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COOPERATIVE STUDY OF METHODS FOR THE DETERMINATION OF OXYGEN IN STEEL

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ABSTRACT

The data from reports of 35 laboratories, comprising more than 2,000 analytical determinations, indicate that the vacuum-fusion method yields accurate results for the oxygen contents of plain-carbon steels either aluminum-killed, silicon-killed, or of the rimming type; the aqueous-iodine method yields accurate results for some types of killed steels and low results for other steels; more data, and particularly more concordant data, are necessary to define the accuracy of the other methods employed in this cooperative analysis.

The vacuum-fusion procedures are reviewed and recommendations given for obtaining optimum results by this method.

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I. INTRODUCTION

The methods employed for the determination of oxides and oxygen in ferrous materials may be roughly classed in two groups, "residue" methods and "reduction" methods. The first group includes the iodine, electrolytic, mercuric chloride, hydrochloric acid, nitric acid, and chlorine methods, all depending upon the action of a selected medium to separate the metallic portions of the sample from the oxygen-containing constituents. Subsequent analysis of the insoluble residue permits the isolation and separate determination of individual oxides and compounds. The reduction methods depend upon the action of carbon or hydrogen, at elevated temperatures, to reduce the oxygen-containing constituents. With the exception of the recently

developed fractional vacuum-fusion method, the reduction methods do not attempt to identify individual oxides and compounds but yield only a single value for the sum of the oxygen contents of several or all of the oxide constituents. With such a diversity in principles and aims, it is not surprising that concordance of results by different methods has usually been difficult to obtain and, consequently, the accuracy and merits of each of the methods of analysis have been subjects of controversial and extended discussion.

The present cooperative attempt to define the accuracy and limits of usefulness of the various methods originated in correspondence between Dr. John Johnston, Director of Research of the United States Steel Corporation, and other metallurgists. The plan was, briefly, to submit identical samples to a number of laboratories for analysis by different methods and to collate the results of these analyses. The project was endorsed by the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers at the Annual Meeting in February 1933, and has been conducted under the joint sponsorship of the Iron and Steel Division and the National Bureau of Standards. The latter organization undertook the preparation and distribution of sample material and the collection of data from the cooperating laboratories. The preliminary stages of the undertaking have been described in progress reports¹ to the sponsors. The results obtained to date, comprising more than 2,000 individual determinations, are described in considerable detail in a paper² presented at the meeting of the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers in February 1937 and are presented in somewhat condensed form in the present paper, together with a few data that were not available when the other report was prepared.

Seven plain-carbon steels and one open-hearth iron were selected, chiefly from commercially available material, covering a range in carbon, silicon, manganese, sulphur, phosphorus, and oxygen contents. Different melting and deoxidation practices insured the presence in the different steels of different amounts and combinations of oxygen. Alloy steels were not included in the selected list, to avoid the additional complications introduced by the presence of alloying elements. The seven steels and the open-hearth iron recorded in table 1 were procured by R. F. Mehl and C. H. Herty, Jr., through the cooperation of the Jones and Laughlin Steel Corporation, the Carnegie Steel Co., and the American Rolling Mill Co.

Many precautions were observed in the preparation of sample material in order that all of the analytical samples of a particular steel should be as nearly identical as possible. For each of the eight compositions a portion of a single large ingot was selected so as to obtain material as free as possible from vertical segregation. Difficulties resulting from horizontal segregation in the ingot, i. e., from skin to core, were avoided by converting the 500-pound selected portion of the ingot into hot-rolled rod approximately 1 inch in diameter. An analytical sample consisting of a complete cross section of a rod therefore represents a complete cross section of the ingot, and adjacent samples should be identical even though neither one is completely homogeneous.

¹ *Mining and Met.* 15, 215 (1934); 16, 184 (1935).

² *Metals Tech.* (December 1936).

TABLE 1.—Type and composition of the selected steels

Steel	Type	Additions			Composition (percent)						
		Furnace	Ladle	Mold	C	Si	Mn	S	P	Cr	V
1	Low-carbon, rimming.....	None.....	FeMn.....	None.....	0.03	0.002	0.31	0.036	0.011	0.004	>.001
2	Medium-carbon, high-manganese, silicon-killed...	FeMn.....	Hot metal, FeMn, FeSi...	None.....	.42	.26	1.15	.025	.020	.022	>.001
3	Bessemer screw stock semikilled.....	None.....	FeMn, S.....	FeSi.....	.12	.024	.72	.168	.101	.006	.004
4	Special, low-carbon, aluminum-killed.....	SiMn, FeMn.....	FeSi, Al.....	None.....	.17	.09	.65	.029	.014	.008	.001
5	Low-carbon, silicon-killed.....	None.....	FeMn, FeSi.....	None.....	.22	.14	.45	.042	.020	.020	.001
6	Medium-carbon, silicon-killed.....	Spiegel.....	FeMn, FeSi.....	None.....	.43	.20	.47	.027	.014	.012	.001
7	Open-hearth iron, rimming.....	None.....	Al.....	None.....	.016	.001	.024	.022	.011	.009	.001
8	Similar to no. 4, but higher in oxygen.....	None.....	Al.....	Al.....	.20	.03	.45	.033	.014	.012	>.001

Samples taken at intervals throughout the length of each rod were subjected to analysis by the vacuum-fusion method. These exploratory analyses confirmed the reproducibility of results obtained from adjacent specimens and showed that the oxygen content of the portion of each rod selected for sample material was satisfactorily uniform from end to end. The maximum difference between the highest and lowest values for each of the seven steels (oxygen content 0.02 percent or less) was 0.003 percent, and for the open-hearth iron (oxygen content 0.10 percent or more) the maximum difference was 0.01 percent.

For further study of segregation, transverse sections taken at intervals along each rod were roughly polished with 1G emery paper and then etched from 10 to 15 minutes in diluted hydrochloric acid (1+1) at 70° C. The characteristic pattern developed in each of the eight steels, figure 1, clearly indicated differences between the core and outer areas of most of the steels, but no significant difference could be detected in samples from different positions in the same rod. Oxygen segregation sometimes accompanies the segregation revealed by deep etching, as was shown by vacuum-fusion analyses of samples representing (1) complete cross sections of the rods, and (2) core areas after removal of the outer layers in a lathe. For example, the results for steel 1 were 0.019 percent of oxygen for the complete cross section 0.96 inch in diameter, and 0.033 percent of oxygen for the core area 0.357 inch in diameter. Likewise, the results for iron 7 were 0.112 percent of oxygen for the complete cross section 1.25 inches in diameter and 0.128 percent of oxygen for the core 0.494 inch in diameter. These results emphasize the necessity for using a complete cross section of a rod for each analytical sample.

Obviously the oxygen-rich scale resulting from hot-rolling must be removed from the sample prior to the determination of oxygen or oxides. To insure uniformity in this respect it was directed that the diameter of iron 7 be reduced to 1.25 inches and the diameter of each of the other steels to 0.95 inch, in a lathe just before the analytical samples were prepared.

At the completion of the exploratory examination the rods were cut into short lengths, each being marked to identify its position in the original rod. Bundles of eight 6-inch rods, one from each of the eight steels, were prepared for the cooperating laboratories.

Meanwhile correspondence had been conducted with laboratories in this country and abroad, that were known to be interested in the determination of oxygen in ferrous materials. The present summary is based on the results reported by the 35 laboratories listed in table 2, together with identification numbers and with indications of the methods of analysis employed. Several of the laboratories reported results by more than one method of analysis. Consequently, there are available 15 reports of determinations by the vacuum-fusion method, 11 by iodine methods, 8 by electrolytic methods, 4 by hydrogen-reduction methods, 3 by the chlorine method, 2 each by the mercuric-chloride and hydrochloric-acid methods, and one by the nitric-acid method, representing a total of more than 2,000 analytical determinations.

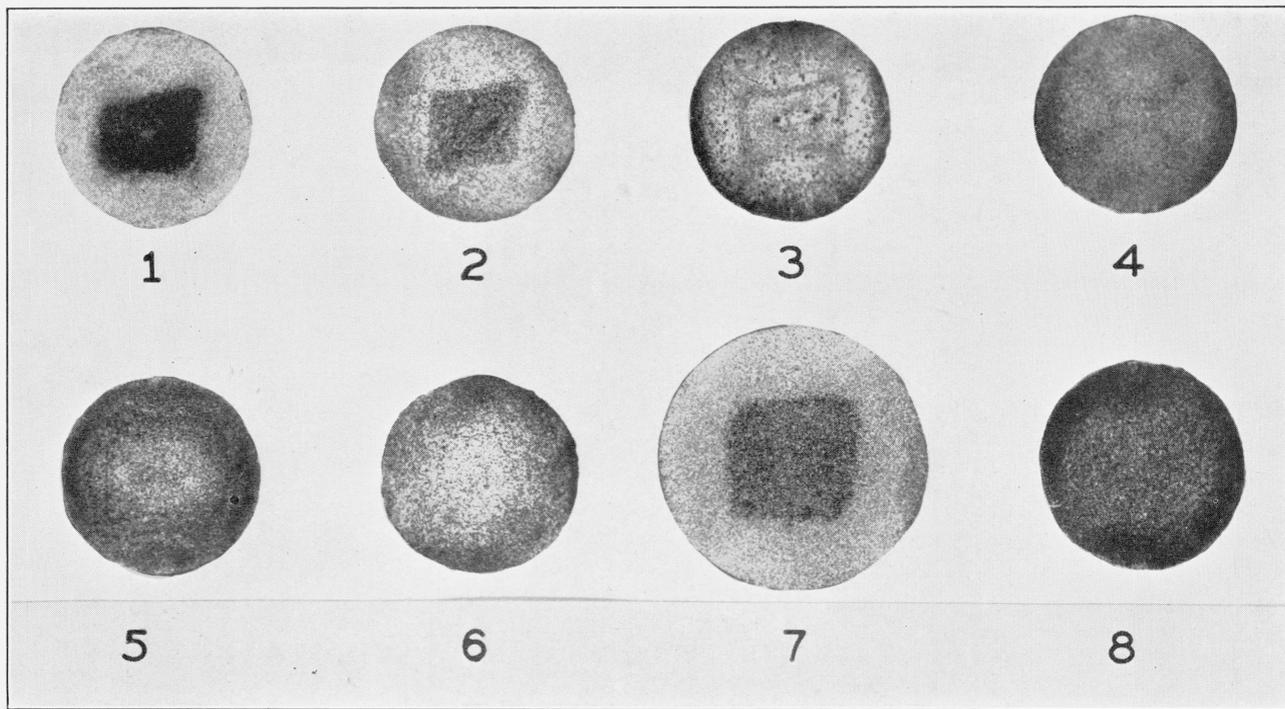


FIGURE 1.—*Appearance of the eight steels after deep etching in 1:1 hydrochloric acid. $\times 1$.*

TABLE 2.—Cooperating laboratories and methods employed

Identification number	Laboratory	Method
1.....	Battelle Memorial Institute, Columbus, Ohio.. S. Epstein, Metallurgist.	Microscopical examination and inclusion count. Metals & Alloys 2, 186 (1931).
2.....	United States Steel Corporation, Kearny, N. J. John Johnston, Director of Research; T. E. Brower, B. M. Larsen.	Hydrogen-reduction method. Trans. Am. Inst. Mining Met. Engrs. 113, 61 (1934).
3.....	Mining and Metallurgical Advisory Boards to the Carnegie Institute of Technology, Pittsburgh, Pa. C. H. Herty, Jr., Director of Research; J. F. Sanderson, B. E. Sockman.	Electrolytic method as described by Fitterer, et al. U. S. Bur. Mines, Report of Investigations 3205 (May 1933).
4.....	Inland Steel Co., Indiana Harbor, Ind..... Frank W. Scott.	Electrolytic method. Ind. Eng. Chem., Anal. Ed. 4, 121 (1932).
5.....	The British (Guest Keen Baldwins) Iron and Steel Co., Ltd., Port Talbot, Wales. F. F. Hunting, Chief Metallurgist; N. Gray, Chief Chemist.	Hydrogen-reduction method. Sample melted with antimony and tin.
6.....	The Babcock and Wilcox Tube Co., Beaver Falls, Pa. Newell Hamilton, Research Metallurgist.	Vacuum-fusion method. Trans. Am. Inst. Mining Met. Engrs. 113, 111 (1934).
7.....	Bethlehem Steel Co., Inc., Bethlehem, Pa..... P. E. McKinney, Metallurgical Engineer; George F. Stammler.	Iodine method, essentially that of cooperator 13.
8.....	Department of Engineering Research, University of Michigan, Ann Arbor, Mich. John Chipman, Research Engineer; M. G. Fontana, C. L. Raynor.	Vacuum-fusion method. Ind. Eng. Chem., Anal. Ed. 7, 391 (1935).
9.....	English Steel Corporation, Ltd., Sheffield, England. T. R. Walker, Chief Research Chemist.	Iodine method of cooperator 13 Nitric acid residue method. J. Iron Steel Inst. 113, 177 (1926).
10.....	Lukens Steel Co., Coatesville, Pa..... Wm. G. Hampton, Metallurgical Engineer.	Iodine method. Solution by Willems' method. Arch. Eisenhüttenw. 1, 655 (1928); analysis of residue by method of cooperator 13.
11.....	The Research Institute for Iron, Steel, and Other Metals, Sendai, Japan. T. Ishiware, Director; T. Yajima.	Vacuum-fusion method. Includes features of several procedures.
12.....	S K F Industries, Inc., Philadelphia, Pa..... Haakon Styri, Director of Research.	Electrolytic method. Trans. Am. Inst. Mining Met. Engrs. 105, 185 (1933); Metals & Alloys 5, 96 (1934).
13.....	Electro Metallurgical Co., Niagara Falls, N. Y. Thos. R. Cunningham.	Iodine method of Cunningham and Price. Ind. Eng. Chem., Anal. Ed. 5, 27 (1933).
14.....	Bell Telephone Laboratories, New York, N. Y. J. H. Scaff.	Vacuum-fusion method. Metals & Alloys 4, 7 (1933).
15.....	Kaiser-Wilhelm Institut für Eisenforschung, Düsseldorf, Germany. F. Körber, Director.	Vacuum-fusion method. Mitt. Kaiser-Wilhelm Inst. Eisenforsch. 13, 215 (1931). Chlorine method. Mitt. Kaiser-Wilhelm Inst. Eisenforsch. 9, 195 (1927).
16.....	Ontario Research Foundation, Toronto, Canada. O. W. Ellis, Director of Metallurgical Research; J. R. Gordon, Research Metallurgist.	Iodine method of cooperator 13.
17.....	Kohle u. Eisenforschung GMBH Forschungsinstitut, Dortmund, Germany. E. H. Schulz, Director.	Chlorine method. Mitt. Forsch. Inst. Ver. Stahlwerke 1, 231 (1930); Chem. Fabrik 2, 51 (1929). Hydrogen-reduction method. Stahl u. Eisen 40, 812 (1920); Arch. Eisenhüttenw. 3, 459 (1929-30).
18.....	Metallografiska Institute, Stockholm, Sweden. Carl Benedicks, Director; G. Phragmén, Metallographer.	Vacuum-fusion method. Jernkontorets Ann. 114, 549 (1931).
19.....	The American Rolling Mill Co., Middletown, Ohio. A. H. Thomas, Supervisor, Service Testing Laboratories; D. L. Reck, Research Engineer; O. B. Ellis, Chemist.	Electrolytic method of cooperator 3. Iodine method of cooperator 13.
20.....	Fried. Krupp Aktiengesellschaft Gusstahlfabrik, Essen, Germany. P. Klinger, Chief Chemist.	Vacuum-fusion method, presumably. Arch. Eisenhüttenw. 6, 189 (1932). Analysis as described in Stahl u. Eisen 45, 1559 (1925). Chlorine method. Arch. Eisenhüttenw. 7, 618 (1933-34). Mercuric-chloride method. Arch. Eisenhüttenw. 8, 391 (1934-35). Electrolytic methods. (A) Ind. Eng. Chem., Anal. Ed. 4, 121 (1932). (B) Jernkontorets Ann. 116, 166 (1932).

TABLE 2.—Cooperating laboratories and methods employed—Continued

Identification number	Laboratory	Method
21-----	Istituto Scientifico Tecnico Ernesto Breda, Milano, Italy.	Vacuum-chloride method. Arch. Eisenhüttenw. 6 , 189 (1932). Iodine method. Essentially method of cooperator 13.
22-----	The United Steel Companies, Limited, Stocksbridge, England. T. Swinden, Director of Research.	Iodine method of Rooney and Stapleton. J. Iron Steel Inst. 131 , 249 (1935).
23-----	Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa. T. D. Jensen, Manager, Magnetic Division; Wilson Scott, N. A. Ziegler.	Vacuum-fusion method. Trans. Am. Electrochem. Soc. 62 , 109 (1932).
24-----	A. O. Smith Corporation, Milwaukee, Wis. S. L. Hoyt, Director of Metallurgical Research; M. A. Scheil, Research Metallurgist.	Fractional vacuum-fusion method. Trans. Am. Inst. Mining Met. Engrs. 113 , 82 (1934). Microscopical examination. Trans. Am. Inst. Mining Met. Engrs. 116 , 405 (1935).
25-----	The Babcock and Wilcox Co., Barberton, Ohio. J. B. Romer, Chief Chemist.	Mercuric-chloride method. Arch. Eisenhüttenw. 8 , 391 (1934-35).
26-----	School of Mines, Columbia University, New York, N. Y. William Campbell, Professor of Metallurgy; S. W. Poole.	Microscopical examination.
27-----	Department of Metallurgy, The University of Sheffield, Sheffield, England. J. H. Andrew, Professor of Metallurgy.	Iodine and vacuum-fusion methods. Iron and Steel Inst., 6th Report of the Heterogeneity of Steel Ingots, section 3, p. 50, 61 (1935).
28-----	The Youngstown Sheet and Tube Co., Youngstown, Ohio. G. A. Reinhardt, Director of Research and Metallurgy; Francis M. Walters, Jr., Research Engineer.	Vacuum-fusion method. BS J. Research 7 , 375 (1931) RP346.
29-----	National Bureau of Standards, Washington, D. C. H. S. Rawdon, Chief, Division of Metallurgy; J. G. Thompson, H. C. Vacher, H. A. Bright.	Vacuum-fusion method. BS J. Research 7 , 375 (1931) RP346. Iodine method of cooperator 13. Hydrochloric-acid residue method. BS J. Research 9 , 615 (1932) RP496.
30-----	War Department, Watertown Arsenal, Watertown, Mass. G. F. Jenks, Col., Ordnance Department, U. S. Army, Commanding Officer; A. Sloan, P. R. Kosting, M. B. Gruzdis.	Iodine method of cooperator 13. Electrolytic method of cooperator 3.
31-----	The National Physical Laboratory, Teddington, England. C. H. Desch, Superintendent, Metallurgy Department.	Iodine method of Rooney and Stapleton. J. Iron Steel Inst. 131 , 249 (1935). Vacuum-fusion method. Sloman, Iron and Steel Inst., 6th Report of the Heterogeneity of Steel Ingots, section 4, p. 71 (1935).
32-----	Central Institute of Metals, Leningrad, U. S. S. R. B. Selivanoff, General Scientific Manager; Gr. Weinberg, Metallurgist; M. Janowsky, Chief of the Chemical Laboratories.	Hydrogen-reduction method. Report of the Central Inst. Metals 18 , 449 (1935).
33-----	Illinois Steel Co., Chicago, Ill. M. A. Grossman, Director of Research; Miss M. Baeyertz.	Microscopical examination.
34-----	Institut für Eisenhüttenkunde der Technischen Hochschule, Aachen, Germany. W. Eilender, Director.	Vacuum-fusion method, graphite-spiral furnace.
35-----	The Timken Steel and Tube Co., Canton, Ohio. Weston Hare.	Electrolytic method of cooperator 4. Hydrochloric-acid method.

The critical review of such a mass of data obviously can be better and more authoritatively accomplished by a small group, comprising experts in the various methods of analysis, rather than by one or two individuals. A subcommittee of the Iron and Steel Division of the American Institute of Mining and Metallurgical Engineers was therefore appointed, consisting of

John Chipman, chairman (American Rolling Mill Co.).
J. J. Egan (Union Carbide and Carbon Research Laboratories).
C. H. Herty, Jr. (Bethlehem Steel Co.).
S. L. Hoyt (A. O. Smith Corporation).
John Johnston (United States Steel Corporation).

On May 14, 1936, the committee, with Messrs. Hoyt and Johnston represented, respectively, by M. A. Scheil and B. M. Larsen, met with representatives of the National Bureau of Standards (J. G. Thompson, H. C. Vacher, and H. A. Bright) and with the following, who were present by invitation:

Thos. R. Cunningham (The Electro Metallurgical Co.).

Frank W. Scott (Inland Steel Co.).

O. B. Ellis (American Rolling Mill Co.).

Louis Jordan (Assistant Secretary, American Institute of Mining and Metallurgical Engineers).

To facilitate the review of the data the committee was divided into two sections. Messrs. Chipman, Larsen, Scheil, Jordan, Vacher, and Thompson considered the data of the vacuum-fusion, hydrogen-reduction, and chlorine methods, and Messrs. Herty, Egan, Cunningham, Scott, Ellis, and Bright reviewed the data of the extraction and residue methods. After 2 days of intensive study the two sections combined for general discussion. The results of these deliberations are given in the ensuing pages of this report, the various methods being discussed in order of the number of data available for each method.

II. REVIEW OF THE RESULTS OBTAINED IN THE COOPERATIVE ANALYSES

1. VACUUM-FUSION METHOD

The principles upon which the vacuum-fusion method, for the determination of total oxygen in iron or steel, is based are briefly as follows:

The sample is melted in a graphite crucible contained in a highly evacuated furnace. Under these conditions, occluded and dissolved oxygen is liberated and the various oxide and silicate combinations that exist in ferrous materials are reduced. In the usual procedure, determination of the amount of carbon monoxide in the evolved gases furnishes a value for the total oxygen content of the material but does not indicate the relative amounts of the different compounds of oxygen that were present. In the recently developed fractional vacuum-fusion method, values for individual oxides are obtained by reduction of the sample in stages at successively increased temperatures, with separate analysis of the gases evolved in each stage. The vacuum-fusion method permits the simultaneous determination of nitrogen and hydrogen, as well as oxygen, in a single sample.

Fifteen reports of determinations by the vacuum-fusion method were available for consideration. Some of the cooperators reported the results of individual determinations, others reported only one value for each steel. The preferred values of each cooperator, or averages of all the determinations in those instances where a preferred value was not indicated, are shown in table 3. Some of the averaged values have been rounded to eliminate meaningless fractions of one thousandth of 1 percent.

TABLE 3.—Results obtained by the vacuum-fusion method

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator	Oxygen	Cooperator
%		%		%		%		%		%		%		%	
0.0215	6	0.018	15	0.0235	23	0.0055	6	0.014	23	0.0085	6	0.125	31	0.022	6
.021	14	.0175	27	.023	27	.005	24	.013	6	.008	29	.112	15	.022	27
.021	28	.016	29	.021	24	.004	15	.012	24	.0075	28	.110	6	.0195	23
.020	20	.016	18	.020	31	.004	27	.011	29	.007	15	.110	8	.019	15
.020	31	.016	31	.0195	29	.003	20	.0105	27	.006	24	.107	29	.019	31
.0195	24	.014	24	.019	15	.0025	28	.010	15	.006	27	.107	14	.0185	28
.019	34	.014	34	.017	8	.0025	18	.010	31	.0055	8	.107	34	.018	14
.019	29	.013	8	.017	14	.0025	14	.0085	8	.0055	18	.105	28	.017	29
.018	15	.013	20	.0145	28	.002	29	.008	18	.005	21	.105	18	.017	18
.018	23	.013	28	.014	21	.002	31	.0075	21	.005	34	.103	24	.016	8
.0175	11	.0125	11	.014	18	.0018	34	.007	14	.005	31	.103	23	.0155	24
.017	8	.012	21	.014	20	.0015	8	.007	20	.005	20	.100	21	.015	20
.016	18	.0115	6	.013	11	.001	21	.0065	11	.004	14	.100	20	.0145	34
.0145	21	.0115	23	.0115	6	.001	11	.0065	28	.003	11	.100	27	.0145	21
.009	27	.004	14	.011	34	.0000	23	.0065	34	.003	23	.096	11	.014	11
BEST VALUES															
0.018	-----	0.017	-----	0.017	-----	0.002	-----	0.009	-----	0.007	-----	0.106	-----	0.017	-----

The review of the vacuum-fusion data proceeded along three lines:

1. Arbitrary establishment of a range of acceptable results for each steel, by eliminating scattered high and low values.
2. Statistical study to determine the apparatus and procedures most consistently yielding results within the acceptable ranges.
3. Detailed study of apparatus and procedure of each cooperator for possible explanation of the failures to obtain consistently acceptable results.

In many cases, final conclusions were based upon consideration of all the foregoing criteria, but for convenience in this report the three items will be discussed separately.

The first impression was that the range of the reported results for each steel was too great to be acceptable. It is evident that no cooperator obtained results consistently higher, or lower, than the others for all eight steels and, in general, the relative position of each cooperator in the columns of table 3 varies considerably from steel to steel. Consequently, the large ranges can be considered to be the result of individual experimental errors rather than of consistent differences in apparatus or procedure, and it is therefore legitimate to eliminate arbitrarily the scattered results, either high or low, in order to obtain for each steel a narrowed range that still includes the results of a majority of the cooperators.

The heavy rules in each column of table 3 inclose the acceptable values, after elimination of the scattered results. Such ranges of acceptable values would be considered satisfactory in determinations of corresponding amounts of elements such as carbon, sulphur, and manganese, for which the analytical methods are much more standardized than is the case for the determination of oxygen. It is evident that scattered values, both high and low, were discarded for all the steels except steel 2. For this steel only low results were eliminated as it was considered improbable that any cooperator would obtain too high a result for oxygen in a steel which contained more than 1 percent of manganese. In the opinion of the reviewing committee the "best" value for the oxygen content of each steel, according to the vacuum-fusion method of analysis, is approximately the mean of the acceptable values, except for steel 2. For this steel the "best" value is probably at or near the top of the acceptable range.

Each of the acceptable ranges in table 3 includes a majority of the reported values for one of the steels, but the personnel of the acceptable majority varies from steel to steel. Consideration of the details of apparatus and procedure of the individual cooperators furnishes plausible explanations for many of these deviations from acceptable results. Some of these details, compiled from the reports of the cooperators and the published references cited in table 2, are shown in table 4.

From the fact that four cooperators, 8, 18, 20, and 29, obtained results lying within the acceptable range for each of the eight steels, it is evident that acceptable results can be obtained in spite of considerable variation in apparatus and procedure. Cooperator 20 used a graphite-spiral furnace; the other three used high-frequency induction furnaces. Operating temperatures ranged from 1,550° C for cooperator 18, to 1,900° C for cooperator 20. The type of crucible support, thermal insulation of the crucible, weight of sample, and the

TABLE 4.—Details of vacuum-fusion procedures

Cooperator	Furnace	Operating temperature	Crucible support	Thermal insulator	Blank correction		Sample weight	Number of samples in a crucible	Surface of melt	Average time of run	Gas analysis	Remarks
					ml CO/hr	Oxygen ^a						
6	High-frequency induction.	° C 1,650	Pedestal.....	Sillimanite.....	<0.08	Percent <0.00015	g 15	6	Open.....	Min.	Low pressure, gravimetric.	
8	do.....	1,650	Graphite-MgO.	Graphite.....	<.2	<.0002	15	1 to 2	Graphite float..	15	Low pressure, volumetric.	
11	do.....	1,650	Quartz.....	Molybdenum....	.056 to .08	<.0002	8	5	Funnel top.....	15	Atmospheric pressure.	
14	do.....	1,600	BeO.....	Alundum.....	.2 to 3.1	.0003 to .008	14 to 27		Graphite sleeve		Selective freezing.....	
15	do.....	1,600	Pedestal.....	None.....				1	Open.....		Atmospheric pressure.	100 g of Fe in crucible.
18	do.....	1,550	do.....	Water-cooled tube.	.06	<.0002	35		Graphite filter and valve.	25	Atmospheric pressure (Oberhoffer).	
20	Graphite spiral.....	1,900			.6	.001	20	3		30	do.....	Low-Mn Fe in crucible.
21	do.....	1,750			.16 to .2	<.001	7			30	Atmospheric pressure (Meyer and Castro).	
23	High-frequency induction.	1,700	Pedestal.....	None.....	3.3	.008	10	Several	Open.....	20	Selective freezing.....	
24	do.....	1,570	Zirconia.....	Sillimanite.....	0.77	.0033	11	1		150	Atmospheric pressure.	Melts sample with tin.
27	Graphite spiral.....	1,700			.08 to .2	<.0003	15	Several	Open.....	20	do.....	9 radiation screens.
28	High-frequency induction.	1,650	Graphite-BeO..	Graphite.....				5	Graphite guide tube.	15	Low pressure, volumetric.	
29	do.....	1,650	do.....	do.....	.3 to .8	<.001	15	1 to 5	do.....	15	do.....	
31	do.....	1,550	Pedestal ^b	Water-cooled tube.	.014 to .05	<.0001	15	Several	Graphite valve..	20	Atmospheric pressure.	
34	Graphite spiral.....											

^a Cooperators 14 and 23 introduced the sample into a cooled crucible and subsequently raised the temperature to the indicated operating temperature. Other cooperators introduced samples at the indicated temperatures.

^b Cooperator 31 surrounded the lower portions of the pedestal with powdered graphite.

^c Based on weight of sample used and time of a determination.

^d Semidisks.

^e 1-inch rods were forged to about 1 cm diameter to provide sample material.

^f Samples not representative of complete cross sections of the 1-inch rods.

^g Total time for determination of FeO, MnO, SiO₂, and Al₂O₃ fractions.

method employed for analysis of the evolved gases, varied considerably in these four procedures. Three of the four employed large furnace connections and four-stage, high-capacity diffusion pumps for rapid evacuation of the evolved gases from the furnace chamber, whereas cooperator 8 obtained acceptable results with a two-stage pump and somewhat constricted furnace connections. Protection of the quartz furnace tube by an external water-jacket instead of internal radiation screens, yielded acceptable results for cooperator 18, although it is interesting to note that Thanheiser and Brauns³ recently reported that the interference of manganese, leading to low recoveries of oxygen, was more severe when the furnace tube was water-jacketed than when it was less drastically cooled by means of a coil of copper tubing.

The four procedures that yielded acceptable results for all eight steels have the following characteristics in common (1) a low blank correction for the apparatus; (2) precautions against interference by manganese; and (3) precautions against spattering of the molten sample. The importance of these three characteristics, common to all four of these procedures, deserves emphasis. A low blank correction, equivalent to not more than 0.001 percent of oxygen in a determination, is a prerequisite of satisfactory operation; larger or variable blank corrections are unsatisfactory for the determination of small amounts of oxygen.

It is the opinion of the reviewing committee that the presence of manganese in the sample causes some degree of interference in many of the procedures employed in this cooperative analysis because of absorption of gas by manganese vapor or sublimate. Cooperator 20 remarked that "the oxygen values for the two manganese-rich samples, 2 and 3, are perhaps somewhat low, in spite of our precautions."

Spattering as a result of gas evolution from the sample during melting or shortly thereafter may result in either high or low values for oxygen. If the spattered globules of molten metal come in contact with refractory oxides of the radiation screen or quartz furnace tube, a reaction resulting in the formation of CO may occur and cause a high value for oxygen. On the other hand, if the portion thrown out from the crucible falls to the cold bottom of the furnace tube, the oxygen of that portion of the sample is lost. The apparatus of each of the four cooperators, who obtained consistently satisfactory results, was arranged to prevent loss of molten spatters or their contact with hot refractory oxides. Cooperator 8 used a graphite float and cooperator 18 a graphite filter to prevent the spattered material from leaving the crucible; cooperator 20 apparently used a deep crucible covered with a graphite funnel in a graphite-spiral furnace that did not contain any refractory oxides. In the apparatus of cooperator 29, a thin-walled graphite tube extended from the top of the crucible to the bottom of the guide tube through which the

³ Arch. Eisenhüttenw. 9, 435 (1935-36).

samples were dropped. With this arrangement, any spattered particles struck the inner surface of the graphite tube and dropped back into the crucible. Only rarely would a spattered particle be evolved with sufficient velocity to reach the guide tube.

Spattering is probably one of the principal causes for the erratic results of individual determinations and for the divergence between the results of different cooperators. It is significant that the greatest divergence of reported results is for open-hearth iron 7, which has the largest oxygen content and consequently the greatest tendency to spatter. The results for steel 3, although less divergent than the results for iron 7, are more divergent than those of other steels of similar oxygen content. However, steel 3 is relatively high in nitrogen and the total volume of gases evolved is appreciably greater than that from other steels of similar oxygen content. Consequently the divergence of results for steel 3 also may be ascribed, in part, to spattering. It has been previously mentioned that gradual melting of the sample is sometimes employed to reduce the tendency to spatter, but this procedure apparently increases the susceptibility to manganese interference.

The fractional vacuum-fusion procedure, which is currently a subject of considerable interest, is represented in these data by the results of only one cooperator, 24, whose values for total oxygen are usually within the acceptable ranges but slightly high for steels 3, 4, and 5. Comparison of the values obtained for the separate fractions with the results of residue methods is given in a later section.

The reports of the other cooperators who used the vacuum-fusion procedure comprise 80 values, of which 47 are within the acceptable ranges, 14 are high, and 19 are low. In several instances it is possible to account for high or low results on the basis of one or more of the following sources of error (1) spattering; (2) interference by manganese; (3) high or irregular blank correction; (4) slow melting; (5) improper sampling; and (6) miscellaneous causes.

(a) RECOMMENDATIONS FOR THE DETERMINATION OF OXYGEN BY THE VACUUM-FUSION METHOD

(1) *Furnace construction.*—Either a high-frequency induction furnace or a graphite-spiral resistor may be used. The presence of refractory oxides in the furnace chamber is undesirable, particularly if they are hot or in contact with hot graphite; beryllium oxide appears to be least objectionable.

(2) *Analysis of the evolved gases.*—The selection of a procedure and apparatus for the analysis of the gases evolved from the sample is apparently a matter of personal preference. The determination may be made volumetrically or gravimetrically, at low pressure or at atmospheric pressure, or by selective freezing.

(3) *Procedure.*—Complete reduction of the oxides in these steels can be obtained in a reasonable time at temperatures as low as 1,550° C.

Preliminary "outgassing" of the furnace is accomplished at a temperature about 200° C higher than the operating temperature. The pressure in the furnace at operating temperature should not exceed 0.001 mm of Hg at the beginning of a determination. The blank correction for the apparatus should not exceed 0.001 percent of oxygen in a determination. The size of the sample depends upon the storage capacity of the apparatus and on the oxygen content of the material, but the sample must be representative. Spattering of the melting sample or of the molten bath should be prevented, but a satisfactorily reliable and convenient means of accomplishing this end has not yet been developed. The evolved gases should be removed rapidly and completely from the furnace chamber to avoid secondary reactions with the walls and contents of the furnace; a four-stage, mercury-diffusion pump of high capacity is frequently employed. Constricted or relatively long connections between the furnace and the diffusion pump should be avoided.

(4) *Manganese interference.*—The presence of 0.5 percent or more of manganese in a steel to be analyzed constitutes a potential source of error in the apparatus generally used, either as a result of the presence of manganese as vapor in the furnace chamber or condensed on the furnace walls, or both. Established precautions to minimize the error from this source include (a) the rapid and complete removal of evolved gases from the furnace chamber; (b) the use of a fresh crucible for each determination or dilution of the sample with manganese-free iron; and (c) frequent cleaning of the furnace chamber. The minimum manganese content that will produce a noticeable error apparently varies with the construction of the apparatus and with the procedure. Two of the cooperators, 27 and 31, believe that their procedures are free from error by interference from manganese contents up to 3 and 12 percent, respectively. Unpublished results of experiments on steel 2 at the National Bureau of Standards showed that two and sometimes three consecutive samples could be melted in the same crucible without appreciable error from manganese interference, provided that a high-capacity pump was used. On the other hand, when a pump of lower capacity was used, with somewhat higher furnace pressure, error from this source was noticeable in the second determination. It was also found that the determination of oxygen in steel 2 was affected somewhat by the size of the sample, slightly higher values being obtained from the smaller samples. A possible explanation is that they melted more rapidly and the gas evolution was completed before appreciable evolution of manganese vapor occurred. This appears to be additional evidence of the usefulness of rapid melting of the sample for minimizing the error from interference by manganese.

(b) DETERMINATIONS OF NITROGEN AND HYDROGEN

Several cooperators reported results for nitrogen and hydrogen, as well as for oxygen. These are summarized in tables 5 and 6. The

results of different cooperators for nitrogen are in quite satisfactory agreement, allowance being made for an occasional high or low result. The good agreement of the single set of results by the solution-distillation method with those obtained by vacuum fusion indicates that both methods are dependable in determining the nitrogen content of these steels.

The results of the four cooperators who determined hydrogen by the vacuum-fusion method indicate that the hydrogen content for each of the eight steels is less than 0.001 percent.

The desirability of accurate determinations of amounts of hydrogen considerably less than 0.001 percent by weight is indicated by recently reported results. Thanheiser⁴ reported that significant differences in the elongation and reduction of area of samples of freshly rolled rail steel occurred when the hydrogen content was reduced from 2 or 3 cc per 100 g to lesser amounts by means of annealing and aging treatments. These figures indicate that a hydrogen content of 0.0002 percent, by weight, may affect the properties of steel to an appreciable extent, and that even smaller amounts may be significant. The accurate determination of such amounts of any element is indeed a problem.

TABLE 5.—*Determination of nitrogen*
(Percent)

Cooperator	STEELS							
	1	2	3	4	5	6	7	8
VACUUM-FUSION METHOD								
8.....	0.0025	0.0044	0.015	0.005	0.004	0.005	0.0045	0.004
11.....	.0024	.0024	.014	.0046	.004	.004	.003	.003
14.....	.0019	.0038	.011	.0035	.003	.0035	.0055	.0035
18.....	.003	.005	.010	.0088	.006	.005	.008	.005
24.....	.003	.003	.015	.002	.002	.003	.004	.0025
29.....	.003	.005	.016	.006	.005	.006	.005	.005
SOLUTION-DISTILLATION METHOD								
2.....	.003	.006	.016	.005	.004	.005	.005	.004

TABLE 6.—*Determination of hydrogen*
(Percent)

Cooperator	STEELS							
	1	2	3	4	5	6	7	8
11.....	0.00014	0.00016	0.00013	0.00007	0.00009	0.00007	0.00054	0.00017
18.....	.0001	.0001	.0001	.0001	.00005	.00004	.003	.0003
24.....	.0006	.0008	.0006	.0003	.0005	.0003	.0001	.0003
29.....	.00002	.00009	.0002	.0002	.0002	.0003	.0004	.00015

2. IODINE METHOD

In the iodine method for determining oxides in steel, the sample is treated with a suitable solution of iodine. Iron, silicon, and manganese are dissolved, and a residue of carbonaceous material (carbides in certain cases) and unattacked oxides remains.

⁴ Stahl u. Eisen 56, 1125 (1936).

In the procedure described by Cunningham and Price (table 2, cooperator 13), a 5- to 10-g sample is treated at 3 to 5° C in a stoppered flask with an aqueous solution of iodine in ferrous iodide.⁵ By the method of Rooney and Stapleton (table 2, cooperator 31) the sample is treated with a solution of iodine in anhydrous methyl alcohol (70 g of iodine in 600 ml of alcohol). Rather elaborate precautions are necessary to exclude all moisture and oxygen from the solvent and containers while the steel is dissolving and during filtration of the resulting solution. Willems (table 2, cooperator 10) recommended the use of a solution of iodine in absolute ethyl alcohol and filtration through an ultrafilter.

The proponents of the alcoholic iodine solutions claim that higher recoveries of oxides of iron and manganese are obtained with these solvents than with aqueous solutions of iodine in ferrous and potassium iodide.

The values for Al_2O_3 , SiO_2 , MnO , and FeO , obtained by the cooperators, are given in tables 7, 8, 9, and 10.⁶ Reports were submitted by 12 cooperators though not all reported values for all of the 8 steels. Eight cooperators used an aqueous iodine solvent, essentially the procedure described by Cunningham and Price; three used a solution of iodine in anhydrous methyl alcohol, as described by Rooney and Stapleton, and one employed a solution of iodine in absolute alcohol, as described by Willems. Some of the values reported by cooperator 31 were obtained by a variant of Rooney and Stapleton's method, but details of the modified procedure are not yet available.

⁵ Prepared as follows: To 5 g of plain-carbon steel drillings in a 300-ml Erlenmeyer flask are added 25 ml of water, 4 g of ammonium citrate, and 30 g of iodine. The flask is shaken for several minutes in ice water and then 30 g of additional iodine is added. The shaking is continued until all the iodine has dissolved, whereupon the solution is filtered. The total volume of the filtrate and washings should not exceed 75 ml and this amount of solution is sufficient for a 5-g sample. For larger samples, proportionally more solvent is used.

⁶ Total Al, Si, Mn, and Fe in the insoluble residues are reported as the single oxides, which may exist in the steel as such, or in combination as silicates or spinels.

TABLE 7.—Determinations of Al₂O₃ by the iodine method

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Percent	Cooper- erator	Percent	Cooper- erator	Percent	Cooper- erator	Percent	Cooper- erator	Percent	Cooper- erator	Percent	Cooper- erator	Percent	Cooper- erator	Percent	Cooper- erator
CUNNINGHAM AND PRICE PROCEDURE															
0.010	9	0.039	9	0.021	9	0.025	9	0.016	9	0.038	9	0.020	9	0.032	29
.005	30	.004	30	.006	16	.011	21	.002	21	.005	7	.018	21	.028	9
.003	21	.003	21	.005	21	.007	7	.002	29	.003	21	.014	16	.027	7
.002	19	.002	29	.003	30	.0055	29	.000	7	.002	30	.004	19	.025	30
.0003	29	.001	19	.002	19	.004	16	.000	16	.000	16	.0015	29	.017	21
.000	7	.000	7	.000	7	.003	30	.000	30			.000	7	.016	16
.000	16	.000	16	.000	29	.0025	19					.000	30	.012	19
SELECTED VALUES															
0.002 ±.002		0.002 ±.002		0.002 ±.002		0.006 ±.002		0.002 ±.002		0.002 ±.002		0.002 ±.002		0.030 ±.003	
ROONEY AND STAPLETON PROCEDURE															
0.006	31	0.014	31	0.021	27	0.008	27	0.0035	22	0.0042	22	0.022	27	0.037	31
.004	22	.0065	22	.0075	22	.0065	31	.0025	31	.0025	31	.013	31	.033	22
.002	27	.003	27	.005	31	.005	22	.001	27	.001	27	.012	22	.031	27
WILLEM'S METHOD															
•0.000	10	•0.000	10	0.010	10	•0.000	10	0.003	10	•0.000	10	0.005	10	0.020	10

• Reported by dash. It is assumed that a determination was made and no detectable amount found.

TABLE 8.—*Determinations of SiO₂ by the iodine method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator
CUNNINGHAM AND PRICE PROCEDURE															
0.018	9	0.041	9	0.037	9	0.015	9	0.049	9	0.049	9	0.012	9	0.040	9
.005	30	.012	21	.012	30	.015	30	.020	30	.014	30	.011	30	.010	30
.005	16	.012	30	.007	19	.008	16	.019	16	.010	13	.004	21	.005	16
.005	21	.010	16	.006	7	.004	21	.015	13	.009	16	.002	16	.0025	7
.0022	29	.006	29	.005	13	.002	7	.015	29	.008	21	.002	19	.002	21
.0015	13	.006	7	.005	29	.0018	13	.013	7	.006	7	.0013	29	.002	19
.009	7	.006	13	.004	21	.0012	29	.012	21			.000	7	.0007	29
-----		-----		.003	16	.0005	19	-----		-----		.000	13	.000	13
SELECTED VALUES															
0.003 ±.002		0.009 ±.003		0.005 ±.002		0.002 ±.002		0.016 ±.003		0.009 ±.003		0.002 ±.002		0.003 ±.002	
ROONEY AND STAPLETON PROCEDURE															
0.0034	22	0.027	22	0.017	31	0.0037	27	0.021	27	0.011	22	0.0013	22	0.0055	27
.0027	27	.025	31	.014	22	.0016	22	.017	22	.011	31	.001	31	.0029	31
.0017	31	.0091	27	.0015	27	.0013	31	.016	31	.009	27	.0009	27	.0026	22
WILEM'S METHOD															
.000	10	0.012	10	0.012	10	0.015	10	0.007	10	.000	10	.000	10	0.006	10

• Reported by dash.

TABLE 9.—*Determinations of MnO by the iodine method*

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator	Percent	Coop- erator
CUNNINGHAM AND PRICE PROCEDURE															
0.013	30	0.029	9	0.025	9	0.007	30	0.010	9	0.015	9	0.030	13	0.006	30
.003	21	.007	30	.021	16	.0065	9	.009	30	.011	16	.030	7	.005	9
.0025	9	.005	16	.013	21	.006	16	.007	16	.011	30	.027	19	.0035	16
.002	7	.005	21	.012	30	.002	13	.006	21	.007	21	.026	9	.002	7
.002	16	.0025	13	.009	13	.0003	29	.003	7	.005	13	.022	21	.002	21
.002	29	.0025	29	.008	29	.000	7	.002	29	.004	7	.021	29	.0015	29
.0015	13	.002	7	.0055	7	.000	21	.002	13			.021	30	.001	13
												.018	16		
SELECTED VALUES															
0.002±.002		0.004±.002		0.012±.004		0.002±.002		0.004±.002		0.008±.003		0.025±.005		0.003±.002	
ROONEY AND STAPLETON PROCEDURE															
0.055	31	0.041	27	0.141	22	0.0061	31	0.011	31	0.012	31	0.027	31	0.025	27
.044	22	.036	22	.120	31	.0057	22	.009	22	.011	22	.023	22	.0075	22
.000*	27	.032	31	.016	27	.000	27	.005	27	.002	27	.019	27	.0071	31
WILLEM'S METHOD															
0.008	10	0.0055	10	0.205	10	0.000	10	0.005	10	0.029	10	0.069	10	0.0026	10

* Reported by dash.

TABLE 10.—Determinations of FeO by the iodine method

Steel 1		Steel 2		Steel 3		Steel 4		Steel 5		Steel 6		Iron 7		Steel 8	
Percent	Cooper-ator	Percent	Cooper-ator	Percent	Cooper-ator	Percent	Cooper-ator	Percent	Cooper-ator	Percent	Cooper-ator	Percent	Cooper-ator	Percent	Cooper-ator
CUNNINGHAM AND PRICE PROCEDURE															
0.015	30	0.024	16	0.015	13	0.018	30	0.014	30	0.021	9	0.43	16	0.018	13
.014	16	.023	13	.014	7	.014	16	.014	13	.018	16	.414	7	.017	16
.012	13	.015	30	.012	30	.011	7	.009	7	.014	7	.393	13	.014	30
.010	7	.013	7	.011	9	.0055	13	.009	16	.013	30	.39	30	.014	29
.010	21	.010	29	.007	21	.0035	9	.008	21	.013	13	.377	19	.010	21
.007	29	.008	21	.005	29	.002	29	.007	29	.007	21	.33	29	.009	7
.002	9	.0047	9	.003	16	.0006	21	.0036	9			.32	9	.0042	9
												.262	21		
SELECTED VALUES															
0.012±.004		0.013±.005		0.011±.004		0.004±.002		0.010±.004		0.010±.004		0.39±.03		0.014±.005	
ROONEY AND STAPLETON PROCEDURE															
0.063	22	0.014	22	0.026	22	0.015	31	0.025	27	0.014	31	0.481	22	0.033	22
.054	31	.0073	27	.021	31	.011	22	.012	31	.010	22	.446	31	.030	31
.004	27	.0065	31	.014	27	.006	27	.008	22	.008	27	.382	27	.005	27
WILLEM'S METHOD															
0.016	10	0.027	10	0.011	10	0.033	10	0.024	10	0.038	10	0.111	10	0.017	10

The values obtained by the iodine method vary rather widely among themselves. Undoubtedly, inaccurate chemical analysis of the insoluble residue is responsible in part. In studying the data of the eight cooperators who used an aqueous solution of iodine, it was observed that the results obtained by some were consistently high or low, and that the values obtained by cooperators 7, 13, 19, 21, and 29 were generally in good agreement. The "selected values" given in tables 7, 8, 9, and 10 were chosen by the committee from the data of those who used the aqueous solvent and were based largely on the results of the five cooperators mentioned. It is believed that these selected values are representative of results that may be expected by carefully following the Cunningham and Price procedure.

Because of the limited number of cooperators who used the alcoholic solvents and the rather wide variation in the reported results, no selected values were chosen for this group. However, a comparison of these results with the selected values for the aqueous iodine method is discussed in a later section.

In the following sections there is recorded a brief discussion of the values reported by the eight cooperators who used the aqueous iodine solvent. These cooperators used the Cunningham and Price method, except for some small changes by some of the analysts. For example, cooperator 7 used an I-FeI₂ solution containing approximately 50 g of iodine and 0.8 g of ammonium citrate per 100 ml; cooperator 19 used an I-KI solution containing 1 percent of ammonium citrate, and cooperator 29 used somewhat larger samples (18 to 20 g).

The permissible variations within the selected ranges may seem rather wide. In general, however, the spread, except for FeO, is of about the same order as obtains in the determination of other constituents present in small amounts in ferrous alloys. Furthermore, it should be noted that a difference of 0.005 percent of FeO or MnO, or 0.002 percent of Al₂O₃ or SiO₂, is equivalent to but 0.001 percent of oxygen.

Of the 53 values for the determination of Al₂O₃, received from cooperators who used an aqueous solution of iodine as the solvent, 33 are within the selected ranges (indicated by the heavy rules in the columns of tables 7, 8, 9, and 10), 14 above and 6 below. On the very low-alumina steels, the errors are usually on the high side, probably because of faulty blank corrections. On the other hand, low values were reported by a number of cooperators for high-alumina steel 8, another indication of the tendency toward inaccurate analysis of the insoluble residues. The values obtained by the Rooney and Stapleton procedure (cooperators 22, 27, and 31) are of the same order of magnitude but frequently are higher than the selected values.

For the determination of SiO₂, 59 values were received from the cooperators who used the aqueous-iodine solvent. Of these, 41 are within the selected range, 15 above and 3 below. The values obtained by following the Rooney and Stapleton procedure (cooperators 22, 27, and 31) are, in general, of the same order of magnitude as the selected values; results obtained by following Willems' procedure (cooperator 10) are within the selected ranges only for steels 2 and 7.

For the determination of MnO, 56 values were received from the group who employed the aqueous-iodine solvent, of which 40 are within the selected range, 13 above and 3 below. The values obtained by the Rooney and Stapleton procedure vary considerably, and, in

general, are higher than those obtained with the aqueous-iodine solvent. Part of this difference undoubtedly can be attributed to the fact that MnS is not as soluble in the alcoholic as in aqueous-iodine solutions, and some MnS is reported as MnO. It is noteworthy that in steel 2 the MnO values of the alcoholic group are distinctly higher than the selected value, which brings up the question of whether or not MnO can be quantitatively recovered by the aqueous solvent from a steel of the 2 type. On the other hand, the values for MnO in iron 7 by the aqueous and alcoholic methods are in good agreement. In this iron the maximum possible MnO would be 0.031 percent if the total Mn (0.024 percent) be calculated to MnO.

For the determination of FeO, 56 values were received from those who used the aqueous-iodine solvent, of which 37 are within the selected range, 8 above and 11 below. It will be noted that the variation within the selected range is greater for FeO than for the other three oxides. This condition naturally complicates the choice of a selected value. The values by the Rooney and Stapleton procedure are frequently higher than the selected values. In general, it appears as though the FeO values obtained by the iodine method are somewhat unreliable. For example, with steel 4, the selection of 0.004 percent of FeO may be questioned.

3. ACCURACY OF THE VACUUM-FUSION AND AQUEOUS-IODINE METHODS

These cooperative analyses were undertaken in the hope that the results of different operators would be in sufficiently close agreement to define the best value, or a reasonable range of values, that should be obtained by each of the analytical methods. Agreement in the results obtained by different methods, for the same steel, would establish the accuracy of the methods that were in agreement. To date this hope has not been fully realized. The outstanding feature of these data is the range of results, i. e., the lack of agreement, in the values obtained by a group of operators using the same method even when each analyst confirms his own results by duplicate or multiple determinations. The information available at present does not suffice to determine whether these discrepancies are primarily the result of inaccuracies in the methods, minor variations in apparatus and procedure of different investigators, or the personal equation.

A selection of representative ranges or "best" values has been possible only for the vacuum-fusion and aqueous-iodine methods as previously described. None of the other methods of analysis are represented by enough concordant results to indicate "best" values, and even in some of the data of the vacuum-fusion and aqueous-iodine methods there is sufficient lack of concordance to render the selection of "best" values difficult and somewhat uncertain. The determination of FeO by the iodine method is a particular illustration of this point.

Direct comparison of the "best" values by the vacuum-fusion and aqueous-iodine methods can be made on the basis of the total oxygen content. This is given directly by the results of the vacuum-fusion analyses and can be computed in the iodine method from the selected values for Al_2O_3 , SiO_2 , MnO, and FeO on the assumption that other combinations of oxygen are not present. This assumption is not

strictly correct; the presence of small amounts of other oxides was detected⁷ by some of the cooperators, but the amount of oxygen combined in these other oxides may be neglected for present purposes.

Values for total oxygen by the two methods are shown in table 11. Entirely satisfactory agreement, well within the permissible limits of error for such determinations, is evident for steels 4, 5, 6, and 8. Such duplication of results by two independent methods is good evidence of the accuracy of both methods, as applied to these four steels, all of the "killed" type. Steels 4 and 8 were killed with aluminum, steels 5 and 6 with silicon. The iodine method is expected to give its most accurate results on steels of this type, in which the oxygen is present principally as Al_2O_3 and SiO_2 . The good agreement of the results by the two methods is evidence that appreciable amounts of Al_2O_3 and SiO_2 do not interfere with the satisfactory operation of the vacuum-fusion method.

TABLE 11.—*Comparison of results by the vacuum-fusion and aqueous-iodine methods*

Steel	Selected values for total oxygen		Steel	Selected values for total oxygen	
	Vacuum-fusion method ^a	Aqueous-iodine method ^b		Vacuum-fusion method ^a	Aqueous-iodine method ^b
	Percent	Percent		Percent	Percent
1.....	0.018	0.006	5.....	0.009	0.013
2.....	.017	.010	6.....	.007	.010
3.....	.017	.009	7.....	.106	.095
4.....	.002	.005	8.....	.017	.020

^a Selected values from vacuum-fusion determinations.

^b Computed from results for Al_2O_3 , SiO_2 , MnO , and FeO obtained by the aqueous-iodine method.

Steel 2, a silicon-killed steel, with a manganese content of 1.15 percent, gave a "best" value for total oxygen by the iodine method only half as great as the "best" value by the vacuum-fusion method. In view of the established fact that the presence of manganese frequently causes low recoveries of oxygen to be obtained, the results of the vacuum-fusion method should not be considered as being too high. It is more probable that the iodine results are low, perhaps because the silicates in this steel are different in composition and more soluble than those in steels 4, 5, 6, and 8. Microscopic studies (cooperators 1, 26, and 33) indicated that the silicate inclusions are larger and more numerous in steel 2 than in steels 5 and 6; in steels 4 and 8 the inclusions are chiefly Al_2O_3 .

For steels of the "rimming" type, 1, 3, and 7, the total oxygen by the vacuum-fusion method was appreciably higher than by the iodine method.⁸ On the assumption that the vacuum-fusion method yields correct results for killed steels, containing the difficultly reducible oxides, Al_2O_3 and SiO_2 , it is reasonable to conclude that this method should yield correct results for rimming steels in which the easily reducible oxides, FeO and MnO , are predominant. It is believed,

⁷ Cooperator 7 reported 0.0013 percent of Cr_2O_3 in steel 2, and 0.010 percent of Cr_2O_3 in iron 7; cooperator 29 reported 0.0015 percent of Cr_2O_3 in steel 2, 0.007 percent of Cr_2O_3 and some Fe_2O_3 in iron 7, and 0.004 percent of P_2O_5 in steel 3; cooperator 22 reported 0.0026 percent of TiO_2 in steel 2; cooperator 31 reported 0.0034 percent of TiO_2 in steel 2 and Cr_2O_3 in four of the steels as follows: 0.0012 percent in steel 1; 0.0014 percent in steel 2; 0.0077 percent in iron 7; and 0.0006 percent in steel 8.

⁸ This statement is based on the actual difference and not on the percentage difference in results by the two methods. In the latter respect the two methods are in fairly good agreement for iron 7.

therefore, that the results obtained by vacuum-fusion for steels 1, 3, and 7 are approximately correct, and, on the other hand, that the results by the iodine method are somewhat low, perhaps on account of analytical difficulty in determining FeO and MnO by this method or because of difficulty in the selection of the best values from the reported data for FeO and MnO. It is not fully apparent why the greatest difference in results by the two methods was obtained for steel 1, unless it is because the MnO in this steel is not combined with SiO₂ and is therefore more readily dissolved than in the other steels.

The evidence of the available data in regard to the accuracy of the two methods may be summarized as follows:

The accuracy of the vacuum-fusion method for silicon-killed and for aluminum-killed steels (4, 5, 6, and 8) is demonstrated by agreement with the results of the aqueous-iodine method. The accuracy obtained for killed steels justifies the assumption of accuracy for un-killed steels. A reasonable value was obtained for the oxygen content of steel 2 and indicates that the presence of 1.15 percent of manganese in a steel does not introduce serious error in the best results obtainable by the vacuum-fusion method.

The accuracy of the iodine method for aluminum-killed steels and for some silicon-killed steels is demonstrated by agreement with the results of the vacuum-fusion method, for steels 4, 5, 6, and 8. The low results obtained for steel 2 indicate that inaccurate results may be obtained on some silicon-killed steels. Low results were obtained on rimming steels. Satisfactory concordance in the results obtained by the iodine method, particularly for FeO, is not yet attainable.

4. HYDROGEN-REDUCTION METHOD

This method depends upon the reduction of oxides in the sample by means of purified hydrogen at elevated temperatures. The amount of water vapor in the hydrogen leaving the furnace indicates the amount of oxides reduced. It is generally believed that FeO and MnO are completely reduced under these conditions, but that refractory compounds such as Al₂O₃ and certain silicates are reduced only partially or not at all.

Four of the cooperators in this project reported results obtained by this method. Essential details of apparatus and procedure, which differed considerably for the four, have been published elsewhere.⁹

The data reported by these four cooperators and shown in table 12, are too few and the concordance of results is not sufficiently close to permit a selection of representative values for the hydrogen-reduction method. For each steel the four values extend over a considerable range, frequently greater than that of the 15 determinations by the vacuum-fusion method.

⁹ Metals Tech. (December 1936).

TABLE 12.—*Determinations of oxygen by hydrogen-reduction methods.*

STEEL

1		2		3		4		5		6		7		8	
Percent	Cooperator														
0.024	2	0.027	2	0.027	2	0.012	5	0.022	2	0.010	2	0.106	5	0.023	5
.021	32	.020	5	.025	5	.008	2	.016	5	.010	5	.100	32	.020	32
.020	5	.012	32	.021	32	.0077	17	.0078	32	.0043	32	.098	17	.015	2
.019	17	.0077	17	.018	17	.0005	32	.0013	17	.0028	17	.076	2	.0028	17

A comparison of the hydrogen-reduction results with the acceptable values for the vacuum-fusion method (see table 3) shows that the results of only one cooperator (32) are consistently near to or within the limits of acceptable values established by the vacuum-fusion method. The available information is not sufficient to account for the lack of agreement between the results of different investigators or between the results by the hydrogen-reduction and vacuum-fusion methods. The hydrogen-reduction method is generally assumed to recover only the oxygen combined as FeO or MnO, but for steel 8, in which the oxygen is present chiefly as Al_2O_3 , three of the four results are as high as the results by the vacuum-fusion method. On the other hand, for the sample of open-hearth iron in which the oxygen is present chiefly as FeO and MnO, the results tend to run lower than those by vacuum-fusion. It is of interest to note that the best agreement within the results by the hydrogen-reduction method is obtained for steel 1, and for this steel the results by hydrogen-reduction and vacuum-fusion are in good agreement, whereas those by iodine and vacuum-fusion are not. More data, and particularly more concordant data, are needed to establish the accuracy of the hydrogen-reduction method.

5. ELECTROLYTIC METHOD

By making the sample the anode in an electrolytic cell with a suitable electrolyte, and by controlling the conditions of electrolysis, the soluble metallic constituents can be separated from the insoluble nonmetallic material. After electrolysis, the loss in weight of the anode is determined and the insoluble residue is collected and analyzed. The four following electrolytes were used by the seven cooperators reporting results by this method:

(a) An aqueous solution containing 3 percent of $FeSO_4 \cdot 7H_2O$ and 1 percent of NaCl, as recommended by G. R. Fitterer and coworkers, MnO, SiO_2 , and Al_2O_3 being determined in the insoluble residues. Values for FeO cannot be obtained since basic ferric sulphate and ferrous hydroxide precipitate during electrolysis and contaminate the residue.

(b) An aqueous solution containing approximately 45 g of magnesium iodide and 2 g of iodine per liter, as recommended by F. W. Scott for the determination of FeO, MnO, Al_2O_3 , and SiO_2 , the claim being made that iron dissolves without hydrolysis in this electrolyte, and that any sulphides, phosphides, and carbides in steel are completely decomposed.

(c) A 3-percent aqueous solution of ferrous chloride, recommended by H. Styri for determining SiO_2 and Al_2O_3 . In some experiments a solution containing 3 percent of sodium citrate and 0.1 percent of ferrous chloride was used in the anode compartment.

(d) A 0.1*N* potassium bromide solution containing about 10 percent of sodium citrate, for the anode compartment and a 10-percent solution of a copper salt, either sulphate or bromide for the cathode compartment, as recommended by Benedicks, whose published description stated that the determination of FeO , Al_2O_3 , and SiO_2 was adequate but that the determination of MnO was not quite satisfactory. This was used for determining the four constituents listed.

The results reported by seven cooperators are shown in table 13. Two cooperators heat treated the samples before electrolysis to see if heat treatment and the resulting redistribution of carbides affected the determination of Al_2O_3 and SiO_2 .

The comparison of results obtained by different observers using the same electrolyte is frequently complicated by variations in methods of analysis and other departures from uniform procedure. There are not enough data available to justify the selection of "best" values for any one electrolyte or for the electrolytic procedure, in general. However, the results obtained by electrolytic methods can be compared with the selected values by the aqueous-iodine method, shown at the bottom of each section of table 13.

Electrolytic methods, in general, are believed to be more reliable for determinations of SiO_2 and Al_2O_3 than for FeO and MnO . The latter determinations are complicated by the presence of carbides and sulphides in the insoluble residue; by the presence of hydrated compounds formed by anodic oxidation during electrolysis; and by the presence of small metallic particles from mechanical disintegration of the anode. The consistently high results for FeO and MnO , by electrolytic methods, as compared with the selected values by the aqueous-iodine method, may reflect the analytical difficulties in the determination of FeO and MnO , rather than a consistent difference in the two methods in separating FeO and MnO from the rest of the sample. The values by the iodine method are believed to be approximately correct for steels 4, 5, 6, and 8, but they are low for steels 1, 2, 3, and 7. Consequently, if the electrolytic determinations of FeO and MnO are accurate, they should coincide with the iodine results for steels 4, 5, 6, and 8 and should be higher than the iodine results for steels 1, 2, 3, and 7. This is not the case; the electrolytic values are scatteringly higher than those by the iodine method by about the same amount for each steel.

There is somewhat better agreement between results, by the two methods, for SiO_2 and Al_2O_3 . However, even in these determinations there is a decided lack of concordance in results obtained by electrolytic methods.

TABLE 13.—Results obtained by electrolytic methods

Method	Cooper-ator	STEEL							
		1	2	3	4	5	6	7	8
DETERMINATIONS OF Al ₂ O ₃ (%)									
Fitterer.....	{ 3 • 3H 30	0.002 nil .0007	0.009 .002 .0007	0.004 .003 .0003	0.025 .024 .003	0.002 .002 .001	0.002 .004 .002	0.006 .005 .0004	0.016 .024 .018
Scott.....	{ 4 20 35	.004 .004 .002	nil ----- .004	nil ----- .003	.006 .009 .006	nil .005 .002	nil .007 .003	.004 .010 .003	.035 .042 .031
Styri.....	{ 12 • 12H	.001 .0015	.005 .004	.002 .003	.032 .022	.0015 .002	.003 .003	.003 .003	.021 .025
Benedicks.....	20	.005	.013	.006	.012	.006	.009	.009	.070
Best values from aqueous-iodine method.....	-----	0.002±.002	0.002±.002	0.002±.002	0.006±.002	0.002±.002	0.002±.002	0.002±.002	0.030±.003
DETERMINATIONS OF SiO ₂ (%)									
Fitterer.....	{ 3 • 3H 19 30	0.005 .011 .004 .001	0.070 .054 .021 .014	0.008 .010 .020 .0045	0.006 .004 .002 .001	0.024 .017 .018 .027	0.081 .014 .018 .042	0.006 .004 .002 .0015	0.006 .007 .003 .0015
Scott.....	{ 4 20 35	.001 .003 .002	.010 ----- .013	.003 ----- .0035	.0004 .004 .004	.013 .024 .016	.007 .013 .009	.0008 .009 .0015	.004 .010 .003
Styri.....	{ 12 • 12H	.003	.047 .051	.004 -----	.0045 .0065	.0055 -----	.046 -----	.004 -----	.004 .007
Benedicks.....	20	.020	.079	.027	.024	.076	.140	.092	.013
Best values from aqueous-iodine method.....	-----	0.003±.002	0.009±.003	0.005±.002	0.002±.002	0.016±.003	0.009±.003	0.002±.002	0.003±.002

DETERMINATIONS OF MnO (%)

Fitterer.....	}	3	^d -0.001	nil	^d -0.021	0.012	0.009	0.079	0.028	0.103
		• 3H	.014	0.017	.080	.017	.019	.041	.018	.030
		19	.029	.097	.041	.030	.053	-----	.019	.065
		30	.018	.102	.055	.083	.049	.051	nil	.052
Scott.....	}	4	.006	.033	.082	.007	.007	.0035	.0235	.009
		20	•.001	•.001	•.004	•.001	•.002	•.001	•.022	•.004
		35	.002	.009	.011	.004	.008	.009	.025	.011
Benedicks.....		20	•.013	•.073	•.184	•.008	•.014	•.016	•.019	•.023
Best values from aqueous-iodine method.....			0.002±.002	0.004±.002	0.012±.004	0.002±.002	0.004±.002	0.008±.003	0.025±.005	0.003±.002

DETERMINATIONS OF FeO (%)

Scott.....	}	4	0.020	0.009	0.005	0.012	0.015	0.008	0.421	0.004
		20	•.185	•.016	•.515	•.080	•.052	•.094	•.480	•.195
		35	.015	.009	.012	.008	.008	.011	.342	.010
Benedicks.....		20	•.091	•.073	•.047	•.040	•.040	•.029	•.347	•.220
Best values from aqueous-iodine method.....			0.012±.004	0.013±.005	0.011±.004	0.004±.002	0.010±.004	0.010±.004	0.39 ±.03	0.014±.005

• Cooperator 3 determined Al_2O_3 , SiO_2 , and MnO in samples as received (3) and after heat treatment (3H). For determinations of SiO_2 the samples were annealed for 18 hours at 650° C; for MnO the samples were held at 1,000° C for ½ hour and quenched in water.

• Cooperator 12 determined Al_2O_3 in "soft" samples as received (12) and in "hard" samples quenched from 1,100° C in saturated brine (12H).

• After a second annealing of steel 2 at 675° C for 18 hours, the value obtained for SiO_2 was 0.018 percent.

• Negative values for MnO indicate discrepancies in the separation of MnO and MnS.

• Including sulphides.

The best agreement with the selected values for the iodine method was obtained with Scott's electrolyte (cooperators 4 and 35). The procedure was varied, however, from the published description (table 2, cooperator 4), particularly in the treatment of the residue to remove sulphides, iron salts, and metallic particles prior to analysis. In one modified method (cooperator 4) the residue was washed with KI solution, then with a 12-percent solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (previously neutralized with MgO), filtered, and the residue digested with 25-percent sodium citrate solution. It was then filtered, washed with 2-percent ammonium citrate solution and, thereafter, treated as described in the published article. In the other modified procedure (cooperator 35) the electrolysis was conducted at constant voltage (about 2 volts) and in a neutral atmosphere and, without removal from the neutral atmosphere, the residue was washed with 5-percent sodium citrate and then with copper sulphate solution. It was rewashed with these reagents and then with hot 5-percent NaOH solution and finally with water.

The results obtained by these two procedures are in excellent agreement in practically all of the determinations. The values for Al_2O_3 and SiO_2 are invariably within or very near the range of the aqueous-iodine values; the results for MnO and FeO are in good agreement with those of the iodine method, except for high results in one case (cooperator 4) in the determination of MnO in steels 2 and 3. Other results obtained with Scott's electrolyte for SiO_2 and Al_2O_3 (cooperator 20) sometimes are higher than, but, in general, in good agreement with the above. It was suggested however (cooperator 20) that the results obtained for SiO_2 may be somewhat high on account of solubility of glass during the prolonged electrolysis, and it was also stated that the sulphides and phosphides of manganese were strongly decomposed but the corresponding compounds of iron only partially in Scott's electrolyte. Furthermore, the residue was observed often to contain appreciable amounts of fine-grained, undecomposed metallic ingredients. The combined effect of these factors, according to cooperator 20, was to yield erroneously high results for FeO and, to a less pronounced extent, for MnO . Comparison with the selected values by the aqueous-iodine method indicates that the error due to these factors is appreciable only in the determination of FeO ; comparison with the values obtained by the modified procedures (cooperators 4 and 35) indicates that the error even in the determination of FeO can be largely eliminated by a suitable purification treatment of the initial residue.

Comparison of results obtained with Benedicks' and with Scott's electrolyte by the same analyst (cooperator 20) shows that consistently higher results for Al_2O_3 and decidedly higher results for SiO_2 were obtained with Benedicks' electrolyte; also that contamination by sulphides seems to have had somewhat less effect on the FeO , and more effect on the MnO , determinations than was the case when Scott's electrolyte was used.

The results obtained by the three cooperators who used Fitterer's electrolyte vary considerably in some of the determinations of SiO_2 and Al_2O_3 and in most of the determinations of MnO . The statement was made (cooperator 3) that previous work (unpublished) with steels containing 0.60 to 0.80 percent of carbon indicated that the annealing

temperature had a tremendous effect on the value obtained for silica. Accordingly, samples of the eight steels were run in the "as-received" condition and after annealing for at least 12 hours at 650° C. The data in table 13 show that this treatment affected the silica results for only two steels, 2 and 6, with carbon contents in excess of 0.4 percent; that the results for alumina were not appreciably affected; that the results for MnO were improved, by bringing them into better agreement with those obtained by other cooperators with samples that had not been heat treated. The opinion was expressed (cooperator 3) that "the electrolytic method must be considerably modified if steels above about 0.35 percent carbon are investigated. There is also the possibility that the results on lower carbon steels might be affected by the heat treatment."

Styri's electrolyte was used for the determination of SiO₂ and Al₂O₃ (cooperator 12) and also to observe the effect on these determinations of structural changes produced by quenching the samples from 1,100° C in brine. The data indicate no marked effect on the results for silica and alumina. For the samples, as received, the determinations of silica yielded good results for five of the steels, high results for steels 2 and 6, and somewhat low results for steel 5. Reasonable values for alumina likewise were obtained, except for steel 4.

More data are needed to establish the accuracy of the electrolytic method. One of the items which should be studied further is the question of anodic oxidation. Cooperator 20 reported the formation of pentabromacetone at the anode during electrolysis and considered this a possible source of anodic oxidation of the sample. The good results obtained with improved methods of purification of the electrolytic residue prior to analysis (cooperators 4 and 35) serve to emphasize the need of further work of this kind.

6. MISCELLANEOUS METHODS

Three reports on the results of microscopic examination were submitted; a "cleanness rating" of the eight steels, based on an inclusion count according to Epstein's method (cooperator 1); and two extended microscopic studies (cooperators 23 and 26). However, these have not been of particular value in the quantitative determination of the oxygen content of these steels.

Few data are available on the oxide content of the eight steels, obtained by the mercuric-chloride, chlorine, fractional vacuum-fusion, nitric-acid, and hydrochloric-acid methods (table 14). In view of the limited number of data available for each of these methods, the most practical comparison is with the selected values for the iodine method, shown at the bottom of each section of table 14.

TABLE 14.—Results obtained by the mercuric-chloride, chlorine, fractional vacuum-fusion, nitric-acid, and hydrochloric-acid methods

Method	Cooper- ator	STEEL							
		1	2	3	4	5	6	7	8
DETERMINATIONS OF Al_2O_3 (%)									
Chlorine.....	15	nil	0.004	0.001	0.002	<0.001	0.001	0.001	0.024
		17	0.006	.012	.003	.003	.003	.005	.008
Fractional vacuum-fusion.....	24	.0075	.002	.0095	.0085	.002	.002	nil	.042
		Nitric acid.....	9	.001	<.001	<.001	.0015	<.001	.002
13					nil	.0055		.002	.027
Hydrochloric acid.....	13	<.001	<.001	<.001	.0035	.001	.001	.0015	.030
		29	.002	.004	.0035	.0066	.002	.003	.0025
Best values from aqueous-iodine method.....	35							.002	.031
		0.002 ± .002	0.002 ± .002	0.002 ± .002	0.006 ± .002	0.002 ± .002	0.002 ± .002	0.002 ± .002	0.030 ± .003
DETERMINATIONS OF SiO_2 (%)									
Chlorine.....	15	0.001	0.015	0.016	0.001	0.016	0.008	0.001	0.004
	17	.001	.096	.012	.003	.019	.007	.005	.009
	20	.008	.025	.020	.012	.019	.015	.004	.011
Fractional vacuum-fusion.....	24	.003	.011	.007	.002	.013	.004	.0055	.017
Nitric acid.....	9	.008	.0015	.011	.011	.014	.007	.011	.013
Hydrochloric acid.....	35	.001	.013	.0035	.004	.014	.0095	.002	.004
	29	.001	.001	.001	>.001	.012	.002	>.001	.001
Best values from aqueous-iodine method.....		0.003 ± .002	0.009 ± .003	0.005 ± .002	0.002 ± .002	0.016 ± .003	0.009 ± .003	0.002 ± .002	0.003 ± .002

DETERMINATIONS OF MnO (%)

Mercuric chloride.....	{	20	0.004	0.004	0.012	0.004	0.006	0.004	0.050	0.005
		25	.0015	.0025	.010	<.001	<.001	.0015	.012	>.001
Chlorine.....		17	.001	.025	.005	.007	.0075	.011	.0035	.011
Fractional vacuum-fusion.....		24	.058	.027	.049	nil	.018	.013	(*)	.009
Nitric acid.....		9	<.001	<.001	.003	<.001	.001	nil	<.001	.001
Best values from aqueous-iodine method.....			0.002 ±.002	0.004 ±.002	0.012 ±.004	0.002 ±.002	0.004 ±.002	0.008 ±.003	0.025 ±.005	0.003 ±.002

DETERMINATIONS OF FeO (%)

Mercuric chloride.....	{	20	0.290	0.038	0.284	0.061	0.068	0.043	0.630	0.288
		25	.313	.135	.323	.316	.115	.135	.720	.472
Chlorine.....	{	17	.001	.013	.005	.002	.007	.019	.068	.023
		20	.013	.035	.040	.040	.034	.037	.187	.024
Fractional vacuum-fusion.....		24	.009	.0045	.007	nil	nil	nil	*.449	nil
Nitric acid.....		9	<.001	<.001	<.001	<.001	<.001	<.001	<.001	<.001
Best values from aqueous-iodine method.....			0.012 ±.004	0.013 ±.005	0.011 ±.004	0.004 ±.002	0.010 ±.004	0.010 ±.004	0.39 ±.03	0.014 ±.005

* In the analysis of iron 7, by the fractional vacuum-fusion method, FeO and MnO were determined together and reported as FeO.

(a) MERCURIC-CHLORIDE METHOD

In the mercuric-chloride method, the sample is subjected to the action of an aqueous solution of mercuric chloride, 120 g per liter, in the absence of air, until the reaction, $\text{Fe} + 2 \text{HgCl}_2 = \text{FeCl}_2 + 2 \text{HgCl}$, is complete. FeO and MnO remain in the insoluble residue. Compounds of manganese and iron with phosphorus, sulphur, and nitrogen are not decomposed quantitatively. The presence in the insoluble residue of these compounds, or of metallic particles from incomplete decomposition of the sample, leads to high results for FeO and MnO. The determination of SiO_2 and Al_2O_3 is not attempted.

The results for FeO of the two cooperators (20 and 25) using this method for the eight steels are consistently higher than those obtained by any other method. High contents of phosphorus and sulphur might account for the high values for FeO in steel 3, but the equally high values obtained for other steels, with lower phosphorus and sulphur contents, indicate contamination of the residue by particles of metal. Contamination of the residue by phosphides and sulphides would produce high values for MnO as well as FeO; on the other hand, contamination by particles of metallic iron would produce high values for FeO but would not appreciably affect the determinations of MnO. The two sets of values for MnO are in good agreement, except for iron 7 and, furthermore, are usually in agreement with the selected results by other methods. This indicates that the presence of metallic particles in the residue, from incomplete solution of the sample, is a more serious source of error than the presence of the phosphide and sulphide compounds in these eight steels.

(b) CHLORINE METHOD

In this method of analysis the sample is heated several hours at a moderate temperature in a stream of purified chlorine, whereby the metallic constituents are converted to chlorides, which are largely volatile under the conditions obtaining, whereas the oxide constituents are not attacked. These are then determined by suitable means in the residue from the chlorination treatment.

Determinations of SiO_2 , Al_2O_3 , and FeO were made on samples chlorinated at 350° C (cooperator 20) and at 500° C (cooperator 17). In addition, SiO_2 was determined on all the steels, and Al_2O_3 on two of them, chlorinated at approximately 380° C (cooperator 15). MnO was determined by one cooperator (17) on steels chlorinated at 500° C.

Approximately half of the results for SiO_2 are in good agreement with those by the iodine method, and those for Al_2O_3 also in reasonable agreement, although occasional high and low values were obtained. The values for FeO obtained on samples chlorinated at 350° C (cooperator 20) are consistently higher than those on samples chlorinated at 500° C (cooperator 17). The latter are consistently in good agreement with results by the iodine method. The high results for FeO after chlorination at 350° C suggest contamination of the residue in this case by particles of undecomposed sample. Both cooperators reported low values for the FeO content of iron 7. Determinations of MnO by the chlorine method (cooperator 17) are not in consistent agreement with the results obtained by other methods.

(c) FRACTIONAL VACUUM-FUSION METHOD

This modification of the vacuum-fusion method is based on the assumption that the oxides in a steel can be separated according to the temperatures necessary for their reduction. The FeO in a steel can be completely reduced at 1,050° C, whereas temperatures of 1,170, 1,320, and 1,570° C, respectively, are necessary for the reduction of MnO, SiO₂, and Al₂O₃. The sample, to which tin has been added to lower the melting point, is maintained at each of these temperatures successively, and the amount of gas evolved at each is used to indicate the amount of one of the oxide constituents.

Only one set of results (cooperator 24) is available. The results for SiO₂ and Al₂O₃ are generally in good agreement with the selected values by the iodine method. For steels 7 and 8 somewhat high results for SiO₂ are compensated by low results for Al₂O₃, indicating faulty separation of the two fractions in these two determinations. The values for FeO obtained in the fractional vacuum-fusion method are in good agreement with, or somewhat lower than, the iodine results. The high value for FeO in iron 7 represents the sum of the FeO and MnO, as the two constituents were not separated in this determination. The MnO values indicated by the fractional vacuum-fusion analyses are consistently higher, sometimes appreciably so, than the values obtained by other methods. These high values for MnO by the fractional vacuum-fusion method, particularly for steels 1, 2, and 3, perhaps explain the low recoveries of oxygen by the iodine method, as compared with the results by vacuum-fusion. However, determinations by one observer cannot be unreservedly accepted, according to the evidence of the data assembled in these cooperative analyses. Further information is needed to establish the accuracy of the fractional separations and the reproducibility of results by the fractional method in the hands of different operators. In the previous discussion of the vacuum-fusion method, the values for total oxygen obtained by the fractional method were compared with the selected values for the regular vacuum-fusion method. For five of the eight steels the fractional method yielded satisfactory values for total oxygen, but for the other three steels high results were obtained.

(d) NITRIC-ACID METHOD

This method depends upon the solubility of metallic constituents and the relative insolubility of oxides, particularly alumina, in approximately 10-percent nitric acid.

Values for Al₂O₃ that are in excellent agreement with selected results by other methods were obtained by two cooperators (9 and 13), but the determination of SiO₂ was less satisfactory, the results being too high, unless the hydrated silicic acid, formed during the solution of metallic silicides, was completely separated from the SiO₂ and silicate inclusions in the residue. On the other hand, low results for SiO₂ may be caused by partial solubility in the acid medium of some of the silicates that may occur in steel. Determinations of FeO and MnO by the nitric-acid method were made (cooperator 9) to illustrate the accepted belief that the method is not applicable to those determinations. The results demonstrate the almost complete solubility, in nitric acid, of FeO and MnO as they exist in these eight steels.

(e) HYDROCHLORIC-ACID METHOD

In this method diluted hydrochloric acid, approximately two volumes of water to one of concentrated acid, is employed to separate the metallic from the oxide constituents. SiO_2 and Al_2O_3 are determined in the insoluble residue, but the method is not applicable to the determination of FeO and MnO .

The values for alumina by this method are in excellent agreement with those by the iodine method, but the determinations of SiO_2 , as in the nitric-acid method, may be affected by the partial solubility of certain silicates or by the presence of hydrated silicic acid. The determinations of cooperators 35 for both SiO_2 and Al_2O_3 are in excellent agreement with the selected values.

III. AUTHORS' COMMENTS AND CONCLUSIONS

The first impression derived from a study of the data of these cooperative analyses usually is that the results as a whole are decidedly unsatisfactory and indicate that none of the methods for determining oxygen or oxides is sufficiently accurate to conform to the requirements of modern metallurgical analysis. On the whole, however, the variation in results obtained in these cooperative determinations of oxides and oxygen is of about the same order of magnitude as is obtained in determinations of other elements, such as carbon, manganese, nickel, chromium, et cetera, when present in very small amounts.

The results of the vacuum-fusion method are in better agreement among themselves than are those obtained by the aqueous-iodine method. However, in consideration of the data obtained by the latter method, further allowance should be made for the complicated procedure and the number of operations that must be performed in one analysis. The approximate magnitude of the best results by the vacuum-fusion method is clearly indicated by the data for each steel. Some of the selected values for the aqueous-iodine method likewise are clearly indicated by concordant results, but in other determinations the lack of concordant data introduces an element of uncertainty in the selection of best values. The upper and lower limits of the acceptable ranges, to include permissible variations from the selected values, represent the considered opinion of the reviewing committee. It is recognized that there may be differences in opinion as to the proper location of some of the acceptable ranges. Raising or lowering the range as a whole, by one or two thousandths of 1 percent, in several cases would appreciably affect the number of cooperators who obtained acceptable results by the vacuum-fusion method.

The conclusions derived from detailed consideration of the cooperative data may be summarized, as follows:

1. The vacuum-fusion method yields accurate results for all eight of the steels, and the best results obtained by this method probably are close approximations of the true oxygen contents of each of the steels. Recommendations have been made in regard to the procedure and apparatus to be employed in order that the best results may be obtained. SiO_2 and Al_2O_3 , as they occur in these steels, are completely reduced in the vacuum-fusion procedure; the error resulting from interference of manganese, at least up to 1 percent of manganese, is not

so serious with the recommended form of apparatus as it was formerly considered to be. The chief cause of erratic results appears to be spattering of the sample, during melting or shortly thereafter. A convenient and reliable means of eliminating this source of error is not yet available.

2. The aqueous-iodine method yields accurate results for aluminum-killed steels and for some silicon-killed steels but for others, especially steels of the rimming type, low results are obtained. The data for steels 1, 2, and 3, and to a lesser extent for iron 7, show clearly that the aqueous-iodine method cannot be relied upon for determining the total oxygen content of all steels. Part of the discrepancy may be due to some of the oxygen being present in the form of dissolved or entrained gases that are not recoverable by residue methods. Further efforts in standardization of the method, down to minute details of procedure, undoubtedly will result in improved agreement in the results obtained by different analysts. Further study of the determinations of FeO and MnO is particularly needed, and the need for greater accuracy in the chemical analysis of the small amounts of insoluble material obtained in the residue methods is to be emphasized.

3. None of the other methods is represented by sufficiently concordant data to justify the drawing of definite conclusions. The hydrogen-reduction method yields results of the same order of magnitude as the vacuum-fusion results, but further work to standardize the procedure of the hydrogen-reduction method is necessary. Likewise, the results of the other residue methods are of the same order of magnitude as the results obtained by the aqueous-iodine method and are more accurate for the determination of Al_2O_3 and SiO_2 than for FeO and MnO. Further standardization of the methods is desirable.

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