III. CONSTANT VOLUME.

	$Bi(NO_3)_3$. cc.	$H_2O(+H\overline{A})$. cc.	$K_3Co(CN)_6$. cc.
1	5	5	15
2	3	12	10
3	1	19	5
4	1	21	3

In 1, 2, and 3 the ratio of $K_3Co(CN)_6$ to $Bi(NO_3)_3$ increases with the dilution. Filtrate from 3 contained 10 per cent. of the bismuth; filtrate from 4 contained 57 per cent. of the bismuth. In 1 and 2, the filtrates showed a trace of bismuth with $(NH_4)_2S$, greater in 2 than in 1, showing that the completeness of the precipitation increases with the concentration.

A RAPID METHOD FOR THE DETERMINATION OF CARBON IN IRON OR STEEL BY COMBUSTION.

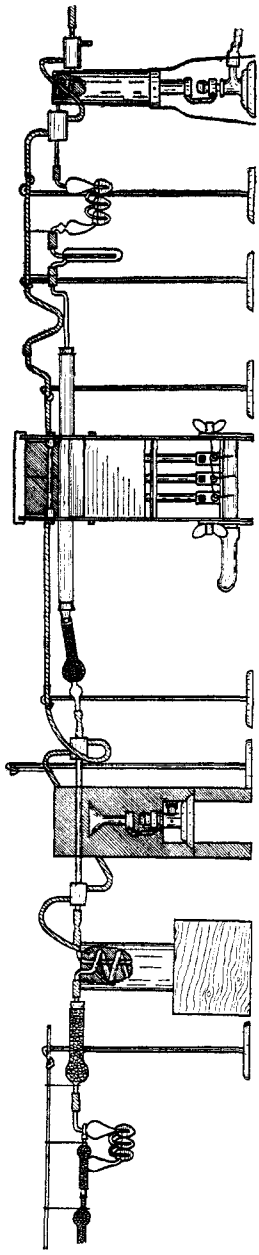
BY GEO. WM. SARGENT.

Received April 5, 1900.

THE part taken by the carbon in determining the utility of steel or iron, especially the effect of slight changes in the quantity, impresses one with the need of exercising the greatest care that its estimation may be accurately made, and yet the large number of determinations required in a limited time calls for greater speed in their accomplishment.

The color method of Eggertz is probably the most rapid, but its application is so limited that it is scarcely used outside of regular furnace work where straight steels only are encountered, and the steel has undergone the same treatment, consequently the carbon is present in always the same condition. The advent of alloys of nickel, chromium, tungsten, molybdenum, titanium, etc., with iron, forces even the furnace chemist back to the most reliable method,—that of the combustion, in oxygen, of the carbon residue from the solution of the drillings. During the past three months the results obtained in this laboratory, by this method somewhat modified, have been so eminently gratifying with regard to accuracy, rapidity, and simplicity of the apparatus used, that I believe it worthy the attention of other chemists.

The apparatus as shown by the accompanying cut consists of, beginning on the right, a small copper or platinum spiral, water-jacketed at each end to prevent the burning of the rubber con-



nections, and suspended in a copper cylinder over a burner; a Geissler potash bulb, followed by an empty "safety" tube, then the porcelain tube resting in a three-burner combustion furnace; a glass tube filled with coarse, wet sand; a copper tube filled with copper oxide and also water-jacketed at each end; a tin can containing a copper worm; then a 6-inch calcium chloride tube; the weighed potash bulb and its calcium chloride tube; and finally the guard.

It will be best to describe in detail each portion of the apparatus and its function.

The spiral is made from a platinum tube 17 inches long and $\frac{5}{32}$ inch in diameter. This gives four close coils $\frac{3}{4}$ inch in diameter and leaves 4 inches extend on either side. The water-jackets are two pieces of $\frac{1}{2}$ inch copper tubing $1\frac{1}{2}$ inches long, closed at the ends by rivet burrs, carefully soldered and containing an outlet and an inlet, the outlet of the one being connected to the inlet of the other by a $\frac{1}{4}$ inch copper tube bent around the support. The latter is a $1\frac{1}{2}$ inch copper tube with $\frac{1}{16}$ inch walls, 6 inches long, resting on three legs sufficiently long to bring the spiral the proper distance from the burner. A two-way cock leads the oxygen or air from the tanks to the spiral where any hydrocarbons are burned. The resulting carbon dioxide is caught in the Geissler potash bulb to which the spiral is connected by rubber tubing, thence the purified oxygen or air passes through the empty tube which is used to catch any potassium hydroxide from the Geissler bulb, into the combustion tube. Both the potash

bulb and the "safety" are suspended from the small copper pipe conveying the water from the outlet of the second water-jacket to the first jacket on the copper oxide tube. The combustion tube is a $\frac{5}{8}$ inch glazed porcelain tube 16 inches long, 5 inches of which extend on either side of the combustion furnace. The curved piece of fire-brick protects the tube from direct contact with the flames of the furnace. The latter is 5 inches long, having but 3 burners and was made from an old 10-burner furnace. To prevent the boat holding the carbon from being pushed into the combustion tube beyond the heated portion, a piece of clay pipe stem is placed at one end. The gases from the combustion tube pass through the coarse, wet sand loosely packed in a $\frac{1}{2}$ inch glass tube 6 inches long and held in place by two small disks of copper gauze placed at either end. This moist sand and the copper disks effectually hold any hydrochloric acid or chlorine that the gases may contain. The copper oxide tube is a straight piece of copper $\frac{3}{8}$ inch in diameter, 1 foot long, water-jacketed at each end, the water flowing from the outlet of the first jacket to the second, and thence into the tin can containing the worm. The copper oxide tube rests on a support of sheet tin, bent as shown in the cut, and slit at each side and at the bottom of the back, the two side openings supporting the copper tube, while the one in the back allows the gas pipe to enter to the burner, which has a spreader so that the copper oxide is heated for a distance of at least 3 inches. The worm consists of 3 very loose coils of $\frac{1}{4}$ inch copper tubing. A piece of tube about 20 inches long will make about the right size worm. From the cooler, the gases are dried by passing through 6 inches of thoroughly dehydrated calcium chloride. They then enter the weighed potash bulb and its calcium chloride tube, which are in one piece. These bulbs are extra large at the part holding the potash solution, being 1 inch long and $\frac{3}{4}$ inch wide, weighing, when filled for use, about 75 grams, and holding 30 cc. caustic potash solution. They, therefore, allow the gases to come in contact with more of the solution for a longer time.[1] The guard tube is the usual calcium chloride tube.

It is absolutely essential that all the calcium chloride used should be thoroughly dehydrated, that none of the fine powder

[1] These bulbs were made to order by Queen & Co., Philadelphia.

be placed in the tubes, particularly that one attached to the weighed potash bulb, and that as little of the space within the tubes as is possible be taken up with cotton, which does no good as an absorbent. It is best to sift out the fine powder from the dehydrated calcium chloride and take that which is about $\frac{3}{16}$ inch diameter, or the size of a dried pea.

The apparatus being ready, the combustion is proceeded with as follows:

A stream of water is started through the water-jackets, the burners under the spiral and copper oxide lighted, also the 3 burners of the furnace, which are regulated so the tips of the flames just touch the curved fire-brick upon which the porcelain tube rests. After ten minutes the burners may be turned on sufficiently far to bring that part of the tube within the furnace to a red heat and hold it there. The water overflowing from the can should be about 15° C. The weighed potash bulb having been connected, a current of air is started through the apparatus at the rate of about 5 bubbles per second in the weighed bulb (this is a little faster than one can count), the stopper at the forward end of the combustion tube is withdrawn and, as quickly as possible, the platinum boat containing the carbon residue obtained by the standard method of solution of steel, is pushed into the tube until it meets the pipe stem, and the stopper immediately replaced. The air is then turned off and replaced by a current of oxygen at a slightly slower rate of speed, about $4\frac{1}{2}$ bubbles per second. At the expiration of ten minutes the oxygen is turned off and the air on at the former speed for ten minutes. The connections are then broken, a new weighed potash bulb placed in the train; a fresh boat containing the carbon is inserted after removing the first one and a new combustion proceeded with. The boats should be taken from the oven, which is kept at 100° C., and at once put into the porcelain tube in order to prevent a cold boat cracking the tube.

The copper oxide is always kept at a red heat, as is also the combustion tube, as long as the apparatus is in use, from the beginning of the day's work until its completion.

A combustion is thus made in twenty minutes, and one man, with two of these pieces of apparatus side by side so arranged that when the oxygen or air is turned from one it goes on to the

other, and six potash bulbs, can make 48 combustions per day of nine hours.

After each day's work it is necessary to wash the sand in the tube by running a stream of water through it; remove any moist calcium chloride from the tube next the cooler and replace it with fresh or, better still, put in an entirely new tube full of freshly dehydrated calcium chloride and dry the moist one to have it ready for use the day following. The worm also should be dried out about every two days by placing it over a burner and blowing air through it.

In our practice we have found that about 25 combustions can be made on each bulb before it will need refilling with calcium chloride and caustic potash solution. If more than this number be run on a bulb it will be found that the calcium chloride has ceased to catch all the moisture carried from the potash solution. The latter has a specific gravity of 1.27 and is capable of absorbing 2.5 grams of carbon dioxide with perfect safety.

I append some of the results obtained by the above method of combustion and by combustion in a platinum tube.

Sample. No	Combustions in a platinum tube. Per cent. carbon.	Combustions in a porcelain tube by new method. Per cent. carbon.
16	0.836	0.832
17	0.850	0.860
17	....	0.864
17	....	0.864
1238 B C 389	0.563	0.566
1238 B C 389	....	0.552
1580	1.111	1.108
1099 C	1.087	1.075
1099 C	1.073	....
1078 C 291	1.162	1.168
1078 C 291	....	1.164
1060 C 283	0.326	0.323
R. J.	0.958	0.958
R. J.	0.955	0.953
R. J.	0.953	0.955
J.	1.067	1.068[1]
J.	1.070	....
B	0.904	0.900[1]

[1] These results were obtained when exhibiting the apparatus before the Philadelphia Section of the American Chemical Society; the carbon content of the steel was unknown to me at that time. The results obtained by combustion in a platinum tube are those of R. Job, chemist of the Philadelphia and Reading Railway Co., also of A. A. Blair.

Some duplicate results obtained by combustion in a porcelain tube by the new method are:

Sample No.	Carbon Per cent.
1	0.839
1	0.839
5	0.838
5	0.832
8	0.776
8	0.779
9	0.850
9	0.855
11	0.843
11	0.842
14	0.848
14	0.853
713	1.012
713	1.019
B X	1.608
B X	1.614

The condenser or worm cools the gases so that when they reach the weighed potash bulb, there is no tendency to carry out moisture while running the bubbles at the speed of five per second. In fact, blanks have shown that the gases can pass through the potash bulb at a speed so great that the bubbles are scarcely to be distinguished and no loss in weight will be sustained.

	Gain or loss in weight of bulb.	Number of bubbles per second.
Blank	0.0000	5
"	0.0000	5+
"	+0.0003	steady stream

Two weighed potash bulbs placed one after the other and a combustion of a high carbon steel made with the oxygen running five bubbles per second and the air a trifle faster, gave the following:

Sample No.		Before. Grams.	After. Grams.	Difference. Grams.
1905 B X 347	Weight of 1st bulb	17.4991	17.5920	0.0929
1905 B H 347	" of 2nd "	23.0177	23.01755	0.00015

A factor weight, 2.7272 grams, of the drillings was taken.

The porcelain tube may be replaced with a copper tube 16 inches long, $\frac{5}{8}$ inch in diameter, and $\frac{1}{16}$ inch walls, water-jacketed at each end for $1\frac{1}{2}$ inches, as these results show:

Sample.	Combustion in a porcelain tube. Per cent. carbon.	Combustion in a copper tube. Per cent. carbon.
Standard No. 1	0.529	0.529
" " 1	0.529[1]	0.527
" " 2	0.544	0.545

The copper tube, however, burns out in about two weeks, while the porcelain tube, with proper care, will last for weeks, especially if at the heated portion, the boat be kept from direct contact with the tube by a sheet of platinum foil.[1]

The life of the copper oxide tube is about three months. When it is burned out, however, it is quickly replaced, by another, the water-jackets being easily melted from the old tube and soldered on the new.

The whole apparatus can be made in any laboratory at a very small cost.

Mr. Job, who now has this apparatus in use in the laboratory of the Philadelphia and Reading Railway Co., has obtained very good results, a few of which he kindly gave me.

	Combustion in porcelain tube.	
	Old method. Per cent. carbon.	New method. Per cent. carbon.
Standard No. 1	1.070	1.068
" " 3	0.937	0.937–0.942
" " 2	0.527	0.531
Blank	....	0.0000
"	....	0.0000

It may be stated that in almost every instance where blanks have been made, the difference in weight of the potash bulb has been zero. This is due, I believe, to the cooler, which permits the gases to pass into the potash bulb at the same temperature, or a slightly lower one, at which it leaves it; consequently the gas is saturated with moisture to the same degree. For this reason, I believe the accuracy of the determinations even exceeds the results obtained by the old method where a dry train is used.

Many of the results that have been given, that is, those coming from this laboratory, have been made in the course of our everyday work by a man turning out a result every ten minutes from two of these pieces of apparatus, and they certainly show that,

[1] Old method combustion in platinum tube.

[2] Since the foregoing was written, Mr. Job has informed me that he has obtained excellent results by using a hard glass tube protected from the flames by a piece of iron, and supporting the boat within the tube in a sheet of platinum foil.

even at this rapid rate, the accuracy attained equals that of the more slow and painstaking method of combustion in a platinum tube.

It may be of interest to know that the copper oxide may be replaced by the electric spark as an oxidant to insure the complete change of the carbon to carbon dioxide. The action of the electric spark on a mixture of carbon monoxide and air, in the presence of moisture, is to produce carbon dioxide, ozone, and a very small amount of nitric acid; therefore, I removed the copper oxide from the system and placed in its stead a small glass tube through which two platinum wires were fused so that a spark would be produced between the points when a current from a Rhumkorff coil passed through the wires. Combustions were then made as usual, except that during the time of burning in oxygen, a continuous stream of sparks played between the platinum wires within the tube. The following table shows the results obtained:

Sample. No.	Method.	Weight of carbon dioxide. Grams.	Carbon. Per cent.
1.30 Standard	Electric spark as oxidant	0.1303	1.303
1257 B D	" " " "	0.0720	0.720
1257 B D	No oxidant	0.0614	0.614
1257 B D	CuO as oxidant—combustion in platinum tube	0.0724	0.724
1254 B D	ditto	0.0747	0.747
1254 B D	Electric spark as oxidant	0.0744	0.744
Pig iron	" " " "	0.4193	4.193
Pig iron	CuO as oxidant—combustion in platinum tube	0.2060	4.120*

Starch paper moistened with potassium iodide and placed just before the weighed absorption bulb was turned blue, showing the presence of ozone.

Owing to the platinum contacts of the induction coil becoming worn away with continued use and the consequent stoppage of the sparks, thus creating error, the hot copper oxide is preferred as an oxidant. Could, however, the trouble with the induction coil be simply remedied, the apparatus without the copper oxide would be the neatest, cleanest, and most compact to use.

Mr. John K. Faust has made most of the determinations in-

*In every case except that marked with an asterisk, where a half factor weight was taken, a whole factor weight, 2.7272 grams, was taken.

volved in perfecting this method of carbon combustions, and its success is largely due to his careful work, for which I sincerely thank him. I also wish to thank Mr. F. Cooper Pullman for his assistance in working up the electric spark as an oxidant.

LABORATORY OF THE CARPENTER STEEL CO., READING, PA.

SOIL HUMUS. SOME SOURCES OF ERROR IN ANALYTICAL METHODS.

BY A. L. EMERY.

Received April 21, 1900.

DURING the past four years we have devoted considerable time in our laboratory to the analysis of California and Hawaiian soils for the purpose of determining the kind of fertilizer best adapted for each separate piece or tract of land. The analytical methods of Dr. E. W. Hilgard have been generally followed in our work and good results have been secured with the exception of the determination of humus and nitrogen in the humus. In order for a method to be practical for industrial work it must be rapid as well as accurate. Time is a very important factor. Many samples of soils require several days' leaching to free them of calcium salts and several days more for the extraction of the humus.

About two years ago while working with one of these slowly leaching soils it was observed that the caustic potash solution of humus was strongly ammoniacal. A slightly ammoniacal solution is, of course, unavoidable, for caustic alkalies will liberate the ammonia present in the form of ammonium salts and also readily decompose some of the weaker compounds of amid nitrogen. But where the time of leaching extended over several days more ammonia was apparently liberated, than was originally present in the form of these easily decomposed salts. Other work prevented further investigation at that time, and the subject was not taken up again until this winter when the rush of soil samples to the laboratory almost compelled experimenting with humus with a view of finding a more rapid method. During these experiments some interesting results developed.

Several samples of soil, washed free of calcium salts with dilute hydrochloric acid, were leached with a 4 per cent. solution of caustic potash. In the course of a few hours, varying with the