DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 141

ELECTROLYTIC RESISTANCE METHOD FOR DETERMINING CARBON IN STEEL

BY

J. R. CAIN, Chemist

L. C. MAXWELL, Laboratory Assistant

Bureau of Standards

ISSUED DECEMBER 6, 1919

PRICE, 5 CENTS

Sold only by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1919

ELECTROLYTIC RESISTANCE METHOD FOR DETERMINING CARBON IN STEEL

By J. R. Cain and L. C. Maxwell

CONTENTS

	Page
Introduction.....	3
I. Resistance of barium hydroxide solution.....	5
II. Absorption apparatus.....	8
III. Temperature coefficients.....	11
IV. Methods for direct reading of carbon percentages.....	12
V. Apparatus for determining electrical resistance.....	14
VI. Procedure for determining carbon.....	16
VII. Operating suggestions.....	18
VIII. Summary.....	20

INTRODUCTION

The purpose of this study was to investigate the accuracy, speed, and practicability of a method for determining carbon in steel, dependent in principle on passing the carbon dioxide produced by direct combustion of the metal into a solution of barium hydroxide of known electrical resistance. After complete absorption of this gas the resistance is again determined, and from the increase in this (due to precipitation of barium ions) the percentage of carbon is deduced. This method is new in principle, and it is believed it can be applied generally in many cases where the substance being determined precipitates another substance from solution with resultant change in resistance. The assembly of apparatus for determining resistance is also new,¹ and offers many advantages for technical work over the methods hitherto in general use for measurement of electrolytic resistance which require the use of induction coils or high frequency generators, tuned telephones, balanced inductances and capacities, etc. Other new features are the application of the nomograph² for

¹ The elements of this are described by Weibel and Thuras, *J. Ind. and Eng. Chem.*, 10, p. 626; 1918.

² The mathematical work in constructing the nomograph shown in Fig. 4 was done by H. M. Roeser of this Bureau at the request of the senior author, who suggested its application to electrolytic resistance data. A paper on this subject is in preparation by Mr. Roeser. References on the nomograph are: *Traite de Nomographie*, by M. d'Ocagne, Gauthiers-Villars, Paris; *Graphical Methods*, by Carl Runge, Columbia University Press, New York; *Graphical Interpolation of Tabulated Data*, by H. G. Deming, *J. Am. Chem. Soc.*, 39, p. 2383, 1917; *The Nomon, a Calculating Device for Chemists*, by H. G. Deming, *J. Am. Chem. Soc.*, 39, p. 2137; 1917.

the graphical representation of resistance data and the use of special conductivity cells with adjustable electrodes to facilitate the manufacture of any number of such cells with the same cell constant.

Much work has been done by others on electrochemical analytical methods. In general, this work falls into three groups in which an end-point is shown electrochemically by the following methods: (1) The unknown concentration is obtained from curves expressing a relation between cubic centimeters of titrating solution and conductivity (or a related quantity) of the solution titrated;³ (2) the unknown is obtained from curves giving the relation between cubic centimeters of titrating solution added and the corresponding electromotive forces of a cell composed of a normal electrode and an electrode not acted upon by the solution being titrated, the latter being the electrolyte;⁴ (3) a special application of method 2 is used for determining hydrogen ion in acidimetry and alkalimetry and in precipitations from neutralized solutions.⁵ Such methods suffer by comparison with the present for the following reasons: (a) A curve must be plotted for every determination, which consumes much time; (b) the apparatus required to determine carbon with an accuracy of 0.01 per cent carbon would be too delicate and inconvenient of manipulation for everyday use; (c) in some cases it is difficult to fix with sufficient definiteness the inflection or break in the curve denoting the end point of the titration. Upon further comparison of these methods with the present, it is seen that the latter dispenses with one operation common to all the others, namely, the addition of successive portions of a titrating solution and the determination of the resistance at each addition, which results in additional timesaving.

From an inspection of the chemical equation for the reaction underlying the present method:

it is evident (when any given conductivity cell is used) that the only factors which act to change the conductivity of the barium hydroxide used for absorption are: (1) the amount of carbon dioxide absorbed, which determines the disappearance from solution of the barium ion, and (2) the temperature. Since carbon dioxide

³ Harned, *J. Am. Chem. Soc.*, **39**, p. 252, 1916; Findlay, *Practical Physical Chemistry*; Ostwald-Luther, *Physik.-Chemische Messungen*.

⁴ Loomis and Acree, *Amer. Chem. J.*, **46**, pp. 585, 621, 1911 (a bibliography is also given); Hildebrand, *J. Amer. Chem. Soc.*, **35**, p. 869, 1913; Kelly, *J. Am. Chem. Soc.*, **38**, pp. 341, 1916.

⁵ Hildebrand, *loc. cit.* See also Weibel and Thuras, *J. Ind. and Eng. Chem.*, **10**, p. 626, 1918, for another electrolytic method.

precipitates barium without leaving reaction products in the solution to increase the conductivity (such as would remain if, for instance, sodium sulphate were the precipitating agent for the barium), it can be seen that the present method should give the maximum possible change of resistance for a given amount of barium removed—a condition which tends to secure a high degree of sensitiveness.⁶ However, since the temperature coefficients of resistance of barium hydroxide solutions in the range of concentrations herein employed (see Fig. 2) average nearly 1.7 per cent per degree, it is evident that the accuracy of the method will be largely affected by temperature if due correction is not made.

In developing this method it was deemed necessary (a) to construct the curve showing resistance as a function of concentration of barium hydroxide solutions ranging from very concentrated to very dilute, and to select the portion of this curve showing the maximum change of resistance for a given change of concentration; (b) to devise an apparatus which, when the selected barium hydroxide solutions were used in it, would completely absorb the carbon dioxide at the highest rates of passage of the gas current, and which, in order that the method might meet the requirements of convenience and rapidity, should permit resistance determinations to be made without transfer of the solution to another vessel, and should also be easy to fill and empty; (c) to determine the temperature coefficients of the barium hydroxide solutions in the selected range of concentration;⁷ (d) to prepare a chart enabling the operator to read directly therefrom the percentage of carbon, all temperature corrections being incorporated; (e) to design an apparatus for the electrical measurements possessing the necessary robustness, reliability, simplicity, and protection from corrosion by the laboratory fumes.

I. RESISTANCE OF BARIUM HYDROXIDE SOLUTIONS

A curve was prepared (Fig. 1) showing the relation between electrical resistance and barium hydroxide concentration when the latter was varied from practically saturation to nearly zero. As the data in the literature were insufficient for this purpose, the determinations were made by Louis Jordan of this Bureau and are represented in Fig 1. The solutions for constructing the curve were prepared from J. T. Baker's analyzed barium hydroxide by diluting a stock solution of this with carbon-dioxide-free

⁶ Compare the conditions in Harned's work with $\text{Ba}(\text{OH})_2$ solutions, loc. cit.

⁷ There is some possibility of placing the absorption vessel in a constant-temperature bath together with a compensating cell in the other arm of the bridge. This would remove the necessity for temperature correction. The method described herein, however, is believed to be simpler.

water and determining the strength by titration against standard hydrochloric acid, using methyl orange as indicator. The resist-

FIG. 1

ance measurements were all made in the same conductivity cell and at practically the same temperature (27°).⁸ No great accu-

⁸ They were not corrected by any temperature coefficient since, as an inspection of Table 1 shows they were made at near enough to one temperature to give roughly the form of the curve, which was all that was desired.

racy is claimed for these results, which are used only for establishing the form of the curve and selecting a portion of it for more exact redetermination. The portion of the curve selected for use in this method is that between *A* and *B*. This region gives the maximum change of resistance per unit change of concentration consistent with the use of solutions sufficiently concentrated to effect complete absorption of carbon dioxide under the conditions imposed. Comparing the resistance changes with changes of concentration of barium hydroxide corresponding to 1 per cent carbon on different parts of the curve, it is seen, for example, that these changes in resistance are approximately six times as great on the curve portion *AB* as on the portion *CD*. The use of the most dilute solutions possible is, of course, also desirable from the saving in barium hydroxide effected. Solutions to the left of *A*, even when used in a very efficient absorbing vessel, will not retain all the carbon dioxide except at rather slow rates of aspiration.

The methods used in Tables 1 and 2 and elsewhere throughout this paper for expressing the strength of the barium solution in terms of "equivalent per cent carbon" was chosen for convenience in using the nomograph described subsequently (pp. 13-14). By "equivalent per cent of carbon" is meant the amount of carbon (expressed as percentage on the basis of 2 g samples used) necessary to precipitate completely all the barium ions from the solution concerned. This amount of carbon is calculated from the equation $\text{Ba}(\text{OH})_2 + \text{CO}_2 = \text{BaCO}_3 + \text{H}_2\text{O}$. For instance, in the first horizontal column of Table 1 it is seen that 2.14 equivalent per cent carbon corresponds to 0.612 g $\text{Ba}(\text{OH})_2$. The former figure was obtained by solution of the proportion:

Molecular weight $\text{Ba}(\text{OH})_2$: Atomic weight carbon :: (weight of $\text{Ba}(\text{OH})_2$ in 200 cc solution : weight of carbon in sample.

or

$$171.38 : 12.00 :: 0.612 :$$

whence $X = 0.0428$ g carbon

or the "equivalent per cent carbon" = $(x/2)100 = 2.14$

TABLE 1.—Data for Resistance Concentration Curve for $\text{Ba}(\text{OH})_2$ Solutions in the Region: 2 to 30 Per Cent Carbon Equivalent Strength^a

[Cell constant=0.715]

Grams $\text{Ba}(\text{OH})_2$ per 200 cc solution	Equivalent carbon	Tempera- ture	Resistance	Grams $\text{Ba}(\text{OH})_2$ per 200 cc solution	Equivalent carbon	Tempera- ture	Resistance
	Per cent	°C	Ohms		Per cent	°C	Ohms
0.612	2.12	27.9	171.6	4.94	17.9	27.2	26.2
1.12	3.92	27.3	97.9	5.31	18.6	27.0	24.7
1.68	5.87	27.3	68.5	5.88	20.6	26.9	22.7
2.20	7.70	27.3	53.5	6.45	22.5	26.0	21.8
2.67	9.35	27.3	44.9	6.93	24.2	26.8	20.1
3.17	11.1	27.2	38.7	7.34	25.6	21.2	20.8
3.64	12.7	27.0	34.6	7.84	27.4	21.2	19.7
4.05	14.2	26.9	31.2	8.45	29.5	27.3	16.4
4.43	15.5	27.0	29.2				

^a See explanation on p. 7.TABLE 2.—Data for Resistance Concentration Curve of $\text{Ba}(\text{OH})_2$ Solutions in the Region: 4 to 5 Per Cent Carbon Equivalent Strength^a

[Cell constant=0.715]

Grams $\text{Ba}(\text{OH})_2$ per 200 cc solution	Equiva- lent carbon	Tem- perature	Observed resist- ance	Cor- rected resist- ance	Grams $\text{Ba}(\text{OH})_2$ per 200 cc solution	Equiva- lent carbon ^a	Tem- perature	Observed resist- ance	Cor- rected resist- ance
	Per cent	°C	Ohms	Ohms		Per cent	°C	Ohms	Ohms
1.164	4.075	23.6	100.9	98.49	1.301	4.553	27.5	85.3	88.92
1.198	4.194	24.2	97.4	96.08	1.303	4.559	26.4	86.8	88.79
1.239	4.337	24.2	94.6	93.26	1.346	4.712	25.1	86.0	86.06
1.242	4.348	23.2	95.8	92.81	1.385	4.848	25.8	82.7	83.90
1.280	4.482	24.4	91.4	90.42	1.403	4.912	24.4	84.2	83.94
1.286	4.500	26.6	87.6	90.01	1.460	5.110	23.1	82.8	80.11

^a See explanation of this term on p. 7.

The portion of the curve selected for use by this method is again shown in Fig. 2. The procedure used in determining the points on it was the same as for constructing the curve shown in Fig. 1, except that more care was taken to secure accurate readings and the results were corrected by the temperature coefficients given in Section III of this paper. Table 2 gives the data used in constructing this curve.

II. ABSORPTION APPARATUS

The essential features desirable in the absorpuon apparatus are: (1) It must retain all carbon dioxide when gas passes at the rate of 300 to 400 cc per minute; (2) it must permit resistance measurements to be made without transfer of the solution to

another cell; (3) temperatures of solutions should be easily read to 0.1° ; (4) the cell should be easy to clean and fill with fresh solution; (5) all cells should be built with the same cell constant,⁹ or the latter should be capable of adjustment to one value for all, so that one chart or set of tables may be used for all cells.

FIG. 2

Fleming¹⁰ and others have shown that the combustion of a sample of steel and the sweeping out of the products of combustion from the apparatus where combustion tubes of the usual length and bore are used, can be accomplished in 5 to 6 minutes; this requires passage of the oxygen at the rate of about 300 to 400 cc per minute. Soda lime has been found to absorb all the carbon dioxide at this and higher rates. However, barium hydroxide solutions of all concentrations are much less efficient absorbents than soda lime. The absorbing efficiency increases slightly with the concentration, but even when the most concentrated solutions are used it is impossible to absorb completely all the carbon dioxide in the usual types of gas-absorption vessels, nearly all

⁹ The "cell constant" is not a constant at all, as Washburn and others have shown, but for want of a better term this expression has been used throughout this paper.

¹⁰ W. R. Fleming, *Iron Age*, 93, p. 64, 1913.

of which were tried. The method used for testing these forms of apparatus was to burn a sample of steel with a gas meter before the furnace to control the rate of passage of the oxygen, and to attach, after the tube being tested, a second absorption vessel containing a little clear barium hydroxide solution. A test was not considered satisfactory if the second tube showed any cloudiness.

Satisfactory absorption was secured in a vessel similar to that described by Weaver and Edwards,¹¹ with suitable modifications, the details of which were developed by S. M. Hull, formerly of the chemical division of this Bureau. For use in the present work electrodes were sealed into this absorption tube in the middle reservoir. In order always to secure the same cell constant, the area and distance apart of the electrodes were originally adjusted before sealing into the reservoir. This was found to be an extremely uncertain and difficult operation, and this difficulty, as well as the general fragility of the apparatus, led to its abandonment and the search for something simpler. After the completion of investigations described in another paper,¹² it was found that by burning the sample as therein described (namely, by placing it on a preheated boat, allowing boat and sample further to preheat for a minute in the furnace, and then admitting oxygen at 300 to 400 cc per minute) it was possible to burn a 2 g sample completely in $1\frac{1}{2}$ to 2 minutes. Since the first few hundred cubic centimeters of oxygen combined with the iron, there was produced a much greater partial pressure of carbon dioxide than would have been secured had the sample burned slowly, and this made it possible to use a very simple absorption tube, such as that shown in Fig. 3, for the carbon dioxide.

It was also found simpler to build a cell whose electrodes could be adjusted to secure a given cell constant than to attempt to obtain the same result with the electrodes sealed in a fixed position in the cell. This fact, and the use of the special method of combustion described, led to the design of the apparatus shown in Fig. 3. This is not fragile and the glass parts can be built by any glass blower of ordinary skill; it meets all the other requirements detailed on pages 8 and 9.

The adjustment of the cell constant is made by moving the electrodes up and down after loosening the stuffing box; a marked change takes place as they approach the meniscus. Initial ap-

¹¹ *J. Ind. and Eng. Chem.*, 7, p. 534; 1915.

¹² Cain and Maxwell, *J. Ind. and Eng. Chem.*, 10, p. 520; 1918.

proximate similarity can be attained by the glass blower with comparative ease. Once the electrodes are set in the proper position, this is maintained by cementing with DeKhotinsky cement. The electrodes are platinized and the cell constant is determined as described under "Operating suggestions." A certain amount of adjustment of the constant of the cell can be secured by removing or adding platinum black to one or the other of the electrodes during the platinizing operation by the use of an auxiliary electrode. Some cells in long use at the Bureau have differed in cell

FIG. 3.—Details of absorption vessel

constant by 0.04 without affecting the accuracy of results. Actually, it is possible easily to adjust cell constants within 0.005, and this practice is to be recommended.

III. TEMPERATURE COEFFICIENTS

The solutions for determination of these coefficients were prepared and standardized as described on pages 5 and 6. The conductivity cells used for the work were kept in a thermostatically controlled chamber where the temperatures were maintained within 0.01°C .

Resistances of barium hydroxide solutions equivalent to approximately 4.0, 4.25, 4.50, 4.75, and 5.0 per cent carbon were determined at 20° , 25° , and 30° . The experimental values and the corresponding calculated values for α and β are shown in Table 3.

These values for α and β were calculated by substituting the values for temperature and resistance from Table 3 for t in the equation:

$$\frac{1}{Rt} = \frac{1 + \alpha[t - 25] + \beta[t - 25]^2}{R_{25}}, \text{ and solving for } \alpha \text{ and } \beta.$$

TABLE 3.—Data for Temperature Coefficients of Resistance

Concentration of Ba(OH) ₂ solution ^a (approximate)	Temperature	Resistance	α	$\beta \times 10^{-4}$
5.0 per cent carbon.....	20	135.25	0.01674	0.2687
	25	124.02		
	30	114.37		
4.75 per cent carbon.....	20	142.18	.01680	.3505
	25	130.36		
	30	120.16		
4.50 per cent carbon.....	20	149.07	.01686	.3085
	25	136.62		
	30	125.91		
4.25 per cent carbon.....	20	156.18	.01687	.1652
	25	143.07		
	30	131.89		
4.00 per cent carbon.....	20	165.18	.01687	.0898
	25	151.28		
	30	139.48		

^a 200 cc of the solution contained barium hydroxide approximately equivalent to the carbon in a 2 g sample with 5 per cent C., or 100 cc of the solution contained barium hydroxide approximately equivalent to the carbon in a 1 g sample with 5 per cent C (i. e., 0.05 g carbon); or approximately 0.7125 g Ba(OH)₂. The other solutions contained barium hydroxide approximately equivalent to 1 g samples with 4.75, 4.50, 4.25, and 4.00 per cent C., respectively.

IV. METHODS FOR DIRECT READING OF CARBON PERCENTAGES

Several methods were tried for graphically representing the relation between carbon percentages and the corresponding observed temperature and resistance measurements. At first tables were constructed in which temperature corrections were calculated and applied for every tenth of a degree and every one-tenth ohm, but these were found to be too cumbersome. Other tables were then constructed which gave the temperature corrections only, with the idea of adding or subtracting these each time a reading was made. This condensed the tables very considerably, but increased the amount of calculation necessary. A series of curves was then constructed showing the relation between resistance and per cent carbon, a curve being constructed for every tenth of a degree. Such curves are convenient to use only if they are plotted on an inconveniently large scale; even then it is very fatiguing to use them for many readings at a time.

After a little study it was found that the β term could be omitted from the equation for correcting temperatures to 25° , provided this equation is applied only between the temperatures

FIG. 4

15° and 35° ; at higher or lower temperatures the correction for the β term is appreciable. If the laboratory temperature is not within these limits, the stock solution in carboy *F* of Fig. 6 must

be brought within this range by placing it in a bath of hot or cold water. The equation: (1) $R_{25} = Rt[1 + \alpha(t - 25) + \beta(t - 25)^2]$ then reduces to: $R_{25} = Rt[1 + \alpha(t - 25)]$, in which $\alpha = 0.01681$, this value being taken from Table 3. After trials of other forms of curves, it was found that the parabolic form answered the requirements of fitting the observations sufficiently well and of permitting the construction of a nomograph. The equation to the curve shown in Fig. 2 was calculated on the assumption that it was parabolic, using the methods of least squares and the observation shown in Table 2. This equation was found to be:

$$\begin{aligned} C^2 - 13.589C + 63.191 - 0.2478R_{25} &= 0 \\ \text{or, } C^2 - 13.589C + 63.191 - 0.2478R(1 + \alpha(t - 25)) &= 0 \\ \text{whence (2) } C &= 6.79 - \frac{1}{2}\sqrt{0.9912R(0.5798 + 0.01681t - 67.11)} \end{aligned}$$

C being the equivalent per cent of carbon in the sense already explained. From equation 2 the nomograph shown in Fig. 4 was prepared. This nomograph can be used for all cells having cell constants not too different from 0.715 (see p. 11), which was the cell constant of the cell used when data for the curve shown in Fig. 2 were obtained. As has been shown, the form of cell used (Fig. 3) allowed the electrodes to be adjusted always to secure this result.

The use of the nomograph is very simple. A straightedge is made to connect the observed values for temperature and resistance, and the intersection with the third (middle) ordinate gives the concentration of the solution in terms of carbon percentage; this may be termed the first concentration. After the combustion is ended a similar set of readings is taken and subtraction of the second concentration reading from the first gives directly the per cent of carbon if a 2 g sample has been taken; or, if a 1 g sample has been used, the result is multiplied by 2. The scales can be read to 0.005 per cent C, 0.05° and 0.05 ohm. It was found by comparison of chart readings in a number of cases with the resistances computed by equation 1 that the error of the chart is less than 0.005 per cent carbon.

V. APPARATUS FOR DETERMINING ELECTRICAL RESISTANCE

With the cooperation of the Leeds & Northrup Co., different forms of apparatus for measuring electrolytic resistances were built and tried. Two forms of high-frequency generator in connection with tuned telephones were used; also one or two forms

of induction coil as sources of alternating current, and an interrupter such as is used in wireless investigations. The latter was quite unsatisfactory, as might be expected, due to polarization. Good results were obtained with the high-frequency generators and tuned telephones, provided that inductances and capacities were used as directed by recent investigators. Such refinements were inconvenient in a method such as the present, intended for works use. There are two other important objections from the same standpoint: (1) The difficulty of detecting a minimum in the telephone when working in a noisy place, such as the usual works laboratory and the fatigue of the operator who would have to make possibly 80 or 90 determinations in an 8-hour day; and

FIG. 5.—Diagram of bridge used for resistance measurements

(2) the liability to deterioration of a high-frequency generator when operating continuously 24 hours per day, as might happen in technical use. These considerations led to the development of a method of measuring electrolytic resistances by the use of commercial 60 or 25 cycle current. It was found after trial of the Weibel¹³ galvanometer, of a vibration galvanometer, and of a direct current galvanometer operating off a crystal rectifier placed in the secondary of a transformer (the cell being in the primary) that the Weibel galvanometer offered a very satisfactory zero instrument for such measurements of electrolytic resistance as had to be made in this work. The bridge shown in Fig. 5 was

¹³ E. E. Weibel, Bureau Standards Scientific Papers No. 297; 1917.

accordingly constructed by Leeds & Northrup. The resistance coils and galvanometer are inclosed in a hermetically sealed box so that they are efficiently protected from corrosion. There are three dials—tens, units, and tenth ohms, respectively—and a fourth which adds 100 to the readings of the others, when this is desired. An accuracy of 0.1 ohm in the readings is all that is necessary, although much better than this can be done. This instrument has been in use several months and has been very satisfactory. A perfect minimum is always registered by the galvanometer, provided the electrodes are well platinized.

VI. PROCEDURE FOR DETERMINING CARBON

A nichrome-wound furnace is used for heating. Porcelain or glazed-quartz tubes may be employed; they should be fitted with a sheet-nickel sleeve for internal protection from fused iron oxide which is thrown off from the burning steel. The two absorption vessels are filled to the 200 cc mark with barium hydroxide solution from the stock bottle *F* (Fig. 6; see also note 1). Oxygen or air freed from carbon dioxide is passed for a few seconds to mix the solutions, and their temperatures and resistances are then recorded. In the meantime the combustion boat filled with alundum sand has been preheating in the furnace, which for this work should be maintained continuously at 1050 to 1100° C, preferably the latter temperature.¹⁴ This is an extremely important point, for if the temperature is too low or the oxygen is not pure or is not admitted at 300 to 400 cc per minute after the combustion starts, the rapid combustion mentioned on page 10, and essential to successful absorption, can not be secured. The boat is removed from the furnace, and when at a low red heat the sample is distributed on the alundum¹⁵ and the boat replaced in the furnace and left to preheat, without oxygen passing, while the next sample is being weighed. Oxygen is now passed at the rate of 300 to 400 cc per minute for the next two minutes; then stopcock *S*, Fig. 6, is turned to position 2, which admits carbon-dioxide-free air; this should pass at the same rate as the oxygen. During this combustion period, if directions have been followed, all carbon dioxide will have been removed from the furnace, but some still remains in the large bulb of the absorption apparatus; the air removes this.

¹⁴ The melting point of gold is a convenient temperature check. If this metal is not melted the temperature is too low. See cited paper by Cain and Maxwell.

¹⁵ Experience has shown that no loss of carbon occurs unless the sample contains dust; with most steels this can first be removed without causing an error in the carbon determination. This point should always be tested, however, in burning new steels.

FIG. 6.—*Assembly of apparatus used*

The advantage of the use of air at this stage is obvious: a saving of oxygen is effected and the furnace is immediately available for burning the next sample. While air is passing through the first tube ($1\frac{1}{2}$ to 2 minutes is necessary for this) the combustion of the next sample proceeds as already directed, using the second absorption tube. The second reading of resistance and temperature on the first tube then follows, and if the solution is not too dilute it can be used for absorbing the carbon dioxide from other samples; otherwise, a little is allowed to flow into the reservoir G, and the tube filled to the mark again with fresh solution. Of course it is an economy in time for the operator, wherever possible, to choose conditions (weight of sample, carbon content of same, etc.) so as to get the maximum number of determinations for a single filling, since in this way the second resistance and temperature readings serve as initial values for the next combustion, and so on. The solution should not be used when it is more dilute than corresponds to 4 per cent carbon (i. e., 99.5 ohms at 25° ; see nomograph, Fig. 4, for the limiting resistances corresponding to other temperatures), since its absorptive power at rapid rates of passage of the oxygen is then less, and some carbon dioxide may be lost. The data relating to combustions should be recorded as obtained. It is convenient to use a tabular form or record showing (1) designation of sample, (2) weight taken, (3) cell used, (4) initial temperature, (5) final temperature, (6) initial resistance, (7) final resistance, (8) initial concentration, (9) final concentration, (10) carbon percentage in sample, and (11) remarks. There is ample time for entering this information while other operations are going on. A very good way is to enter "final temperature" below "initial temperature," and "final resistance" after "initial resistance" for each sample, since this relates these quantities in an easy manner for reading the nomograph.

The speed of the method naturally depends on the skill of the operator and the ingenuity displayed in arranging a cycle of operations which secures the best speed under his working conditions. Operators at the Bureau when working on a series of Bureau of Standards analyzed samples averaged one determination per four and one-half to five minutes. The accuracy of results is shown in Table 4.

TABLE 4.—Results by Electrolytic Resistance Method

Sample used	Grams used	Bureau of Standards value for carbon (average by direct combustion)	Value by electrolytic resistance method	Analyst
		Per cent		
11a.....	2.0	0.223	0.21	Maxwell.
11a.....	2.0		.21	
	2.0		.41	
12b.....	2.0	.409	.41	Swindells.
	1.0		.42	
	2.0		.81	
14a.....	1.0	.813	.82	Swindells.
	2.0		.80	
	.5		1.00	
16a.....	.5	.990	1.00	Cain.
	1.0		1.00	
	2.0		.98	
21a.....	2.0	.617	.62	Cain.
21a.....	2.0		.62	
	0.00421		0.0046	
Sugar (grams carbon).....	.00421		.0042	Do.
	.00421		.0040	

VII. OPERATING SUGGESTIONS

1. Stock barium hydroxide solutions are conveniently made in one to two carboy lots by adding solid barium hydroxide to the carboy nearly filled with water (agitating with air) until the equivalent strength approaches 5 per cent carbon. Subsequent additions can then be made by adding a saturated barium hydroxide solution. Of course, it is not necessary to make up exactly to the equivalent of 5 per cent carbon. An approximation to this is all that is desired. The strength of the solution is determined from time to time during the standardization by running a portion of the solution into the cell and measuring its resistance. If a set-up like that shown in Fig. 6 is used in measuring the resistance, it is not necessary to remove the carboy from the shelf or to break any of the connections during these operations. If it is desired to economize in the use of barium salt, the waste solution in reservoir *G* can be brought up to strength as described, after first decanting it off from the barium carbonate that has settled out. A still further economy can be effected by drying and calcining to oxide the precipitated barium carbonate. This oxide can then, of course, be used again.

2. The cell constants should be checked from time to time. This may be done (1) by burning standard samples or (2) by determining the resistance of a N/10 solution of pure potassium chloride. This solution should be prepared on the day it is to be used, since stock solutions have been found to change during the course of this work. Table 5 shows the resistivities at various

TABLE 5.—Specific Resistivity of N/10 KCl Solution at Various Temperatures

[From Landolt-Bornstein Physik. Chemische Tabellen 4 Aufl., p. 1117]

Temperature	Resist- ance	Temperature	Resist- ance	Temperature	Resist- ance
	Ohms		Ohms		Ohms
15.0.....	95.42	22.0.....	82.30	29.0.....	72.10
16.0.....	93.28	23.0.....	80.71	30.0.....	70.82
17.0.....	91.32	24.0.....	79.11	31.0.....	69.59
18.0.....	89.37	25.0.....	77.64	32.0.....	68.40
19.0.....	87.49	26.0.....	76.16	33.0.....	67.20
20.0.....	85.69	27.0.....	74.79	34.0.....	66.09
21.0.....	83.96	28.0.....	73.42	35.0.....	64.98

temperatures of N/10 potassium-chloride solutions. The cell constant is computed from the formula: $R = NS$, or $N = \frac{R}{S}$, where R is the observed resistance, N the cell constant, and S the resistivity, taken from Table 5, for the same temperature. If a change in cell constant has taken place, it is most probable that the electrodes need replatinizing. Directions for this are given in paragraph 4 of this section. If method 1 is used, any marked deviation from the correct carbon value of the standard steel may be due to a change in the cell constant, and this should then be checked by method 2, unless it is suspected that the error in the carbon determination is due to some other cause. In the present work no deviation of cell constants has been observed until after several months' use, and then the change is sudden and erratic. When the cell constant changes, it should be brought back to the original value by the methods already described in Section II of this paper.

3. If the absorption vessels are not to be used for some time, they should be cleaned with hydrochloric acid (not over 2 to 3 per cent HCl) followed by distilled water. Extreme care should be taken that none of the hydrochloric acid or chlorides enter the reservoir for waste barium hydroxide solution if this is to be used again.

4. To platinize the electrodes, the cap carrying them (Fig. 6) is removed from the cell, and they are first cleaned with sulphuric acid and chromic-acid mixture, followed by distilled water. Then they are immersed in a vertical position in a solution made of 100 g water, 3 g chloroplatinic acid, and 0.02 to 0.03 g lead acetate. Current is passed through the solution by connecting the electrodes to three dry batteries in series. The current is passed for five minutes, reversing every half minute. Finally, an auxiliary platinum electrode is introduced and current passed with this as anode for another two minutes, after which the electrodes are washed thoroughly with distilled water and are then ready for use.

VIII. SUMMARY

1. This paper describes the fundamental principles of a method for determining carbon dioxide by absorbing it in barium hydroxide solution and measuring the resistance change of the solution in relation to its concentration.

2. A suitable absorption vessel with electrolytic resistance cell incorporated is illustrated and described.

3. Resistance measurements of barium hydroxide solutions varying in concentration from 3.08 g Ba(OH)_2 per liter to 42.25 g Ba(OH)_2 per liter were determined approximately and determinations accurate within 0.10 ohm were made of the resistances of 12 different solutions varying from 5.820 g Ba(OH)_2 per liter to 7.300 g Ba(OH)_2 per liter.

4. Temperature coefficients of resistance of these 12 solutions were determined in the range 20.00° to 30.00° C.

5. Based on the measurements of resistance of the barium hydroxide solutions, solutions with concentrations varying between 5.820 g Ba(OH)_2 per liter and 7.300 g Ba(OH)_2 per liter were chosen as most suitable for this method.

6. Special resistance-measuring apparatus was developed which simplified these measurements by dispensing with tuned telephones, high-frequency generators, and balanced inductances and capacities.

7. A convenient nomographic method of applying necessary temperature corrections to resistance measurements was developed.

8. The method permits of accurate determinations of carbon in steel (i. e., within 0.01 per cent carbon) by the direct-combustion method in four and one-half to five minutes.

H. E. Cleaves carried out some preliminary measurements, and Messrs. Silsbee, Agnew, and Isler, of the electrical division of the Bureau, cooperated effectively in the selection of a suitable alternating-current galvanometer. The Leeds & Northrup Co. also cooperated fully by constructing and loaning electrical measuring apparatus for experimental work, and, finally, by building in practical form the apparatus that was developed.

WASHINGTON, October 8, 1918.