

The saving effected by reusing the copper potassium chloride solution is no inconsiderable amount, especially where much of the salt is used. Roughly estimating, 1 pound of black oxide of manganese, and 1.5 pounds of hydrochloric acid, are sufficient to reconvert 3 quarts of the double chloride, worth about \$1.00.

LABORATORY OF THE CARPENTER STEEL CO.,
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ON THE DETERMINATION OF CARBON AND HYDROGEN BY COMBUSTION IN OXYGEN USING COPPER OXIDE.¹

BY CHARLES F. MABERY AND WILLIAM R. CLYMER.

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IN a former paper² on combustion with copper oxide it was stated that some experiments were in progress to determine the conditions of efficiency, and limits of accuracy when applied to the analysis of oils containing only carbon and hydrogen.

In the long and tedious experience in the analysis of the great number of hydrocarbons that have been under examination in this laboratory, there have been ample opportunities to observe the working details in the hands of a large number of operators who have served at different times as assistants.

The difficulties in the way of securing results with oils containing only carbon and hydrogen, that will calculate closely to 100 per cent., are much greater than with substances containing smaller proportions of these elements, and require great skill and patience on the part of the operator.

Our experience shows that copper oxide is reliable after it has been brought to a constant condition by blank trials. The gases that are evolved in the combustion of some of the hydrocarbons require the highest temperature in presence of oxygen that can be brought to bear, without too great strain on the combustion tube.

The first essential is a drying apparatus that will remove water and carbon dioxide from air and oxygen, and remain in good condition without too frequent renewal. The apparatus now in

¹ The work described in this paper formed the subject of a thesis by Mr. Clymer for the Degree of Bachelor of Science.

² This Journal, 20, 510.

use in this laboratory which does not need renewal oftener than once in a year or two, consists of two pieces of combustion tubing 1.75 meters long, with a bend 30 cm. from one end, with an angle of about 105° , and placed on the wall in front of the combustion furnaces. One of these tubes for air and another for oxygen are nearly filled with broken glass and concentrated sulphuric acid. A second set of tubes are filled to the same extent with glass and a 40 per cent. solution of potassium hydroxide, one for air and another for oxygen. Air is supplied from a large iron tank under water pressure and the flow is regulated by a mercury seal. Oxygen is supplied from a smaller tank under water pressure regulated by an overflow.

For absorbing water from combustion, there is no more convenient nor efficient means than concentrated sulphuric acid. One point must be borne in mind and that is the retention of carbon dioxide by the acid. Since it is well known that concentrated sulphuric acid dissolves carbon dioxide to the extent of 75 per cent. of its volume, some experiments were made to ascertain just the conditions necessary to avoid retention in analysis.

In one experiment dry carbon dioxide was passed for one hour through 2 cc. of the acid in a U-tube, just sealed by the acid. Then dry air was passed through the acid for two hours, when the tube was found to have gained 1 milligram in weight. At the end of another hour the gain was reduced to 0.0008 gram, and at the end of the third hour the weight was just the same as at the beginning of the experiment.

In a second experiment conducted in the same manner the original weight was reached in two and one-half hours. In a third experiment a larger sulphuric acid tube was used containing 7 cc. of the concentrated acid. After passing carbon dioxide for one-half hour and air for one hour and fifteen minutes the gain in weight was 0.0075. In continuing the passage of air at the rate of 500 cc. per hour for different lengths of time the following results were obtained.

Minutes.	Increase.
15	0.0058
15	0.0047
15	0.0037
1 hour	0.0029
1 "	0.0018
1 "	0.0018
1 "	0.0001

It was, therefore, only after air had been passed five hours that the weight was reduced to the original. In a third experiment a potash bulb was placed in front of the sulphuric acid tube, and carbon dioxide was passed one hour, and air for one hour. The potash bulb was now attached and the gain in weight (with air) compared with the loss in the acid tube.

Hour.	Loss in acid tube.	Gain in potash tube.
I	0.0014	0.0014
I	0.0008	0.0007
I	0.0005	0.0005
I	0.0002	0.0002
I	0.0000	0.0001

In a fourth experiment, carbon dioxide was passed for one hour through 2 cc. of acid, then air for one hour, then air for one hour more and weighed; the gain in weight was 0.0007 gram. Carbon dioxide was then passed for one hour and air for another hour, then at the end of a second hour the weight was 0.0004 gram. In three repetitions the gains were respectively 0.0006, 0.0004, and 0.0006 gram showing that passing air the same length of time leaves the same weight of carbon dioxide in the acid. These experiments indicate that when a small volume of acid, 2 to 3 cc., is used with the large volume of oxygen and air used to expel carbon dioxide from the tube, very little of the gas remains dissolved in the acid. But with larger volumes of the acid there is danger of retention of carbon dioxide.

In testing the capacity of sulphuric acid to retain moisture, moist air was passed through 2 to 3 cc. of the acid at the rate of 100 cc. per hour for four hours. At this rate the bubbles cannot be counted. In front of the sulphuric acid tube was placed a high tube filled with phosphorus pentoxide but there was no gain in the latter tube. There is therefore no danger of loss in water if sulphuric acid is used. The only value of this experiment was to ascertain the conditions since Morley showed several years ago that sulphuric acid is a most efficient drying agent. The form of sulphuric acid tube we have used for several years has a bulb for collecting the greater part of the condensed water which is poured out after weighing. The forward bend of the U is 10 cm. in height from the bottom and a side tube is attached for connection to the potash bulb. When containing 3 cc. of concentrated acid, and 0.2000 gram water is weighed in each

combustion, the tube may be safely used without replacing the acid in ten or twelve combustions and probably longer. That sulphuric acid is preferable to calcium chloride has frequently been shown, since the best fused calcium chloride may contain basic chloride which retains carbon dioxide. It was shown by Winkler¹ that lime in the chloride cannot be completely saturated by carbon dioxide, since the inside of the granules remain caustic for a long time.

It is doubtful whether there is a more convenient apparatus than the Geissler potash bulb for the absorption of carbon dioxide, especially if the substance analyzed consists, for the most part, of carbon and hydrogen. There is no danger of loss of carbon dioxide if the solution of $33\frac{1}{3}$ per cent. potash be not used in more than four or five analyses. But there is danger of loss of moisture from the potash bulb unless care is taken to prevent it.

Some experiments were made to ascertain the conditions of safety. In one experiment the calcium chloride tube in front of the potash bulb was filled with freshly fused calcium chloride, broken to the size of grains of rice. Air was passed through at the rate of 550 cc. per hour with no loss in weight of the potash bulb, and the result was verified by placing a sulphuric acid tube in front of the calcium chloride tube which showed no gain in weight. Any faster rate than this showed a loss in the potash bulb and a corresponding gain in the sulphuric acid tube. On replacing the granular calcium chloride with other more finely ground, in a slightly longer tube, and passing air at the rate of 1050 cc. an hour, or 120 bubbles a minute, there was no change in weights. With a calcium tube of common length, 6 cm., a rate of 880 cc. per hour caused a loss of 0.0004 gram in the potash bulb and a gain of 0.0005 gram in the sulphuric acid tube. It is therefore safe to pass 500 cc. per minute through a tube filled with freshly fused finely granular calcium chloride. Such calcium chloride may be used in a considerable number of analyses. This rate can not be exceeded in the combustion of oils that are in part or all volatile without decomposition, or that yield gaseous products in burning. But this rate is in any sense in excess of the rate of evolution of gas from the combustion, since the carbon dioxide is, for the most part, immediately absorbed as

¹ *Ztschr. anal. Chem.*, 545, 1882.

soon as it meets the potash solution. By replacing the fused calcium chloride with phosphorus pentoxide, there was no loss even when the rate exceeded 1000 cc. per hour, or 120 bubbles a second. But the oxide offers no advantages over the fused chloride in ordinary analysis.

In preparing for a long series of combustions a combustion tube should be selected that promises to stand 50 to 100 analyses, since it requires a long time to get the tube and its contents and connections in good working order. A long time is required to remove all the volatile impurities from the best copper oxide, and the moisture from the tube and oxide. Rubber stoppers are the only means for satisfactory connections, but before they become constant in weight probably some of the sulphur must be volatilized and moisture expelled. It is therefore necessary to test carefully all parts of the apparatus by means of blank experiments in the beginning, and even after the apparatus becomes constant it is well occasionally to apply a blank test.

In conducting analyses of such bodies as the high-boiling constituents of petroleum, the closest attention to details is necessary. The tube must be as hot as it will stand, and yet not hot enough to lessen its durability, on account of the labor involved in getting it in good condition. If the combustion tube be filled with oxygen before the substance is inserted and the rate of volatilization be carefully controlled, any hydrocarbon may be burned in a furnace with 20 burners. Many analyses were lost before these conditions were fully understood. In view of the possibility that a longer combustion tube might insure complete combustion and shorten the time of the analysis, two furnaces were placed together, and a tube nearly two meters in length was used. But the results were not more satisfactory than with a tube of ordinary length.

As a general summary of what is necessary to insure desirable accuracy in such determinations, it must be fully understood at the outset that no operation in analytical chemistry demands greater precautions, closer attention to details, or more skill and patience on the part of the operator to insure results within 0.20 per cent. of the maximum 100 per cent. in substances composed solely of carbon and hydrogen, such as petroleum oils.

In view of the great amount of work that will have to be done in determining the constitution of the large number of hydrocarbons with high molecular weights in Pennsylvania, California, and other petroleum, it would be a great advantage if a method for the determination of carbon and hydrogen could be devised that would avoid the tedious routine of the present method. But with present knowledge of this subject this method is probably all that can be hoped for. The Geissler potash bulb and the sulphuric acid tube seem to be as convenient forms as can be devised and they are capable, as shown above, of retaining carbon dioxide and water with as rapid delivery as is consistent with complete combustion. Rubber corks are objectionable, but they are the only convenient and reliable means of connection available.

We have tried successfully weighing the bulbs full of oxygen, thus avoiding the expulsion of oxygen by air. But since the time necessary to carry forward all the carbon dioxide is equivalent to that necessary to displace oxygen by air, there is nothing gained by weighing the bulbs filled with oxygen. The precautions necessary to insure cleanliness of the bulbs and constant conditions of moisture and temperature in weighing must be carefully observed.

CIDER VINEGAR : ITS SOLIDS AND ASH.

BY R. E. DOOLITTLE AND W. H. HESS.

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DURING the past few years the question of vinegar adulteration has received considerable attention from food chemists. Heretofore the sophistication has consisted almost entirely of the sale of colored distilled vinegar for pure fermented apple juice. As distilled vinegar contains little or no solids or ash this fraud was easily detected by very simple determinations. During the year 1899, however, there appeared for sale on the markets of this state, vinegar containing the necessary amount of solids and ash required by the statute for cider vinegar; but on ordinary analysis of this the solids and ash did not have the usual appearance of solids and ash of vinegar from pure apple juice. It was to ascertain the character of these vinegars