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A STUDY OF THE GOUTAL METHOD FOR DETERMINING CARBON MONOXIDE AND CARBON DIOXIDE IN STEELS

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I. INTRODUCTION

In 1910 Goutal [1] published a method for determining carbon monoxide and carbon dioxide in steel, which consisted in dissolving the metal in a 40 per cent copper-potassium-chloride solution in a rubber-stoppered flask through which purified nitrogen passed and carried with it the gases liberated upon solution of the steel. The gases carried by the nitrogen were first passed through barium-hydroxide solution to absorb carbon dioxide, and then washed with concentrated sulphuric acid saturated with bromine to remove hydrocarbons generated from the steel. Following the sulphuric-acid vessel was (1) a tower filled with stick potassium hydroxide to remove bromine carried over from the preceding wash bottle; (2) a U-tube which contained pumice

[1] E. Goutal, Rev. de Met., 7, pp. 6-15; 1910.

saturated with concentrated sulphuric acid for completely drying the gas; (3) a U-tube filled with iodine pentoxide. This was heated by an oil bath to 75° for the purpose of oxidizing carbon monoxide according to the equation: $5CO + I_2O_5 = I_2 + 5CO_2$. The iodine thus liberated was carried on by the current of nitrogen to a wash bottle containing chloroform covered with water. Here it was absorbed and the chloroform solution was subsequently titrated against sodium thiosulphate. From the amount of iodine thus determined the carbon monoxide was calculated.

As part of a general study of the determination of gases in steel, it was decided to study this method at the Bureau with the idea of coordinating results obtained by it and by the Ledebur method of determining oxides in steels when both methods were applied to the same sample. As will be seen later this was not done because the Goutal method did not yield the results expected of it.

In attempting to repeat Goutal's work, it seemed desirable to make certain changes in his apparatus and method. These related to (1) choice of apparatus, (2) purity of reagents used, (3) blank corrections, and (4) methods for estimating the carbon monoxide and dioxide.

II. AUTHORS' MODIFICATION OF GOUTAL'S PROCEDURE AND APPARATUS

1. APPARATUS

In this work a reaction flask fitted with ground-glass stopper was substituted for the rubber-stoppered flask used by Goutal. The elimination of rubber is an obvious advantage. The apparatus for washing with a solution of bromine in concentrated sulphuric acid was omitted, after determinations of carbon monoxide on several steels with and without it in the train showed no appreciable difference. The tube containing pumice saturated with concentrated sulphuric acid was also omitted as being unnecessary. The wash bottle containing chloroform which followed the iodine pentoxide and which was used by Goutal for absorbing the iodine liberated was replaced in the authors' apparatus by a Meyer tube filled with barium-hydroxide solution, since the carbon dioxide formed by oxidation of the carbon monoxide was determined instead of the equivalent iodine liberated, as in Goutal's work.

2. REAGENTS

(*a*) *Copper-Potassium-Chloride Solution.*—Goutal makes no statements as to impurities in the copper potassium chloride he used. His procedure in preparing for a determination was to place in the reaction flask 500 cm^3 of the 40 per cent copper-potassium-chloride solution, replace the stopper, and boil for one-half hour while passing a slow current of nitrogen. Then the flask was connected to the train containing the absorbents for carbon monoxide and carbon dioxide, and the boiling and passing of nitrogen was continued for 15 minutes; the flask was now allowed to cool for one hour with the nitrogen still passing. He says: "Apres ce temps, on ne doit constater aucun trouble dans le solution de baryte et aucun coloration dans le chloroform bien que le tube a anhydride iodique se troube portè dè le dèbut a 75°." If Goutal actually secured this result, his blank determinations could, of course, be considered satisfactory.

In the present work such blank determinations were obtained only after very special precautions, as is shown by Table 1, which gives the results of several experiments. It was found in this work that different preparations of copper potassium chloride contained varying and sometimes very large amounts of impurities, which cause a blank correction such as Goutal's preliminary treatment would not eliminate. Such impurities may be removed in part by recrystallizing the salt, and Table 1 gives some blank experiments made by using solutions of copper salt so prepared. The procedure in making these determinations was that subsequently described in this paper for determining carbon monoxide and carbon dioxide in steel with omission of the steel.

TABLE 1.—Results of Blank Determinations [a] When Using Various Preparations of Copper Potassium Chloride

Source or method of preparation of salt	CO	CO_2
	mg	mg
Baker & Adamson's	0.5	1.1
	.6	1.1
J. T. Baker's	1.2	2.5
	1.0	2.5
J. T. Baker's recrystallized	.9	1.8
	1.1	1.5
	1.0	1.1
Salt recovered from mother liquors from recrystallization	2.9	6.9
Specially prepared by authors (see text)	.0	.0

[a] These blank determinations were made by carrying out the method as described on pp. 5-6, omitting the steel.

Since it was found impossible either to obtain commercial preparations of this salt which gave no blank correction, or to purify them so that an appreciable blank correction was not necessary, a special reagent was made for some of the work. Electrolytic copper was dissolved in hydrochloric acid to which was added slightly more than the theoretical amount of nitric acid to convert to cupric salt. The solution was evaporated on the steam bath until dry, then covered with concentrated hydrochloric acid and again evaporated on the steam bath until dry. Potassium chloride was freed from possible organic contaminants by fusion in an electric furnace through which air was circulated. The reagent for dissolving the two steels was prepared in quantity by dissolving the two salts in correct proportion and filtering. The reagent thus prepared gave no blank corrections whatever.

(*b*) *Hydrogen and Nitrogen* (*for Displacing the Liberated Carbon Monoxide and Carbon Dioxide*).—Goutal used air or nitrogen interchangeably for this purpose. In this work either pure hydrogen or nitrogen was used, comparison tests on a sample of steel having shown that the amounts of carbon monoxide and carbon dioxide obtained under otherwise similar conditions were practically identical. (See Table 2.)

TABLE 2.—Results When Using Nitrogen and Hydrogen as Displacing Gases

Sample	Hydrogen		Nitrogen	
	CO	CO_2	CO	CO_2
	Per cent	Per cent	Per cent	Per cent
B. S. Bessemer 0.8 per cent C	0.026	0.011	0.026	0.019
	.029	.016	.029	.013

3. AUTHORS' METHOD OF DETERMINING MONOXIDE AND DIOXIDE

Carbon dioxide was absorbed in barium hydroxide solution, but instead of converting the precipitated carbonate to sulphate and weighing it in that form, as Goutal did, the authors determined it by the barium-carbonate-titration method,[2] which method has been proved here and elsewhere to be accurate and reliable. The carbon dioxide produced as a result of the reactions in the iodine-pentoxide tube was also absorbed in barium-hydroxide solution and determined in the same way. It was found necessary, by tests, to heat the iodine-pentoxide tube to 150° instead of to 75°,

[2] J. R. Cain, B. S. Tech. Paper No. 33; 1914. Also J. Ind. and Eng. Chem., 6, p. 465; 1914.

as Goutal recommended; the data given in Table 3 show that known amounts of carbon monoxide were converted to carbon dioxide only at or above this temperature.

The carbon monoxide for the experiments shown in Table 3 was obtained by decomposing known amounts of pure sodium oxalate with concentrated sulphuric acid; the gas evolved was carried into the iodine-pentoxide tube with pure hydrogen. From the table it is seen that at 80° only 63.4 to 71.7 per cent of the carbon monoxide was oxidized to carbon dioxide, while at 150° 97.3 per cent or more was so oxidized.

TABLE 3.—Oxidation of CO by I_2O_5 at Different Temperatures

Temperature	Amount of CO present	Amount of CO found	Recovered
	g	g	Per cent
80°	0.0103	0.0065	63.4
	.0082	.0059	71.7
100°	.0234	.0211	92.7
	.0128	.0121	94.5
	.0173	.0158	91.3
150°	.0157	.0154	98.1
	.0189	.0184	97.3
	.0154	.0157	[a] 101.8

[a] A little SO_3 passed over.

III. GOUTAL'S METHOD AS USED BY AUTHORS

Four hundred cubic centimeters of the copper-potassium-chloride solution were placed in the solution flask together with 4 cubic centimeters of 1–1 hydrochloric acid and the solution was boiled for one hour with air (purified from carbon dioxide) passing. At the end of this period, when using the specially prepared copper reagent, the solution was free from substances yielding carbon monoxide and carbon dioxide; with the purified commercial preparations small amounts of these gases were generally still evolved, for which appropriate blank corrections were applied. The solution was now cooled to room temperature, the steel put in and the flask connected to the hydrogen apparatus on one side and the gas-collecting apparatus on the other. Hydrogen was passed slowly for two hours during solution of the steel, the oil bath heating the iodine-pentoxide tube, having previously been brought to 150°. The solution was then boiled vigorously for an additional hour with a more rapid current of hydrogen passing during this period. The tubes which served for collecting

the carbon monoxide and dioxide were then disconnected and the flask cleaned and filled with fresh solvent in preparation for the next determination. The barium carbonate in each tube was determined as described, and calculated, respectively, to carbon dioxide and monoxide after any necessary blank corrections were made.

Table 4 shows the results obtained by the authors when using various kinds of steels. The results were intended to illustrate the effect (1) of carbon percentage, (2) weight of sample, and (3) effect, if any, of process of manufacture. The first two effects are discussed later; no distinction based on the process of manufacture is evident.

TABLE 4.—Results by Authors with Goutal's Method (Modified)

I. CONSTANT WEIGHT OF SAMPLE FOR SERIES

Sample used [a]	Weight used	CO_2	CO
	g	Per cent	Per cent
Bes. 0.8 per cent C	10	0.018	0.029
		.020	.026
Bes. 0.6 per cent C	10	.019	.029
		.016	.024
Bes. 0.4 per cent C	10	.010	.019
		.014	.019
Bes. 0.2 per cent C	10	None	.017
Bes. 0.1 per cent C	10	.004	.003

II. VARYING WEIGHT OF SAMPLE

Bes. 0.8 per cent	5	0.032	0.008
	20	None	.046
A. O. H. 0.8 per cent C	5	.039	.002
	10	.010	.014
	20	None	.037
B. O. H. 1.0 per cent C	2.5	.078	.038
	5	.044	.016
	10	.053	.010
A. O. H. 1.0 per cent C	5	.058	.016
	10	.023	.009
	20	.009	.007

[a] All are Bureau of Standards analyzed samples.

The results of this table show that the carbon monoxide and dioxide content of steels by the Goutal method vary greatly according to the weight of sample relative to the quantity of copper salt; hence such gas contents are apparent and not real. Thus in one case when 5 g samples are used over six times as much carbon dioxide is shown as is obtained from the same steel when 20 g samples are used (A. O. H. 1.0 per cent C); with this steel, the

carbon-monoxide content with 10 g samples is only about one-half as large as that of the 5 g samples. It seems very likely that the carbon dioxide is generated from action of the cupric salt on the carbides present; when 5 g of metal are used a considerable excess of cupric salt remains to act upon the carbides liberated during solution of the steel. When, however, 20 g of metal are used, no cupric salt is left and hence the oxidizing action is much less vigorous, as is shown by the lowering of the carbon-dioxide content. This is even more true when the 2.5 g samples are used. (See Table 4.) It is very doubtful whether the results in the "carbon-monoxide" column represent entirely or even approximately the amount of that gas formed by the oxidizing action of the cupric salt, since during this action there are also liberated hydrocarbons recognizable by their odor, and many of these, as is well known, are oxidized by iodine pentoxide.

Determinations of carbon monoxide and carbon dioxide were made by the Goutal method on a white iron containing about 3.7 per cent combined carbon, i. e., carbide carbon. Such an iron might be expected to give a very high percentage of "carbon monoxide" and carbon dioxide because of the large percentage of carbide present. Actually, using 10 g samples, 0.11, 0.13, 0.13 per cent carbon dioxide were found, whereas determinations of carbon dioxide by solution of the metal in dilute hydrochloric acid, employing the apparatus and in other respects the procedure used for conducting the Goutal method, showed no carbon dioxide when 2 g and 3 g samples were used.

If the cupric salt oxidizes the carbides, then the longer the time of contact the more carbon monoxide and dioxide should be formed, providing an excess of cupric salt is always present. To test this point a 5 g sample of a high-carbon steel was dissolved and the carbon dioxide and carbon monoxide determined as usual. The flask was closed to prevent access of air and allowed to stand overnight. Hydrogen was then passed with the absorbing apparatus connected and the contents of the flask boiled for an hour with the hydrogen still passing and the carbon monoxide and carbon dioxide then determined. This was repeated for four successive days. The results (corrected for blanks) are shown in Table 5 and indicate that there is a continuous oxidizing action by the cupric salt. The one-hour treatment was sufficient to expel all the carbon dioxide and carbon monoxide formed after each period of standing.

TABLE 5.—Action of Cupric Salt on Carbides as a Function of Time

Sample used (5 g)	Time of boiling	Day	CO	CO_2
			g	g
Bes. 0.8 per cent C	One hour	First	0.016	0.014
	do	Second	.012	.012
	do	Third	.004	.012
	do	Fourth	.010	.006

IV. CONCLUSIONS

From the work herein described the following conclusions may be drawn:

1. If Goutal's method is to be used for the purpose intended, various modifications should be made in the procedure as originally described with a view to eliminating errors in the methods of measuring the carbon monoxide and dioxide and for reducing or eliminating blank corrections.

2. The method does not give the true carbon-monoxide or carbon-dioxide content of steels and irons, but instead a fictitious value for these gases since they appear to be generated by action of the cupric salt on the carbides present.

3. This fictitious content of carbon monoxide and dioxide varies (*a*) with the weight of sample relative to the amount of reagent; (*b*) with the time of boiling of the solvent; and (*c*) with the carbon content of the metal.

WASHINGTON, December 26, 1918