

be checked by running a government standard.¹ A fresh bulb may show slightly low results on the first three analyses. When filled with ascarite, one bulb will absorb from 10 to 15 g. of carbon dioxide without refilling.

3. DETERMINATION OF CARBON BY THE CORLEIS METHOD²

Principle.—Iron and steel samples of suitable fineness are dissolved by boiling with a mixture of chromic and sulfuric acids, which causes the oxidation of nearly all the carbon to carbon dioxide. A little of the carbon is usually set free as carbon monoxide or as hydrocarbon unless certain precautions are taken. Corleis found that the formation of such carbon compounds is greatly reduced by the addition of copper sulfate solution, but it is always best to heat the gases mixed with air in order to be certain that all the carbon is in the form of carbon dioxide. The carbon dioxide formed is absorbed by soda-lime contained in a U-tube or by caustic potash solution in a Geissler bulb. From the gain in weight, the amount of carbon in the sample is calculated.

Apparatus and Necessary Solutions.—For combustion with chrome-sulfuric acid, the Corleis flask *K* with condenser is used (Fig. 7). There is a ground-glass connection between the condenser and the flask.

To keep the flask from breaking when it is heated, either support it on wire gauze or cover the bottom with asbestos paper as shown in Fig. 8. In the latter case, cut out suitably shaped pieces of asbestos paper (about 0.5 mm. thick), wet them with water, stick them to the bottom of the flask, and allow them to dry a little while in a drying closet at 110°.

The arrangement of the entire apparatus is shown in Fig. 8. Air is passed through the apparatus either by applying suction

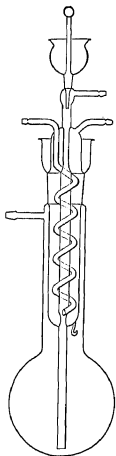


FIG. 7.

¹ Carefully analyzed samples of various kinds of steel can be obtained from the Bureau of Standards at Washington, D. C.

² *Stahl u. Eisen*, 14, 381 (1894).

at W or from a gasometer leading to W_1 . To purify the air, place concentrated caustic potash solution (1:1) in the wash bottles W_1 and W_2 and soda-lime in the U-tube, U . Instead of these three tubes, a single soda-lime tower, with concentrated caustic potash solution at the bottom may be used.¹

The gases from the combustion flask pass first through a small wash bottle, S , containing concentrated sulfuric acid. The glass tubing through which the gas enters should not dip into the sulfuric acid, but should end a few millimeters above the surface of the liquid. This flask has the function of holding back water vapor and sulfuric acid fumes from the boiling solution, without any danger of retaining appreciable quantities of the hydrocarbons in the sulfuric acid.

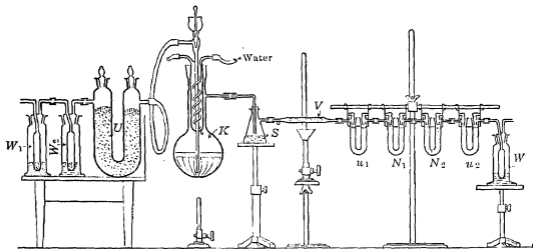


FIG. 8.

To S , attach a small combustion tube, V , made of difficultly fusible glass or of porcelain and containing copper oxide or platinized asbestos.²

If a glass tube is used, wrap it in iron gauze to prevent it from breaking when heated. The purpose of this combustion tube is to convert traces of carbon monoxide, or of hydrocarbons, into carbon dioxide.

The use of copper sulfate in the oxidizing liquid, however,

¹ cf. TREADWELL-HALL, "Text-book of Analytical Chemistry," Vol. II.

² The platinum capillary combustion tubes so frequently recommended have not given satisfaction; on continued use the platinum crystallizes

prevents the loss of more than 2 per cent of the total amount of carbon present in any sample of ordinary iron or steel. In commercial work, therefore, this combustion tube may be omitted. Moreover, results obtained in test analyses with pure sodium oxalate show that the tendency of the method is to give results that are slightly high, which is another reason why this combustion tube may be omitted. In that case, connect the flask *K* directly with a small tube containing solid chromic-acid anhydride, between plugs of glass wool, and from this lead the gas into a U-tube containing a few glass beads wet with concentrated sulfuric acid. Place a little glass wool in each arm of this U-tube to break up any bubbles of sulfuric acid that may form during the analysis. Then, with the omission of *S* and of *V*, the arrangement is the same as shown in the drawing.

The last traces of moisture must be removed from the gases before the carbon dioxide is absorbed. This is accomplished by means of the small U-tube, *u*₁, containing calcium chloride or phosphorus pentoxide between plugs of cotton wool.

From this drying tube, the gases pass into the weighed soda-lime tubes *N*₁ and *N*₂, in which the carbon dioxide is absorbed. Usually all of the carbon dioxide is absorbed in the first tube. If the second tube begins to gain in weight, it is a sign that the first tube is nearly exhausted. When this happens, refill the first tube and then use it as the second tube in the train.

When carbon dioxide reacts with soda-lime, water is set free. To prevent the loss of this moisture, each tube must contain a little calcium chloride or phosphorus pentoxide. Fill the arm through which the gas enters with small pieces of soda-lime and fill half of the other arm with soda-lime. Then cover the soda-lime with a small piece of glass wool and fill up the tube with dry calcium chloride (or phosphorus pentoxide). In the top of each arm of the U-tube, place a plug of cotton wool. The kernels of soda-lime and of drying agent should be from 1 to 1.5 mm. in diameter; if much powder is present, it must be sifted out to avoid stopping up the tube. Too large lumps of either soda-lime or drying agent must not be used and the tubes must be filled tightly, or some gas may escape that should be absorbed.

As an added precaution, the second soda-lime tube is connected

with a calcium chloride (or phosphorus pentoxide tube) u_2 and this in turn is connected with a safety wash bottle, W , containing concentrated caustic potash solution; there is then no chance of water vapor or carbon dioxide being drawn back into the weighed tubes from the atmosphere. The wash bottle, W , also serves to indicate the rate at which the gas is passing through the apparatus.

Connections between the different parts of the apparatus are made by rubber tubing. In setting up the apparatus, take care that all the connections to the right of the Corleis flask are tight (glass on glass); in no case should the ends of the glass tubing be separated by empty sections of rubber tubing.

The following solutions are necessary:

(a) *Chromic Acid Solution*.—Dissolve 720 g. of chromic acid anhydride, which need not be chemically pure but should be practically free from organic matter, in 700 c.c. of water.

(b) *Copper Sulfate Solution*.—Dissolve 400 g. of copper sulfate crystals in water and dilute the solution to 2 liters.

Preliminary Boiling of the Chrome-sulfuric Acid Solution.—Remove the condenser from the flask K , and introduce 35 c.c. of the chromic-acid solution (a), 150 c.c. of the copper sulfate solution (b) and 200 c.c. of concentrated sulfuric acid (d. 1.84).

Replace the condenser and start a stream of water running through it. Boil the mixture in the flask to remove any organic matter which may be present, with the soda-lime tubes disconnected from the flask. While the solution is boiling, pass a slow stream of purified air through the apparatus and heat the small combustion tube V . Boil the solution for at least an hour in order to be sure that in subsequent work no carbon dioxide, or other gases absorbed by soda-lime, will be generated from carbon in the reagents. Then remove the flame and allow the apparatus to cool in a current of air.

Before starting an analysis it is advisable to run a blank on the apparatus, to find out how much the soda-lime tubes change in weight without the introduction of any substance to be analyzed.

Blank Run.—Rub the soda-lime tubes with a piece of chamois or a clean linen cloth, allow them to stand in the balance case for at least half an hour, then open the stopcocks for an instant to

Connect the weighed tubes to the rest of the train, open the stopcocks and pass a slow stream of air free from carbon dioxide through the apparatus. Boil the contents of the Corleis flask and heat the combustion tube for 2 or 3 hr. (the usual length of time for a combustion). Then remove the soda-lime tubes, close the stopcocks and place the tubes in the balance case. Remove the flame from beneath the Corleis flask and weigh the tubes, under the same conditions as before, after they have remained at least $\frac{1}{2}$ hr. in the balance case.

If much more than 0.001 g. gain in weight is found in the blank determination, something is wrong. Besides possible impurities in the chromic acid, it may be that small particles of soda-lime or of drying agent have lodged in the glass tubing beyond the stopcocks, either due to a too rapid passage of the air current or to faulty filling of the tubes. In such a case the tubes would gain in weight constantly if left in the air, owing to absorption of carbon dioxide or of water. Care should be taken, therefore, to see that the tubing is free from soda-lime or drying agent. If necessary, the inside of the tubes may be wiped clean with small rolls of filter paper.

Slight gains in weight in the absorption tubes, which are almost always observed in the blank, should be allowed for in the determination.

Procedure.—While the acid solution in the flask is cooling, weigh the soda-lime tubes as previously described and also the sample of iron or steel, the carbon content of which is to be determined.

The weight of sample taken for analysis should be determined by its probable carbon content. Of cast iron, with 3 per cent or more of carbon, take 1 g.; of steel with 0.3 per cent or more take 3 g.; and of mild steel or wrought iron take 5 g.¹ Weigh the

¹ In weighing out samples it is a waste of time to weigh accurately to decimal places beyond those which affect the analysis. In the determination of carbon in steel, the absolute accuracy is determined largely by the degree of accuracy to which the soda-lime tubes, used for absorbing the carbon dioxide, can be weighed. Unless particular precautions are taken, such as reducing the weighings to vacuum, etc., the difference between the weights of the soda-lime tubes before and after the analysis cannot be assumed to be nearer than 0.001 g. to the truth. As a general rule, the next to the last significant figure in any value should not vary by more than one or

sample into a porcelain crucible, a glass-stoppered weighing tube, or, if it can be obtained in powder form (*e.g.*, gray cast iron), into a small glass basket which can be suspended, by means of fine platinum wire, from the hook which is usually provided on the end of the condenser, so that the sample is immersed in the liquid in the flask.¹ After the chrome-sulfuric acid solution has cooled sufficiently, connect the soda-lime tubes with the apparatus and pour a little sulfuric acid into the funnel at the top of the condenser to act as a seal; then test the entire apparatus to see if it is tight. To do this, close all the stopcocks in the absorption train and open the cock at the air supply to the Corleis flask. After a short time no more bubbles should pass through the Corleis flask. If bubbles do form, a leak is indicated between the Corleis flask and the calcium chloride tube u_1 . When this section is found to be tight, open the first stopcock in the calcium chloride (or phosphorus pentoxide) tube; if after waiting a short time the current of air through the Corleis flask again stops, open

two units. According to this rule, therefore, the soda-lime tubes should be weighed as carefully as possible to four decimal places, which is possible with the usual analytical balance. In the case of a sample of steel with 1 per cent carbon, a 3-g. sample will yield 0.110 g. of carbon dioxide and an error of 0.001 g. in this weight will correspond to 0.01 per cent carbon, or to one-hundredth of the entire carbon content. This precision is satisfactory here. An error of 0.03 g. in the original weight would correspond to the same fractional error. If, therefore, the original sample is weighed to the nearest centigram, any error introduced by neglecting the following decimal places will not have an appreciable effect upon the final result and any balance accurate to 0.01 g. can be used for weighing out the sample. It is not only a waste of time, but unscientific in principle, to determine values smaller than those which have a noticeable effect upon the result.

In weighing out smaller samples it is usually necessary to weigh more accurately but with cast iron the sample is rarely perfectly homogeneous so that in carbon determinations even with a 1-g. sample, it is sufficient if the original weighing is accurate to 0.01 g.

¹ For obtaining representative samples and for the method of weighing small samples for analysis the precautions mentioned in Part II of the book should be taken.

The shavings for the combustion with chrome-sulfuric acid treatment should not be more than 1 mm. thick if the combustion is to be finished in 2 or 3 hr. Thicker pieces should be hammered, broken or rolled before cutting. Hard-drawn wire or high-silicon tungsten steel often requires 3 or 4 hr. for combustion even if it is finely divided.

the next stopcock and so on up to the last stopcock on the final calcium chloride tube u_2 . After the apparatus has been shown to be tight¹ and the air supply has been shut off, slowly open the last stopcock so that the excess of air will escape from the apparatus without rushing. A sudden rush of air might carry calcium chloride (or phosphorus pentoxide) dust either into or out of the weighed tubes, in each case causing a change in weight.

When the excess of air has escaped, remove the condenser and pour the weighed sample into the flask, or, if the sample has been weighed into a small glass basket, hang this on the hook. Replace the condenser at once and pour a little strong sulfuric acid over the connection between the condenser and the flask to make a tight joint. Raise the condenser again, just a trifle, so that a little of the sulfuric acid can run into the flask to wash down any particles of the sample which may have stuck to the glass.

Now light the gas under the combustion tube V and cause a slow stream of air, free from carbon dioxide, to pass slowly through the apparatus. Heat the Corleis flask, slowly at first, until the acid boils.²

Continue the boiling for about 3 hr., which is usually long enough to insure the complete solution and oxidation of the sample, unless it was in too coarse a condition. During this time the apparatus should be watched to see that the acid does not boil too violently, and that the air is run at the proper rate, not more than three bubbles a second. At the start if the contents of the flask are heated too quickly, particularly just before the solution boils, there is some danger of liquid sucking back toward the purification train. This is prevented by lowering the flame and increasing the speed of the air current. If, by accident, some of the liquid gets back into the tube U , the determination is

¹ If, instead of using an air reservoir in the experiment, suction is applied at the other end of the train, the manner of testing for leaks is the reverse. Gentle suction should be used in making the test and care should be taken not to let the air in too rapidly after the test.

² The current of air must be started as soon as the sample has been introduced. As the cold chromic-acid mixture has slight oxidizing power it is possible for small amounts of hydrogen and hydrocarbons to form. If these gases are not diluted and removed by the air current, they form mixtures with the air in the apparatus which, at certain concentrations of hydrogen and hydrocarbon, may explode in the combustion tube.

spoiled. During the last 15 min. of the boiling, it is well to increase the rate at which the air is passing so that it will drive over the last traces of carbon dioxide into the absorption train.

When the combustion is complete, stop the current of air and turn out the gas flames. Close the stopcocks of all the U-tubes that are in front of the flask and remove the soda-lime tubes. Allow these tubes to stand in the balance case for at least $\frac{1}{2}$ hr. and weigh them with the usual precautions.

When the contents of the Corleis flask have cooled, remove the condenser and observe carefully whether there is any undissolved sample in the bottom of the flask. In case of doubt, this can be seen easily by pouring the contents of the flask into a large beaker containing considerable water. In most cases this is unnecessary and the solution may be used again for another determination. The quantities of reagents used are sufficient for the combustion of at least 10 g. of steel.

If some undissolved material should be noticed in the bottom of the flask, it is necessary on repeating the experiment to use finer material or to continue the boiling for a longer period. In no case, however, is it permissible to sift a sample of cast iron because the fine powder is likely to contain more graphite than the larger particles. Some kinds of iron alloys will not dissolve in the acid; the carbon in such alloys should not be determined by this method.

Computation.—If p represents the gain in weight of the soda-lime tube (or tubes) in the analysis of a sample weighing s g., then

$$\text{Per cent C} = \frac{27.3 \times p}{s}$$

ACCURACY OF THE VALUES FOUND BY THE CHROME-SULFURIC ACID METHOD

Allowing for differences in the composition of the samples, as discussed in Part II of this book, the errors which may occur in the chrome-sulfuric acid method are traceable chiefly to errors in weighing and to the gain in weight of the soda-lime tube from some source other than the carbon in the sample.

Assuming that the errors of weighing are not greater than

of 0.002 g. too high the total error in a properly conducted analysis probably lies between +0.001 to +0.003 g. carbon dioxide.

The error in all cases would be found in the second decimal place of the calculated percentage and would be, for example, between 0.01 and 0.03 per cent with a 3-g. sample or between 0.005 and 0.02 per cent with a 5-g. sample.

It follows from this that the carbon content is uncertain in the second decimal and it is sometimes customary, for this reason, to write the second figure small.

The use of a third decimal, except in such cases where very unusual precautions have been taken, is not only unnecessary but also shows that the analyst is ignorant of the probable error of the method.

If the carbon determination is carefully carried out, the following values may be taken as permissible variations in the analysis of samples weighing about 3 g.

With a carbon content		Greatest allowable deviation
from	to	
0.02	0.15 per cent	± 0.005 per cent
0.15	1.00 per cent	± 0.010 per cent
1.00	2.00 per cent	± 0.020 per cent
2.00 and higher	per cent	± 0.030 per cent

Greater accuracy, as for example, that given by Bischoff¹ for low carbon material, can scarcely be attained.

APPLICABILITY OF THE CHROME-SULFURIC ACID PROCESS

The chrome-sulfuric acid method is suitable for all sorts of irons, steels and special steels as well as for numerous other metals and alloys used in the steel industry. The following substances can be decomposed without leaving a residue; ferro-manganese, chrome-manganese, ferro-vanadium, ferro-molybdenum, ferro-titanium, manganese-titanium, ferro-boron, metallic nickel and metallic molybdenum in the form of fine powder. The method cannot be used for the following materials which are scarcely attacked after 4 hr. treatment; ferro-silicon, ferro-tungsten, metallic tungsten, ferro-phosphorus, ferro-chromium, and metallic molybdenum either as wire or as sheet.

¹ *Stahl u. Eisen*, **22**, 727.