

DETERMINATION OF CARBON IN HIGH SULPHUR STEELS BY DIRECT COMBUSTION

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ABSTRACT

Oxides of sulphur are formed in the direct combustion method for carbon in steel and cause positive errors if they are not removed. The absorbents commonly used for this purpose, as well as promising new ones, have been tested. A description is given of the absorption train that has been developed at the National Bureau of Standards as well as one that has been developed by the Jones & Laughlin Steel Co.

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I. INTRODUCTION

The method used largely at the present time for the determination of carbon in steel or iron is that of direct combustion in oxygen and absorption of the evolved carbon dioxide in soda-asbestos (ascarite) or soda lime. The increasing use of high sulphur steels ($S > 0.10$ per cent) has led to difficulties in securing accurate results for carbon, with consequent disagreements between different laboratories. This is caused by the fact that the sulphur in the steel burns to form oxides of sulphur. If these are not removed completely from the gas stream positive errors for carbon will result in the gravimetric method, and in any method in which the excess of barium hydroxide is titrated.

In the direct combustion of low sulphur plain carbon steels most of the sulphur is converted to sulphur trioxide. Some sulphur dioxide is also formed, and the amount will vary according to such factors as the rate of oxidation of the steel, the temperature, the type of furnace, and the kind of steel.¹

In the present study it was desired to develop an absorption train which could be constructed readily in the ordinary laboratory. For this reason the possibility of using special apparatus such as electrical precipitators² was not investigated. It is doubtful in any case whether the oxides of sulphur could be quantitatively precipitated by electrical precipitation under the conditions prevailing in the direct combustion method for carbon.

¹ For example, from 2 to 10 per cent of their sulphur content was given off as sulphur dioxide when 2 g samples of steels containing 0.13 to 0.22 per cent of sulphur were burned. On the other hand, nearly 50 per cent was given off as dioxidesulphur from a stainless steel containing 14 per cent of chromium and 0.43 per cent of sulphur and from a plain carbon steel containing about 0.7 per cent of sulphur. It is evident that with low sulphur plain carbon steels the chief problem is to provide for the removal of sulphur trioxide, while with high sulphur steels the removal of the dioxide is as important as that of the trioxide. In fact it may be more important, for the absorption of the dioxide by alkaline reagents is more complete than is that of the trioxide.

² F. Oschwald, Determination of C in Al, thesis, Eidgenössische Tech. Hochschule, Zürich, No. 356; 1923. H. Remy and C. Koch, Examination of Chemical Fogs for Electrical Charges, Z. anorg. allgem. Chem., 139. p. 69; 1924.

II. ABSORBENTS USED FOR REMOVING OXIDES OF SULPHUR

Asbestos.—A practice for removing oxides of sulphur that is employed by quite a few chemists³ consists in packing the exit end of the combustion tube (usually 30 inches long) with a 6 to 8 inch section of ironized asbestos.⁴ The ironized asbestos retains more or less sulphur trioxide in the cool section at the exit end and may also cause the oxidation of some sulphur dioxide to sulphur trioxide. If asbestos is used ferric sulphate will accumulate in the exit end of the combustion tube, and it is necessary, periodically, to draw the section containing the asbestos back into the hot zone of the furnace and burn out the sulphur trioxide by heating to about 900° C. while a stream of air or oxygen is passed through the tube. How often this must be done depends on the number and the sulphur content of the samples that are burned each day.⁵ If this periodic burning out is neglected high and erratic results for carbon are obtained, particularly with steels containing more than 0.1 per cent of sulphur.

It is also well to mention that sulphur trioxide which has been fixed as ferric sulphate at a low temperature will be liberated again and carried along in the exit gas stream when the temperature becomes high enough to decompose ferric sulphate. Even though no trioxide is thus liberated, some may still remain in the gas stream through failure of the ironized asbestos to retain all of it. In addition, the ironized asbestos is not an efficient oxidizer of the sulphur dioxide that is always present.

The small amount of sulphur trioxide that may pass the asbestos when steels of less than 0.2 per cent sulphur are burned will usually be retained by the solid desiccant (phosphorus pentoxide, anhydrous, of 20 to 25 mesh, etc.) interposed between the furnace and the absorption tower for carbon dioxide. If such provision is made to retain any sulphur trioxide which may pass by the asbestos and if the tube is burnt out regularly, it is believed that acceptable results for carbon in steels containing less than 0.2 per cent of sulphur can be obtained by this procedure. However, these precautions are not adequate to avoid high results for steels of higher sulphur content. For continuous runs on plain carbon steels containing more than 0.15 per cent of sulphur or on any high-sulphur stainless steels, it is probably better to omit the asbestos in the combustion tube and to absorb the oxides of sulphur after they leave the combustion tube.

Zn.—Granulated zinc of 20 to 80 mesh is used by a number of chemists for removing oxides of sulphur. Tests indicate that it acts as a baffle for condensing more or less sulphur trioxide, but does not remove sulphur dioxide. Like asbestos it has a limited value when used with low-sulphur steels ($S < 0.06$ per cent), but is not satisfactory for high-sulphur alloys.

³ Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Alloy Steels, Carnegie Steel Co., Pittsburgh, Pa., p. 9; 1921.

⁴ Prepared by digesting asbestos in a solution of ferrous sulphate (150 g of the salt in 1 liter of 1 per cent sulphuric acid), drying and igniting at 1,000° C.

⁵ W. D. Brown, chief chemist of the Carnegie Steel Co., Duquesne, Pa., informs us that they burn out combustion tubes every fifth day. About 75 determinations a day are made on a tube and approximately 10 per cent of the steels contain more than 0.10 per cent of sulphur. F. Garman, of the Pennsylvania R. R. Laboratories, Altoona, Pa., states that tubes are burned out after each 100 samples of plain carbon steels, none of which exceed 0.05 sulphur. With cast irons and screw steels a tube is burned out at least once a day.

P_2O_5 .—In this laboratory and elsewhere it has been noted that phosphorus pentoxide, because of its fine state of subdivision, will also act as a baffle and condense and retain sulphur trioxide to a certain extent. It is not effective for sulphur dioxide.

PbO_2 .—Tests made by passing a mixture of approximately 95 parts of oxygen and 5 parts of sulphur dioxide through a U tube containing specially prepared lead dioxide showed that sulphur dioxide is quantitatively absorbed. The lead dioxide was purified by digesting for several hours at $25^\circ C$. with nitric acid (1:3), filtering, washing with water, and drying at $105^\circ C$. Sulphur trioxide mist secured by passing dry oxygen through fuming sulphuric acid was also absorbed to a certain extent at $25^\circ C$. and very well at $250^\circ C$. It was found, however, that the lead dioxide absorbed small amounts of carbon dioxide at $25^\circ C$. and even at $100^\circ C$. No absorption of carbon dioxide was observed at $250^\circ C$.

The use of lead dioxide as an absorbent for oxides of sulphur was further tested by determining carbon in 2 g samples of steel to which 0.05 g portions of pyrite had been added. The exit gases from the combustion tube were passed through a 15 cm

U tube, loosely packed with lead dioxide and heated to a temperature of $250^\circ C$. The gases from this tube were passed next through a 10 cm U tube filled with anhydrous magnesium perchlorate (anhydron) and then into ascarite. Similar tests were made on 2 g samples of the

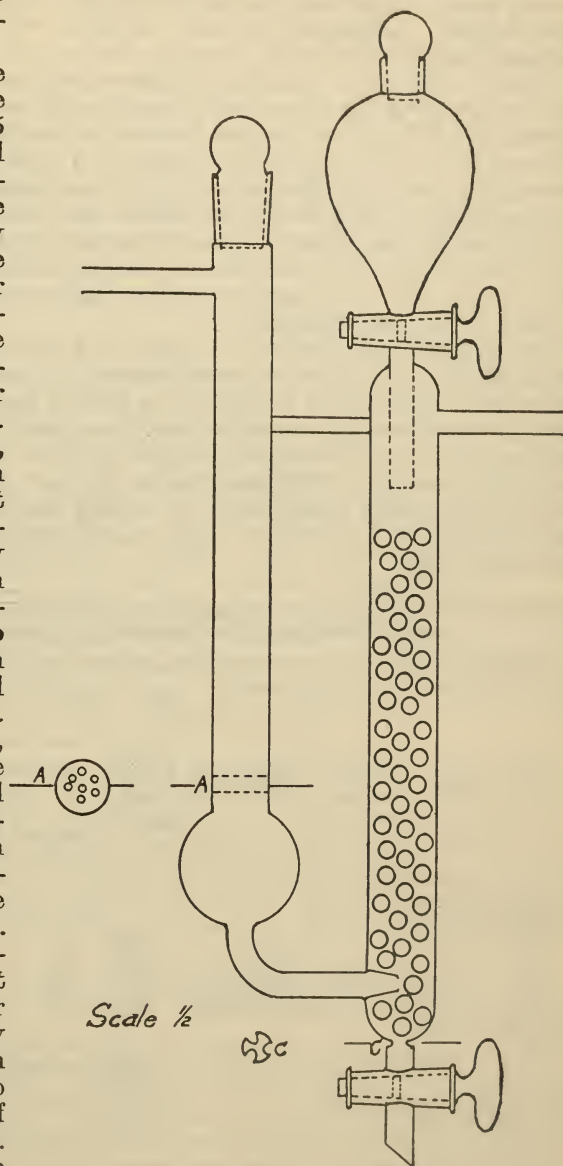


FIGURE 1.—Absorption tube

same steel to which 0.03 g portions of ferric sulphate were added. In both cases correct results for carbon were obtained.

Lead dioxide has certain disadvantages in that it requires an additional furnace and must be heated at 250° C. until a uniform blank is obtained. Moreover, it must be kept out of contact with the carbon dioxide of the air when not in use.

$H_2SO_4-H_2CrO_4$.—Arnold and Ibbotston⁶ used a dilute sulphuric acid solution (1:1) saturated with chromic acid for oxidizing and removing the sulphur dioxide formed in the burning of steels containing about 0.09 per cent sulphur. At the National Bureau of Standards an absorption tube (fig. 1) containing, in the right arm, concentrated sulphuric acid saturated with chromic acid and a 9 to 10 cm column of closely packed asbestos in the left arm has been used for the same purpose during the past 10 years. Previous tests had shown that this procedure was satisfactory for steels with less than 0.08 per cent sulphur.

Qualitative tests made by passing a mixture of dry air and sulphur dioxide, containing about 5 per cent of the latter, through the absorbent at a rate of about 200 to 250 ml per minute showed that neither concentrated nor dilute sulphuric acid (1:1) saturated with chromic acid would oxidize sulphur dioxide completely. Further tests, the results of which are given in Table 1, show that this absorbent is not entirely satisfactory for regular use with steels containing more than 0.10 per cent of sulphur and not at all for high sulphur stainless steels.

TABLE 1.—Results for carbon obtained by using concentrated sulphuric acid saturated with chromic acid as an absorbent for oxides of sulphur

[Figures in parentheses indicate the number of determinations from which the average was obtained]

Type of steel	Weight of sample	Sulphur compound added	Total sulphur present	Carbon			
				Per cent present		Per cent found	
				Average	Range of determinations	Average	Range of determinations
Bureau of Standards standard B. O. H.	g	g	g	Per cent		Per cent	
No. 11d.....	2		0.0008	0.202		0.201 (8)	0.200-0.204
Do.....	2	0.01 FeS ₂	.0058	.202		.22 (8)	.201-.26
Do.....	2	.02 FeS ₂	.0108	.232		.23 (5)	.22-.30
Do.....	2	.05 FeS ₂	.0258	.202		.43 (2)	.41-.45
Do.....	2	.01 Fe ₂ (SO ₄) ₃	.0032	.202		.208 (2)	.203-.213
Do.....	2	.03 Fe ₂ (SO ₄) ₃	.0080	.202		.214 (2)	.21-.218
Bessemer screw stock: ^b							
No. 1.....	2.73		.0036	.088 (3)	0.086-0.092	.093 (3)	.092-.093
No. 2.....	2-3		.0024- .0036	.131 (11)	.127-.138	.137 (21)	.134-.14
Plain carbon.....	2-2.73		.0044- .0060	.171 (5)	.168-.175	.182 (11)	.17-.187
High sulphur stainless steel ^d	1.5-2		.0054- .0085	.090 (16)	.084-.096	.160 (6)	.124-.196

^a Certificate value.

^b Supplied through the courtesy of H. E. Slocum, chief chemist, Jones & Laughlin, Pittsburgh, Pa.

^c Value obtained on the train adopted for high sulphur steels described on p. 948.

^d Supplied through the courtesy of P. Tyson, chief chemist, Carpenter Steel Co., Reading, Pa.

⁶ The Chemical Analysis of Steel-Works' Materials, 3d. ed., p. 35; 1907.

Aqueous solution of CrO_3 and dry chromates.—Blair⁷ used a saturated aqueous solution of chromic acid for removing sulphur dioxide. This absorbent oxidizes sulphur dioxide completely, but does not remove all of the sulphur trioxide present in the exit gas stream when high sulphur steels are burned. Tests of crystals of potassium dichromate, dry barium chromate, and lead chromate showed that these substances do not absorb sulphur dioxide completely. Wetted crystals of potassium dichromate remove sulphur dioxide but because of lower solubility do not have as great an oxidizing capacity as a saturated aqueous solution of chromic acid.

Compounds added to the sample.—It is claimed by some that sulphur is retained in the slag if the drillings are mixed and burned with red lead (Pb_3O_4) or lead chromate. It is quite unlikely that lead sulphate or lead sulphite would be stable at the high temperature ($>1,000^\circ\text{C}.$) occurring in the combustion boat.

Platinized silica gel and ironized asbestos.—For high sulphur steels H. E. Slocum⁸ uses a train in which the gases from the combustion tube are passed first over platinized silica gel heated to $440^\circ\text{C}.$ The catalyst,⁹ of 6 to 8 mesh size, is contained in a pyrex glass U tube of a size to give a column approximately 1.2 cm in diameter and 30 cm in length. A small electric furnace with a rheostat is used to heat the catalyst. The gases are next passed through a tower containing a column (approximately 4 by 13 cm) of closely packed ironized asbestos for removing sulphur trioxide, on top of which is a 4 by 5 cm layer of anhydronite for absorbing moisture. From the second tube the gases are passed to the usual carbon dioxide absorption tube.

Slocum also uses a specially designed combustion tube which is bent down at an angle of 90° at the point where it issues from the heating furnace. The exit end of the tube is tapered to facilitate connecting with the silica gel tube. It is claimed that there is less sulphuric acid condensed and collected in this form of combustion tube.

The chief function of the gel is to oxidize, catalytically, sulphur dioxide to the trioxide. A secondary function is to oxidize carbon monoxide to carbon dioxide should any have been formed in the combustion. With a properly functioning catalyst all of the sulphur that enters the tube containing the gel leaves the tube as sulphur trioxide and must afterwards be removed from the exit gases by collecting in a suitable absorbent, such as closely packed ironized asbestos.

This train has been tested by Slocum on samples of plain carbon steels to which sulphur had been added. Correct results for carbon were obtained.

It should be recognized that the efficiency of a catalyst may, and generally will, fall off in continued use. No data are available at present as to how long the platinized silica gel will function satisfactorily for this particular use. However, Slocum states that several catalysts have been in daily use in the Jones & Laughlin Co.'s laboratory for four months and have given satisfactory service. The use

⁷ A. A. Blair, *The Chemical Analysis of Iron*, 8th ed., p. 128; 1918.

⁸ *The Laboratory*, 3, No. 2, p. 24 (1930); Fisher Scientific Co., Pittsburgh, Pa.; *Burrell Bulletin* 1017, Burrell Tech. Supply Co., Pittsburgh, Pa.

⁹ Prepared according to Holmes et al., *J. Ind. Eng. Chem.*, 21, p. 850; 1929.

of red lead in the combustion boat is not recommended, since it tends to poison the catalyst.¹⁰

Tests of platinized silica gel made during this investigation indicate that it is entirely satisfactory if sufficient contact surface is provided. For example, with a 0.55 by 29 cm column of a silica gel containing 0.15 per cent of platinum¹¹ small amounts of sulphur dioxide were found in the gas stream issuing from the tube containing the catalyst when burning a 2 g sample of a stainless steel containing 0.43 per cent of sulphur, while with a 1.1 by 30 cm column of the same catalyst only negligible traces of sulphur dioxide were detected. Tests of a second catalyst of somewhat higher platinum content¹² and the smaller column referred to above showed a slight improvement over the same volume of the first catalyst, but did not show quite as complete oxidation of the sulphur dioxide as the larger volume of the first catalyst.

In using platinized silica gel it is therefore necessary to be sure that the particular lot of catalyst and the size of the column are adequate to oxidize all of the sulphur dioxide which may be present in the gases issuing from the combustion tube.

III. DESIGN OF COMBUSTION TUBE AND ABSORPTION TRAIN

As a result of the foregoing experimental work the following type of combustion tube and absorption train was developed for use in the determination of carbon in high sulphur steels. The porcelain combustion tube is about 48 cm long, of an internal diameter of 2.5 cm and is made with a rather sharply reduced diameter at the exit end. The reduced section is approximately 1 cm in outside diameter and 14 cm in length. The end of this section has a short taper to a 6 to 8 mm outside diameter. No asbestos packing is used in the tube, as with high sulphur steels less trouble is experienced from accumulations of sulphuric acid during the run. However, a short roll (3 to 4 cm) of oxidized copper gauze is placed in the 700° to 800° zone of the exit end to make sure that no carbon escapes as the monoxide. The gauze becomes coated with ferric oxide and copper sulphate and must be renewed occasionally.

The exit gases from the combustion tube are first passed through an absorption tube (fig. 1) containing about 8 to 10 ml of a 50 per cent aqueous solution of chromic acid¹³ in the right arm and a 9 to 10 cm column of closely packed asbestos, plain or ironized,¹⁴ in the left arm. All of the sulphur dioxide is removed by the chromic acid. Some, but by no means all, of the sulphur trioxide is condensed during the passage through the asbestos and the solution.¹⁵ The first tube is followed by another of identical design which contains sulphuric acid (97 per cent) in the right arm and asbestos in the left arm. This tube serves to dry the gases and to remove more of the sulphur trioxide. The water vapor which is carried over from the aqueous chromic

¹⁰ Private communication from H. E. Slocum.

¹¹ Grade 1 No. 150-G-1200-0. 15 Pt. 6 to 8 mesh, obtained from the Silica Gel Corporation, Baltimore, Md.

¹² Made by treating the 0.15 platinum catalyst with H_2PtCl_6 as per Holmes et al., loc. cit. p. 947.

¹³ A saturated solution tends to salt out and clog the tube.

¹⁴ Our experience indicates that in this particular use, there is no difference in the absorbing or condensing efficiency of plain or ironized asbestos for sulphur trioxide.

¹⁵ For the condensation of SO_3 mists see: H. Remy and Ruhland, *Z. anorg. allgem. Chem.*, **139**, p. 51; 1924; Z. agnew, *Chem.*, **39**, p. 147; 1926.

acid solution is not excessive (approx. 0.01 g per run). After passing through the second tube the gases enter a small U tube (12 cm) containing 20 to 30 mesh anhydron. This tube serves to complete the drying of the gases and also to condense sulphur trioxide mist which may have passed through the first two tubes. From this third tube the gases are passed into a Fleming tube containing ascarite and anhydron.¹⁶ The chromic acid should be renewed about every 35 runs, the sulphuric acid about every 100 runs and the anhydron should suffice for about 400 runs.

The pressure required for a gas stream of 200 to 250 ml per minute in a train of this construction is a little higher than in the ordinary train, but is not excessive and approximates about 4 cm of mercury. It is advantageous to use a mercury gage in the line as it serves to detect any leaks and also acts as a safety valve in case of a stop-up.¹⁷

TABLE 2.—Results for carbon obtained by using a purifying train consisting of an aqueous solution of CrO_3 , asbestos, 97 per cent sulphuric acid and anhydron.

[Figures in parenthesis indicate the number of determinations from which the average was obtained]

Type of steel	Weight of sample	Sulphur compound added	Total sulphur present	Carbon		
				Present	Average	Range of determinations
Bureau of Standards standard B. O. H. No. 11d.....	g 2	g	g	Per cent	Per cent	
Do.....	2	0.05 FeS_2	0.0008	¹ 0.202	0.201(12)	0.199-0.206
Do.....	2	.03 $\text{Fe}_2(\text{SO}_4)_3$	.026	.202	.201(17)	.197- .208
Do.....	2	.02 H_2SO_4	.0080	.202	.200(5)	.197- .204
Do.....	2		.0065	.202	.200(1)	

¹ Certificate value.

Results obtained for steels to which sulphur compounds had been added are given in Table 2. The data show that an absorption system containing asbestos, 50 per cent aqueous chromic acid, 97 per cent sulphuric acid and fine anhydron is entirely satisfactory for removing oxides of sulphur in any steel that is likely to be analyzed for carbon. Values for carbon that were obtained with this train on high sulphur steels are shown in Table 1.

WASHINGTON, July 16, 1930.

¹⁶ After the completion of the experiments incident to the adoption of the absorption system just described it was learned that P. Tyson, chief chemist of the Carpenter Steel Co., Reading, Pa., is also using a train consisting of 50 per cent aqueous chromic acid for removing sulphur dioxide, followed by sulphuric acid (98 per cent) and phosphorus pentoxide for removing sulphur trioxide and moisture.

¹⁷ No trouble from leaks has been experienced by us. If desired the special tubes can be sealed together and a small tower substituted for the U tube.