that care should be taken in the selection of samples for an oxygen determination. As a rule, adjacent samples taken transversely to the original ingot have been found to vary considerably in oxygen content, but if taken longitudinally, the variations are usually small enough to be within the limits of the method. There does not seem to be any general rule to follow in sampling pig irons or steel castings.

2. INTERFERENCE BY VAPORIZED METALS

In the earlier work on the vacuum fusion method, it was observed that, in the case of certain materials, duplicate samples would not yield duplicate results for oxygen, no matter how carefully the samples were selected. The variation in results was greater than could be ascribed to segregation in the material, and it was observed that in any such series of samples the first analysis invariably produced much higher results for oxygen than did subsequent samples of the same material. Analyses No. 1, 2, 3, and 4 in Table 6 illustrate the results obtained on a typical series of samples. This difficulty occurred chiefly with materials which were relatively high in manganese and it was observed that after a series of runs on such material, a ring of metallic condensate had been formed on the inner wall of the heat insulator and on the silica tube just above the graphite crucible. Analysis of this condensate showed that it was chiefly manganese. The samples were all of the same composition and, therefore, should evolve the same amounts of gas when melted under the same conditions. The higher recovery of oxygen from the first sample must be due not to incomplete evolution of gas from the succeeding samples, but rather to incomplete recovery of the gases evolved. It was shown that the presence of the metallic condensate on the walls of the furnace above and near the crucible was the source of the trouble. Presumably a secondary reaction occurred, between some of the carbon monoxide evolved from a fresh sample and the condensed manganese evolved from previous samples, perhaps, according to the reaction:



This manganese oxide is retained in the metallic condensate on the furnace walls and the amount of carbon monoxide recovered in the analytical train is correspondingly lowered.

It was found that, if the furnace was carefully cleaned after each run and all traces of metallic condensate were removed, the difficulty

disappeared and all samples of a series yielded comparable results. It was also found that if lower pressures were maintained in the apparatus throughout an analysis, comparable results could be obtained from successive samples even though the manganese condensate was present. Analyses 5, 6, 7, and 8 in Table 6 illustrate a series of results obtained at a lower pressure. It is believed that at these lower operating pressures the carbon monoxide evolved from the sample is removed from the furnace so rapidly that no appreciable reaction can occur between the carbon monoxide and the manganese condensate.

It was evident, therefore, that if manganese condensate was allowed to accumulate in the furnace, and if the carbon monoxide evolved from the samples was allowed to remain in contact with this condensate for appreciable lengths of time, low results for oxygen were obtained. This difficulty is avoided by carefully cleaning the apparatus before each determination or by operating at very low pressures.

The above discussion applies to the older procedure²⁵ in which a new crucible was employed for each determination. In the newer apparatus a sample loading device allowed the analysis of a number of consecutive samples without opening the furnace between runs. In this procedure the second and successive samples are melted in a crucible which contains the molten residues from the preceding determinations.

TABLE 6.—Oxygen determinations, by the vacuum-fusion method

Analyses No.	Type of sample	Condensed manganese	Content of crucible before addition of sample	Oxygen
				Per cent
1	Cast-iron "E," 1.29 per cent Mn.	{ Absent.....	Empty.....	0.040
2		{ Present.....032
3		{ ..do.....016
4		{ ..do.....003
5	} ..do.....	{ ..do.....do.....	.038
6		{ ..do.....do.....	.036
7		{ ..do.....do.....	.039
8		{ ..do.....do.....	.042
9	} ..do.....	{ Absent.....	Mn free residue of Ni.....	.045
10		{ Present.....	Mn free residue + residue No. 9.....	.012
11		{ ..do.....	Mn free residue + residue No. 9 and 10.....	.010
12		{ ..do.....	Mn free residue + residue No. 9, 10, 11.....	.016
13	} Ingot iron, 0.059 per cent O ₂ .	{ ..do.....	Residue from run 12.....	.033
14		{ ..do.....	Residue from runs 12 and 13.....	.037
15		{ ..do.....	Empty.....	.058
16	} Cast steel "270," 0.74 per cent Mn.	{ ..do.....do.....	.006
17		{ ..do.....	1 residue of 0.74 per cent Mn.....	.001
18	} Cast steel "5922," 0.74 per cent Mn.	{ ..do.....	Empty.....	.005
19		{ ..do.....	2 residues of 0.74 per cent Mn.....	.000
20	} Cast steel "5923," 0.74 per cent Mn.	{ ..do.....	Empty.....	.006
21		{ ..do.....	3 residues of 0.74 per cent Mn.....	-.001
22	} Ball-bearing steel, 0.40 per cent Mn.	{ ..do.....	Empty.....	.006
23		{ ..do.....do.....	.006
24		{ ..do.....	1 residue of 0.40 per cent Mn.....	.004
25		{ ..do.....do.....	.005
26	} Si Steel No. 1, 0.09 per cent Mn., 4.0 per cent Si.	{ ..do.....	Empty.....	.080
27		{ ..do.....	1 residue of 0.09 per cent Mn., 4.0 per cent Si.....	.077
28	} Si steel No. 2, 0.06 per cent Mn, 4.24 per cent Si.	{ ..do.....	Empty.....	.076
29		{ ..do.....	1 residue of 0.06 per cent Mn, 4.24 per cent Si.....	.074

²⁵ See footnote 4, p. 375.

It was found that, under these new conditions, the troubles due to manganese reappeared even though the furnace was operated at very low pressures. If the material contained appreciable amounts of manganese the first sample of a series invariably yielded higher results for oxygen than could be obtained from the second or subsequent samples. It was concluded that, in the case of the first sample of a series, carbon monoxide is evolved from the molten sample and is carried to the absorption train, before appreciable amounts of manganese are volatilized. The second and subsequent samples, however, are melted in the residues from the preceding runs and these residues are constantly evolving manganese vapor. The carbon monoxide evolved from the second, or subsequent samples, therefore, must pass through an atmosphere relatively rich in manganese vapor before it can escape from the furnace and reach the absorption train. Carbon monoxide and freshly evolved manganese vapor might be expected to react in the same way as did carbon monoxide and condensed manganese in the earlier work. That the reaction between carbon monoxide and manganese vapor does occur, and produces low results for oxygen in the second and latter determinations of a series, is illustrated by analyses 9 to 15 in Table 6. The comparison of analyses 16 to 25, in Table 6, further shows that whenever manganese is present in appreciable amounts in the residual matter in a crucible, subsequent analyses made in that crucible will be low in oxygen but that if the crucible is empty or contains only manganese-free material, the manganese present in the sample itself does not appear to cause trouble.

TABLE 7.—Oxygen values obtained by the vacuum-fusion method from commercial steels

Steel No.	Chemical analyses			Vacuum-fusion analyses		
	Manga- nese	Silicon	Carbon	Empty crucible, oxygen	Crucible contain- ing Mn free iron, oxygen	Crucible contain- ing resi- dues of same steel, oxygen
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
C-1.....	0.37	0.013	0.07	{ 0.041 .041 .043	{ 0.045 .043 .042	{ 0.032 .029 .029
C-2.....	.72	.02	.13	.020	{ .019 .020	{ .013 .007 .005
C-4.....	.80	.15	.34	.010	{ .009 .010	{ .004 .001 < .001
C-6.....	.50	.24	.41	.003	.003	} (1)
C-5.....	.65	.17	.63	.007	.008	
C-3.....	.24	.12	1.29	.003	{ .003 .004	{ .001 .003 .001

¹ Less than blank.

The use of the sample loading device, melting successive samples in the residues from previous determinations, presents such a saving in time and convenience, in the determination of a number of samples, that further information was desired as to the maximum amount of manganese which could be present in the residues without affecting

the results. Diergarten²⁶ concluded that more than 0.7 per cent manganese would cause trouble. The data in Table 6 show that manganese contents from 1.29 per cent to 0.4 per cent produce noticeable effects. In a further study of this phenomenon several steels, of different manganese contents, were each run in three different ways: (1) In an empty crucible, (2) in a crucible which contained a residue of iron quite low in manganese (about 0.05 per cent Mn), and (3) in a crucible which contained a residue with approximately the same manganese content as the sample. The results of these experiments, presented in Table 7, show that as little as 0.24 per cent manganese in the residue may produce a definite effect on the oxygen determination, and that the residue in the crucible must be essentially free from manganese if oxygen results comparable to those obtained in an empty crucible are desired. A study of these data further shows that for a given manganese content the amount of the error varies with the amount of oxygen present. It is evident, therefore, that complete recovery of oxygen can be anticipated only when an empty crucible or one containing only a manganese-free residue is used. It has been shown that as little as 0.24 per cent manganese in the residue is dangerous. It is believed that in the general run of ferrous materials the manganese present in the sample does not affect the oxygen determination, since the carbon monoxide usually is completely evolved before appreciable amounts of manganese are volatilized. Exceptional cases in which the carbon monoxide is evolved slowly, so that evolution is not complete before volatilization of manganese occurs, will be discussed in subsequent sections of this paper.

In view of this observed effect of the presence of manganese in the crucible residue, the question arose whether other metallic vapors would act in a similar manner. Analyses 26 to 29 in Table 6 indicate that the presence of about 4 per cent silicon in the residues has only a slight effect, if any, on the oxygen recovery, and certainly has no effect comparable to that of manganese.

It might be expected that aluminum, if present in appreciable amounts in the residue, would vaporize and that the aluminum vapor would interfere with the oxygen recovery as did manganese. Diergarten²⁷ has reported that the presence of more than 0.3 per cent aluminum caused difficulties. Metallic aluminum, at least in appreciable amounts, is not a common constituent of ferrous materials but its presence should be considered in connection with oxygen determinations.

To summarize this interference by metallic vapors in the determination of oxygen; manganese, as low as 0.24 per cent, if allowed to accumulate in the crucible will cause low results to be obtained for oxygen. This is due presumably to a secondary reaction, between evolved carbon monoxide and manganese vapor, through which some of the oxygen of the carbon monoxide is retained in the upper portions of the furnace, probably in the form of nonvolatile manganese oxide. It is evident that if 0.24 per cent manganese, or more, is present in the samples, accurate results for oxygen can be obtained only if the sample is melted in an empty crucible or in one which contains a residue free from manganese. In other words, if manganese is present in the samples the successive analysis of consecutive sam-

²⁶ See footnote 11, p. 377.

²⁷ See footnote 11, p. 377.

ples in the same crucible will yield low results for oxygen. The presence of manganese in a single sample is not believed to affect the results of that determination appreciably, for the usual run of ferrous materials; that is, for samples from which the gases are evolved rapidly. The effect of condensed manganese on the upper walls of the heating chamber, from previous runs, can be largely avoided by rapid withdrawal of the evolved gases, through the use of low pressures in the furnace. A clean furnace obviously is desirable.

Some experimental evidence indicates that metallic silicon in the residues does not interfere appreciably with the determination of oxygen.

It is believed that metallic aluminum, if present in appreciable amounts, would generate vapors which would interfere with the oxygen determination in a manner similar to the interference by manganese vapor. However, metallic aluminum in appreciable amounts is not a common constituent of ordinary ferrous materials.

3. REDUCTION OF CERTAIN OXIDES

Oxygen may be present in ferrous materials in a variety of forms, such as oxides of iron, manganese, silicon, and aluminum, or in more complex combinations, such as silicates of different compositions. Furthermore, these compounds may be present in solution in the metal or as separate particles, commonly referred to as oxide inclusions. The number and size of these oxide inclusions will depend upon the steel-making practice employed, but in clean steel the total amount of inclusions and the average size are relatively small. Occasional large inclusions, if present, should be avoided in the selection of samples.

The different oxide compounds will vary in ease of reduction and for a given compound the rate of reduction will vary inversely with the size of the particles. Obviously, complete reduction of the oxide compounds is essential. It is also important that this reduction be completed within a reasonable time, since the blank correction becomes unreliable and too large if the determination is unduly prolonged. Oxides of silicon and aluminum and complex silicates obviously will be more difficult to reduce than the oxides of manganese or iron. It is believed that these latter oxides are quickly and completely reduced under the conditions of a vacuum-fusion analysis, namely, saturation of the melted sample with carbon in a graphite crucible maintained at about 1,600° C., and the maintenance of a low pressure (about 2 mm. of mercury) over the fused sample during reduction.

Jordan and Eckman²⁸ investigated the reduction of silica and silicates in a number of synthetic samples. In the preparation of these samples electrolytic iron was freed from oxygen by vacuum fusion in a graphite crucible. The resulting iron-carbon alloy, oxygen free, was divided into portions of about 20 g. each, and a small hole was drilled in each piece. A weighed amount of silica was placed in the hole and the sample of iron-carbon alloy plus silica, in a graphite crucible was subjected to a vacuum fusion determination for oxygen. The high recoveries of oxygen obtained from this relatively coarse silica led to the belief that satisfactory recovery could be expected for

²⁸ See footnote 4, p. 375.

the oxygen present as silica or silicates in steel, in the finely divided form normally encountered. Diergarten²⁹ confirmed this belief but Thanheiser and Müller³⁰ reported that oxygen combined as silica was only partially recovered by the vacuum-fusion method. Their conclusions were based on the observation that only 70 per cent of the oxygen in a low-carbon steel was recovered when the sample was melted in a crucible which already contained a high-silicon residue. This experiment was repeated in the present investigation. Approximately 12 g. of ingot iron which contained 0.06 per cent oxygen was dropped into a residue which contained 4 per cent silicon. After one hour of heating at 1,500° to 1,550° C., twice the time required for decomposition of a normal sample, the pressure within the furnace was still above the base pressure, indicating that reduction of oxides was not yet complete. During this hour about 70 per cent of the oxygen present in the sample was recovered in the analytical train. Visual observations during the run indicated the presence of relatively large particles floating on the surface of the melt. From these observations and from the fact that the pressure in the furnace remained higher than usual, it was concluded that the oxygen present in the ingot iron had reacted with silicon of the residue, to form relatively large agglomerates of silica which were decomposed only slowly. It is believed that this agglomeration of silica into relatively large particles, which are only slowly decomposed, is a phenomenon peculiar to the conditions of this and Thanheiser and Müller's experiment; that is, the addition of a sample rich in iron oxide to a residue rich in silicon. The presence of a high-silicon residue in the crucible did not produce a definite effect on the recovery of oxygen in analyses 26 to 29 cited in Table 6. Many samples of steel known to contain silicon and silica or silicates have been analyzed by the vacuum-fusion method and in the great majority of cases decomposition has proceeded rapidly to completion, as indicated by the observations of pressure within the furnace. Comparison of results for oxygen by the vacuum-fusion method and by the HCl residue analysis method, discussed in subsequent sections of this paper, indicates that complete recovery of oxygen from silica and silicates is obtained by the vacuum-fusion method.

It is believed, therefore, that oxygen is satisfactorily recovered, by the vacuum-fusion method, from the silica or silicates ordinarily present in steel, but that the presence of unusually large silica or silicate particles may require an abnormal length of time for complete reduction. If manganese is present in the sample it has been shown that satisfactory results for oxygen can be obtained only when the gas evolution is rapid as well as complete. Since manganese is present in practically all ferrous materials, large silicate inclusions or any other compounds which extend the time required for complete reduction are undesirable. It is believed, however, that in a normal determination the rapid return of the pressure in the furnace to the initial pressure indicates the complete reduction of silica or silicates present. If difficulty develops it will be indicated by abnormal pressures in the furnace.

Alumina is another difficultly reducible oxide which must be considered. Jordan and Eckman³¹ and Diergarten³² concluded that

²⁹ See footnote 11, p. 377. ³⁰ See footnote 10, p. 376. ³¹ See footnote 4, p. 375. ³² See footnote 11, p. 377.

alumina could be decomposed in a vacuum-fusion analysis. This conclusion is believed to be correct for the amount of alumina (a very few thousandths of 1 per cent) ordinarily encountered in commercial ferrous materials. However, experiments have shown that if unusual amounts of alumina are present, decomposition is not always complete within the time limit imposed by the presence of manganese. This statement is based on the identification of unreduced alumina in the residues from vacuum fusion determinations on certain steels known to contain relatively large amounts of alumina.

The data presented in Table 8, discussed in subsequent paragraphs, show that when the alumina in steel is not more than the few thousandths of 1 per cent ordinarily encountered, the amount of oxygen recovered by a vacuum fusion determination is at least as great as, and usually greater than, the oxygen recovered by residue methods of analysis. The results for sample C-6 in Table 8 particularly show that as much as 0.003 per cent alumina is completely recoverable within reasonable limits of error by a vacuum fusion determination. This is about the maximum amount of alumina present in most commercial steels. However, the data in Table 8 also show that if larger amounts of alumina, one or two hundredths of 1 per cent, should be present as in the TA samples, the oxygen recovered by a vacuum fusion is definitely less than that recovered by residue methods of analysis. Attention is called to the fact that in these TA samples the greater part of all the oxygen present is present as alumina due to unusually large additions of aluminum to the ladles. It is evident that these amounts of alumina are not completely reduced rapidly enough to avoid the interference of secondary reactions such as that with manganese vapor.

It is concluded that the vacuum-fusion method of an analysis is applicable to steels which contain only the customary few thousandths of 1 per cent of alumina, but that if unusual amounts of alumina are present in the sample, low recoveries of oxygen will be obtained.

4. PROBABLE ACCURACY OF THE OXYGEN DETERMINATION

It is obvious that the successful application of the vacuum-fusion method for oxygen depends upon the complete decomposition of the oxides present in the sample. Earlier investigators concluded that all of the oxides normally present in ferrous materials could be decomposed in a vacuum-fusion analysis. This conclusion was based on analysis of synthetic samples. More recently, it has been recognized that this decomposition in many cases must be rapid as well as complete, to avoid interference by the vapors of volatile metals, such as manganese, which are present in many ferrous materials. The determination of the accuracy of the method for oxygen is made difficult by the lack of reliable, independent methods of analysis, to confirm or disprove the results obtained by the vacuum-fusion method.

TABLE 8.—Analyses of steels

Steel No.	Analyses of HCl residue ¹			Vacuum-fusion oxygen	Chemical analyses		
	Silica oxygen	Alumina oxygen	Total oxygen		Silicon	Manganese	Carbon
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
98T-----	0.004	0.002	0.006	0.013	0.40	0.72	0.22
98TA-----	.003	.013	.016	.012			
99T-----	.009	.001	.010	.015	.30	.67	.21
99TA-----	.001	.016	.017	.011			
04T-----	.012	.001	.013	.019	.37	.69	.25
04TA-----	.004	.009	.013	.008			
05T-----	.014	.002	.016	.025	.35	.73	.19
05TA-----	.001	.020	.021	.016			
C-1-----	.002	.002	.004	.043	.013	.37	.07
C-2-----	.002	.001	.003	.020	.02	.72	.13
C-4-----	.003	.001	.004	.010	.15	.80	.34
C-5-----	.001	.001	.002	.007	.17	.65	.63
C-6-----	.001	.003	.004	.003	.24	.50	.41

¹ These values were obtained from an analysis of the hydrochloric acid residue; the details of procedure are briefly described in B. S. Jour. Research, 5, p. 1141; 1930.

The data in Table 8 illustrates results obtained for certain samples of steel. Each pair of T and TA samples represent material from the same ladle of finished steel, the T sample containing no ladle addition and the TA sample representing the T metal after a ladle addition of 1 pound of aluminum per ton of steel. The C samples were selected from stock material. The results for the T series (0.70 Mn) show that when appreciable amounts of silica, but only small amounts of alumina are present, more oxygen is recovered by the vacuum-fusion method than by the residue methods. The difference between the oxygen values by the vacuum-fusion method and by the HCl-residue method averages 0.006 per cent in favor of the vacuum-fusion oxygen. Herty ³³ has calculated that iron prepared under steel-making conditions to contain 0.2 per cent carbon, will probably contain about 0.03 per cent dissolved oxygen, whereas if 0.2 or 0.3 per cent silicon is present the steel will contain approximately 0.006 per cent of dissolved oxygen. If this amount of dissolved oxygen is added to the total from the residue analysis of each of the T samples, the agreement with the corresponding vacuum-fusion results is almost perfect. This indicates that the vacuum-fusion results for oxygen correctly represent the total oxygen present in the case of samples which contain appreciable amounts of silica and small amounts of alumina, even in the presence of about 0.70 per cent manganese.

In the C series, samples 1 and 2 contain less of both carbon and silicon than do the T series. The dissolved oxygen, therefore, would be greater and, hence, the vacuum-fusion results are higher than the sum of the residue analyses. Samples 4 and 5 approach the previous composition and for these two samples the assumption of 0.006 per cent dissolved oxygen brings excellent agreement between the vacuum fusion and residue determinations. In sample 6 evidently more heavily deoxidized with aluminum than were the other C samples, it appears that little or no dissolved oxygen is present. In this case the vacuum fusion and residue oxygens agree directly without correction. It appears, therefore, from consideration of these C samples, that

³³ C. H. Herty, Jr., and coworkers, The Physical Chemistry of Steel Making, Min. and Met. Investig. Bull., 34, and Bull. 36, Carnegie Inst. of Tech., Pittsburgh, Pa.

complete recoveries of oxygen can be obtained when small amounts of silica and alumina are present, even in the presence of appreciable amounts of manganese.

In the case of the TA samples different conditions are encountered. Deoxidation of the steel in the ladle, through the addition of unusually large amounts of aluminum, resulted in the presence of unusually large amounts of alumina in the samples. The fact that the silica content of each TA sample is lower than that of the corresponding T sample indicates that the dissolved oxygen has been eliminated from the TA samples, since the reaction between aluminum and dissolved oxygen presumably would precede any reaction between aluminum and silica. In view of this absence of dissolved oxygen, and the previous discussion of the slow decomposition of alumina, it is not surprising that in these TA samples the oxygen recovered by the vacuum-fusion method is less than the sum recovered by residue methods of analysis. Attention is directed to the fact that the T and TA samples were identical except for the addition of aluminum in the ladle in the case of the TA samples. The total oxygen of the T and corresponding TA samples, therefore, should be the same although the oxygen is present in different states of combination. In the TA series the sum of the oxygen combined as alumina and silica, determined by residue analyses, is in good agreement with the vacuum-fusion oxygen for the corresponding samples of the T series. This is further evidence of the correct determination of total oxygen by the vacuum-fusion method for samples such as the T series, where manganese and only small amounts of alumina are present. If larger amounts of alumina are present, and if all the oxygen present is combined as silica and alumina, as in the TA series, the vacuum-fusion results for total oxygen will be low, but for such material the HCl-residue method of analysis will indicate the correct result. The vacuum-fusion method, therefore, is preferable when dissolved oxygen is present, and residue methods of analysis are preferable when a large part of the oxygen is combined in difficultly reducible forms.

The oxygen, presumably present as ferrous oxide, in ingot iron or in other forms of relatively pure iron, is readily determined by the vacuum-fusion method. The only exception to this statement so far encountered, was in the case of a high oxygen ingot iron melted in the presence of a high-silicon residue. Under these conditions silica was formed and for some unknown reason the silica agglomerated to form a few unusually large masses which decomposed very slowly. Oxygen recovery in this case was low, but the circumstances were unusual and the results are not at all representative of results for this type of material.

The cooperative analysis in Table 9, previously published elsewhere,^{34 35} illustrate the results which may be obtained on material such as ingot iron. Samples prepared at the National Bureau of Standards were submitted to Prof. C. H. Desch, at the University of Sheffield, Sheffield, England, and to the late Prof. P. Oberhoffer, at the Institute für Eisenhüttenkunde, Aachen, Germany. After the death of Professor Oberhoffer the analyses at Aachen were completed by Doctor Hessenbruch. At Sheffield the hydrogen reduction method

³⁴ B. S. Tech. News Bull. No. 128, December, 1927.

³⁵ W. Hessenbruch, Procédé rapide amélioré pour la détermination des gaz dans les métaux, en particulier de l'oxygène dans l'acier, Rev. Met., 26, pp. 93-114; 1929.

was employed, with the addition of antimony-tin alloy. At Aachen the samples were decomposed by vacuum fusion in graphite and the gases were determined by volumetric methods. At the National Bureau of Standards the samples were decomposed by vacuum fusion and the gases were determined by a gravimetric method. These results for the hydrogen reduction and vacuum-fusion methods, show that the oxides in this type of material are completely decomposed by the vacuum-fusion procedure. The data also illustrate the agreement which can be obtained between different operators using the vacuum-fusion method. Similar agreement has been obtained in other cooperative analyses.

TABLE 9.—*Cooperative analyses of ingot iron*

(0.04 C, 0.03 Mn, 0.02 S, 0.006 Si.)

Sheffield hydrogen reduction (oxygen)	Aachen vacuum fusion, vol- umetric (oxygen)	National Bureau of Standards vacuum fusion, gravimetric (oxygen)
<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
0.056	0.055	0.057
.057	.059	.059
.049	.062	.058
.048	-----	.058
.049	-----	-----
.051	-----	-----
Ave. 0.051	0.059	0.058

It is believed, therefore, that the total oxygen in many ferrous materials is correctly indicated by a vacuum-fusion determination when the oxygen is present in the sample in the form of ferrous oxide, manganese oxide, and finely divided silica or silicates. Large particles of silica or silicates require too much time for complete decomposition, but the presence of such large particles in a sample indicates either poor material or faulty sampling. If alumina is present in ordinary amounts, not more than 0.003 per cent, satisfactory results are obtained by the vacuum-fusion method for oxygen. If unusual amounts of alumina are present (more than 0.01 per cent) low recovery of oxygen will result because of the slow decomposition of alumina. The presence of manganese in a sample does not interfere with the vacuum-fusion determination of oxygen unless the evolution of carbon monoxide from the sample is unduly prolonged on account of the presence of refractory oxides, particularly alumina. However, the successive determination of a series of samples, using the sample loading device to drop each fresh sample into the crucible which contains the residues from previous samples, is not feasible if the samples contain manganese. Any manganese present in the crucible, in residues from previous fusions, evolves manganese vapor which will result in low recoveries of oxygen from subsequent samples melted in that crucible.

The foregoing considerations and data are interpreted to indicate that the total oxygen in ingot iron, in other forms of relatively pure iron, and in plain carbon steels, is correctly indicated by the results of a vacuum-fusion analysis. The principal difficulty encountered

has been due to the presence of unusually large amounts of alumina and this difficulty is increased by the presence of manganese in the sample. It is difficult to determine the effect of metallic alloying elements on the recovery of oxygen by a vacuum fusion, but so far none of the common alloying elements, except manganese, has been shown to be dangerous. It is believed that the method is adaptable to many alloy steels as well as to the plain carbon steels. The presence of refractory oxides, such as alumina, causes low recovery of oxygen by the vacuum fusion method. With such samples, better recoveries of oxygen are obtained by residue methods.

5. ACCURACY OF THE NITROGEN DETERMINATION

Analyses of synthetic nitrides by solution methods and by the vacuum-fusion method³⁶ showed that the nitrides, which might be present in ordinary steels, are decomposed as completely, sometimes more completely, by the vacuum-fusion method than by the solution methods. In these experiments the nitrogen evolved in the vacuum fusion was absorbed in calcium vapor and was subsequently determined by a solution-distillation method. This required the use of separate samples for the nitrogen and for the oxygen determinations. In the procedure described in this paper, the residual gas in the analytical train, after the absorption of carbon dioxide and water vapor, is assumed to be nitrogen. The amount of this gas is determined by a volumetric method, thus permitting the determination of hydrogen, oxygen, and nitrogen on the same sample. Comparison with results obtained by a solution method, illustrated by the data in Table 10, indicates that this vacuum-fusion method yields correct values for nitrogen. The data in Table 10 also show that the presence of manganese does not affect the determination of nitrogen. In fact, no interferences of any kind have been observed in the determination of nitrogen by the vacuum-fusion method.

It is believed, therefore, that the present vacuum-fusion procedure for nitrogen in ferrous materials yields correct results and is not subject to interference.

No attempt has been made to establish the accuracy of the vacuum-fusion method for hydrogen, since hydrogen is present only in insignificant amounts in most ferrous materials.

³⁶ L. Jordan and F. E. Swindells, *Gases in Metals: I. The Determination of Combined Nitrogen in Iron and Steel and the Change in Form of Nitrogen by Heat Treatment*, B. S. Sci. Paper No. 457; 1922.

TABLE 10.—Nitrogen values obtained from commercial steels by vacuum fusion and solution methods

Steel No.	Nitrogen by vacuum-fusion method			Nitrogen by solution method, nitrogen	Manganese
	Empty crucible, nitrogen	Crucible containing Mn free iron, nitrogen	Crucible containing residues of same steel, nitrogen		
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
C-1.....	{ 0.009 .008 .010	{ 0.008 .007 .007	{ 0.008 .009 .008	{ 0.007	0.37
C-2.....		{ .014 .013	{ .013 .012 .010	{ .014	.72
C-4.....	.004	{ .004 .005	{ .004 .004 .003	{ .006	.80
C-6.....	.004	.004	.003	.005	.50
C-5.....	.004	.004	{ .002 .002	{ .005	.65
C-3.....	.007	{ .006 .008	{ .006 .007 .007	{ .006	.24

IV. SUMMARY AND CONCLUSIONS

Apparatus and procedure for the determination of hydrogen, oxygen, and nitrogen in ferrous materials by the vacuum-fusion method are described in detail.

The results of a number of analyses of ferrous materials are discussed. The data indicate that the method, (in the absence of interferences) gives values reproducible to within 0.002 per cent for either oxygen or nitrogen. The data also indicate that the accuracy of the oxygen determination is affected only when the steel contains a relatively large amount of alumina and manganese or when the fusion is made in a crucible which already contains a residue in which manganese is present. No similar influences have been encountered, which would affect the accuracy of the nitrogen determination.

The oxides commonly encountered in ferrous materials, with the exception of alumina, are probably completely decomposed shortly after the sample has melted. The time of decomposition, when the sample does not contain relatively large amounts of alumina, is approximately five minutes. If the decomposition should require a longer time, the harmful effect of manganese is increasingly evident.

Manganese affects an oxygen determination when it is simultaneously present as vapor with carbon monoxide immediately above the crucible. Such a condition results in the formation of a non-volatile compound, presumably manganese oxide, which deposits in the cooler parts of the furnace and, consequently, is not determinable with the present apparatus. The effect of manganese vapor has been detected from residues containing as little as 0.2 per cent manganese. Therefore, it is recommended that analyses be made in crucibles

free from manganese. A relatively slow decomposition of oxides in the presence of manganese vapor is considered to be the most serious source of error so far identified in the oxygen determination.

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