dioxide with oxalic acid, the first action being the reduction of the oxide by the oxalic acid with evolution of carbon dioxide, and then the formation of the complex salt, which has the formula $M_3IrOx_3.nAq$. The oxaloiridite is a fairly stable ion, and all its salts are hydrated, but the amount of water is variable.

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[CONTRIBUTION FROM THE INSTITUTE OF ANIMAL NUTRITION OF THE PENNSYLVANIA STATE COLLEGE.]

THE DETERMINATION OF CARBON BY MEANS OF THE BOMB CALORIMETER.

BY J. A. FRIES.

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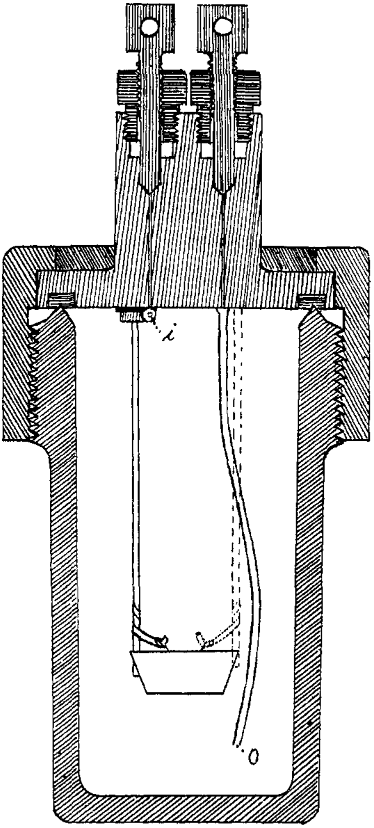
In the investigations carried on by this institute, the problems of animal nutrition are being studied from the standpoint of energetics and hence the heats of combustion of numerous samples of feed, excreta and other materials are determined by means of a bomb calorimeter. Having, therefore, the charges of these samples completely oxidized in the bomb calorimeter at the time of the heat determinations, the idea naturally suggests itself to try to determine the CO_2 pent up in the bomb. The writer made an attempt several years ago to determine carbon by means of the ordinary Atwater-Hempel bomb, but the results were unsatisfactory. This was due, in part, to the fact that the construction of the bomb used was not well adapted to this particular purpose, and in part to the quality of the oxygen supply which was then in use. The work was, therefore, dropped until a more suitable bomb could be obtained. During the past summer, the work of determining carbon has been taken up again with a new Atwater-Hempel bomb, which has the top modified according to the suggestions of Dr. H. P. Armsby and the writer. This time it has been satisfactorily demonstrated that the carbon in organic compounds can be determined accurately, in less time, and with less expense, by means of the bomb than by the ordinary copper oxide method.

While this method for carbon is especially to be recommended to those who desire to determine both energy and carbon in the same material, it can also be recommended for carbon alone. Where the bomb calorimeter is in use already, a new top suitable for this work would, undoubtedly, in many instances prove to be a good investment. The top which we have used has two separate openings and valves, an inlet terminating on the under side of the cover, and an outlet extending by means of a fine platinum tube to within about 5/8 inch of the bottom of the bomb.

The figure shows the arrangement of the two valves, and the general construction of the top, as well as of the other parts of the bomb. For the excellent practical execution of the proposed modification of the top, we are indebted to Mr. S. C. Dinsmore, New York, the maker of the bomb calorimeter.

The platinum tube in the bomb is used only as a gas outlet and need not, therefore, be very heavy. The platinum capsule containing the substance to be burned is supported on one of the two heavy platinum wires, which conduct the electric current for ignition. Outside on the bomb cover, or top, the threaded projections of the gas inlet and outlet point in opposite directions, so that each is easy of access in making connections to absorption tubes, etc.[1]

Method for Carbon Determinations.—Weigh out a charge large enough, when possible, to produce 4000 to 5000 calories, and prepare it exactly as for a determination of heat of combustion, that is, voluminous or powdered material is pressed into tablets to prevent it from spattering and jumping off the capsule. The pressed charge is carefully weighed in a small platinum capsule. This is then attached to one of the platinum wires in the bomb in such a manner that the substance to be burned comes in direct contact with the fuse wire. Next, the bomb is charged with oxygen, twenty atmospheres pressure, a sufficient supply for the quantity of substance mentioned. Immediately after filling, the bomb is completely immersed in water long enough to demonstrate that there is absolutely no leak of gas. This precaution should never be omitted when carbon is to be determined. This done, the substance is ignited. It is best to have the bomb standing in cold water at the time, and for a



Bomb calorimeter, cross-section top modified for carbon determination.

[1] As for the general description of the bomb calorimeter, directions for the manipulation of it in heat determinations, and for the calculation of the results, for the determination of the water value of the apparatus, and a method for determining the heat corrections for impurities in the oxygen, they are all topics which do not belong to this paper. Information concerning these things is to be found in THIS JOURNAL, **25**, 659; Wiley's "Principles and Practice of Agricultural Analysis," Vol. III, and Bull. **94**, of the Bureau of Animal Industry, U. S. Department of Agriculture.

minute or so after the substance has been ignited, since condensation on the sides of the bomb of the water and acids formed is then more quickly completed.

After ignition, the bomb is removed from the water, carefully wiped, secured in the iron clamp and connected to the absorption apparatus.

The carbon dioxide is absorbed by finely granulated soda lime, the absorption train consisting of a series of four glass-stoppered U-tubes 5 inches long and of about 5/8 inch diameter. The first and last tubes contain granulated pumice stone in pieces 1/16 inch or a little more in diameter, saturated with sulphuric acid, and the two middle tubes contain finely granulated soda lime. One of the acid tubes is connected directly to the gas outlet on the bomb. The other acid tube is connected to a small two-holed stoppered bottle containing a little water which serves as a flow indicator when the gas is allowed to bubble through it. A dilute solution of palladium chloride was used instead of the water, while this method for carbon was being tested, but no carbon monoxide was found, hence the palladium chloride is an unnecessary precaution. This small bottle is connected with a large aspirator bottle filled with water. When the system is thus connected, the water in the aspirator is started, all the stoppers in the tubes opened and all the connections back to the bomb tested. The system should stand the suction of a couple of feet of water pressure without showing any leak whatever, before the gas is turned in.

If the system is tight, while the outlet of the aspirator bottle and stoppers of the U-tubes remain wide open, the valve on the bomb is slowly opened, and by watching the bubbling in the small bottle, and the overflow of water from the aspirator, the flow of gas can be regulated.

The amount of soda lime contained in a U-tube of the size named, will absorb from 1.5 to 2.0 grams of carbon dioxide completely from the gas mixture, when it is being passed through the tubes at the rate of one-half liter per minute, and the sulphuric acid tubes can be used repeatedly, if always connected in the same position, until several grams of water have been absorbed in each.

After the pressure in the bomb has been reduced to normal air, freed from water and carbon dioxide, is drawn through until all the carbon dioxide has been removed. With this bomb, capacity about 400 cc., it was found that when the gas was taken out from the bottom of the bomb, and the dry air allowed to enter at the top, there was no carbon dioxide left in the bomb after four liters had passed through, but in order to meet any exceptional cases, the writer always allows about 9 liters of air to pass through the bomb and tubes after the pressure in the bomb has been equalized. Care must be taken, when the gas current through the tubes is as fast as was mentioned, that no moisture is condensed in the side connecting arms of the soda lime tubes.

After cooling to room temperature, the tubes can be weighed. The total increase in weight of the two soda lime tubes and last acid tube gives the weight of carbon dioxide. At ordinary room temperature and at the rate of from 0.25 to 0.5 liter per minute flow, practically none of the nitric and other acids formed in the combustion go over from the bomb with the first 9 liters of air, but with more air, small portions of the acids may leave the bomb.

The following simple words of caution about handling the bomb, if heeded, may save many a determination for beginners. From the time the charge of the substance is placed in the bomb until it has been ignited, the bomb should not be tilted or receive sudden knocks or jars. If the substance falls from the capsule to the bottom of the bomb during ignition, or blotches of carbon are found on the side of the bomb, the determination is faulty and altogether useless if great accuracy is required.

There are certain signs which indicate more or less perfectly the completeness of the combustion in the bomb calorimeter. When there is no sign of any unburned carbon, and no strange odor to the gases, the combustion is always found to be complete. A small black spot of carbon, like a thin layer of soot, weighing not more than 0.1 to 0.2 milligram, will usually mean that the results of heat combustion as well as carbon are a few hundredths of a per cent. too low. If a small spot or blotch of brownish black substance, of a soft gummy nature, is found on the side or bottom of the bomb, even if it weighs only a very few tenths of a milligram, it indicates that the results may at times, at least, be several tenths of a per cent. uncertain, and hence useless. The same may be said when benzene-like odors, or an odor like that of a damp chimney, are noticed in the bomb; there is then uncertainty about the results, even if there is no sign of any unburned carbon. With most substances, however, there is little or no difficulty from incomplete combustion.

Comparison of Results Obtained by Different Methods.—A number of carbon determinations have been made by the bomb calorimeter method on various substances which also have had carbon carefully determined by the copper oxide method by W. W. Braman, one of the chemists. The bomb calorimeter determinations have mostly been done in connection with determinations of the heat of combustion on the same charge. With the exception of the benzoic acid samples, which were used in determining the heat value of the bomb calorimeter, only single determinations of carbon were made. But, as may be seen from the following table, these determinations agree remarkably well with the average of the results obtained by the other method. In the table, the samples are arranged in the order in which the carbon determinations were made with the bomb.

COMPARISON OF CARBON DETERMINATIONS BY THE BOMB CALORIMETER METHOD AND BY THE COPPER OXIDE METHOD.

Sample.		Carbon by the copper oxide method.		Carbon by the bomb method.	
Character.	Lab. No.	Single determ. Per cent.	Average. Per cent.	Single determ. Per cent.	Carbon, theoretical. Per cent.
Benzoic acid (Merck)	...	...	...	68.83 68.73[1]	68.83
Hay	44677	44.88 44.86 44.60 44.73	44.77	44.64	...
Dung	45026	46.03 46.14 45.89	46.02	46.24	...
Hay	44521	44.58 44.67 44.20 44.70	44.54	44.51	...
Hay	44781	44.42 44.66 44.28 44.36	44.43	44.43	...
Naphthalene	...	...	...	93.71	93.70
Corn meal	44517	43.15 43.21 43.18 43.22	43.19	43.27	...
Linseed meal	44518	45.82 45.76 45.80	45.79	45.65	...
Wheat bran	44519	43.24 43.33 43.26	43.28	43.31	...
Compositive grain	44673	44.42 44.39 44.52 44.36	44.42	44.47	...
Benzoic acid (Kahlbaum)	...	...	...	68.80 68.77 68.74[2]	68.83
Hair	45163	43.74 43.79	43.77	43.97	...

Judging from the results shown in the above table, it can be said that the bomb calorimeter method for carbon determinations is absolutely

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[1] This charge was burned in the bomb with a pressure of 10 atmospheres oxygen.

[2] For this charge 12 atmospheres oxygen pressure were used.

reliable and gives very accurate results. In the four determinations of carbon in the pure chemical compounds, benzoic acid and naphthalene having very high percentage of carbon, the greatest variation from the theoretical was 0.054 per cent. In the case of only two other samples did the difference between the single determinations by the bomb calorimeter and the average results obtained by the other method reach the limit of analytical error usually allowed in such determinations. Since, however, some of these samples were reported as having been troublesome to analyze, the bomb result may be as reliable as the other.

Oxygen.—To the writer's knowledge there is in this country no perfectly pure oxygen put up in high pressure cylinders; all contains more or less impurity such as combustible gases, carbon dioxide and nitrogen. A little nitrogen in the oxygen does not in any way interfere with the accuracy of the carbon or heat determinations, nor does a little carbon dioxide with the latter. For carbon determinations, on the other hand, it is desirable to have as little carbon dioxide present in the oxygen supply as possible, thus minimizing the correction. The quantity of carbon dioxide present in the oxygen must be determined so that the proper correction can be made for the amount of oxygen used in the bomb. Oxygen made from liquid air has been found to contain only a small amount of carbon dioxide and is the kind of oxygen which has been used in the determinations referred to in this paper.

To ascertain whether there is any carbon dioxide formed in the bomb from the combustible gases in the oxygen supply, the oxygen can be tested by burning some pure substance of known composition and heat of combustion. If the corrected heat of combustion and the carbon determinations both agree with the theoretical, no carbon dioxide is formed, and hence no correction is necessary. On the other hand, if the heat is correct, but the carbon dioxide is too high, the excess of carbon dioxide is a correction to be applied.

Soda Lime.—The soda lime used for the absorption of carbon dioxide is made in the following manner: An iron pot of about eight to ten liters capacity is fastened securely to a piece of plank sufficiently heavy to prevent upsetting, yet not too heavy to be handled by two men. Into this pot are placed one kilogram of freshly burned, best white lime, 1 kilogram of dry sodium hydroxide powder and 850 grams of water. The sodium hydroxide and water are first added and the sodium hydroxide dissolved, then the lime is added. Soon a violent reaction sets in and during this the mass is stirred and worked with an iron rod or pipe as long as possible. After the reaction has ceased and before the mass has cooled fully, the soda lime is removed from the pot and transferred to an earthen jar which will stand the heat, and new charges are made and added until the desired quantity has been made. The best proportion of the ingredients will vary with the purity of the lime, that of ordinary so-called good lime it may require 1.25 kilos to 1 k of sodium hydroxide and sometimes a little less water than stated befo The best proportion of the ingredients at hand to use may, therefo at times have to be determined experimentally.

The pieces of soda lime should be porous, light gray in color and ha enough to break and crumble when pounded. They are broken up a sifted and the granules of about 1/16 inch or a little more in diamet are used in the U-tubes for carbon determinations.

Hydrogen Determination.—By means of the bomb calorimeter it possible also to determine hydrogen, but it is a much more difficult an tedious operation, and it is very hard on the bomb, and with the kind bombs in use at present, the writer considers it too costly and henc impracticable. Trials were made and it was found that the escapin acids attack the apparatus too much; but as soon as the bomb ca be made with platinum or other non-corroding lining all through the ga outlet, a method for hydrogen can doubtless be worked out successfully

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES
I. HYDROXYLAURONIC ACID AND ISOCAMPHOLACTONE.

BY W. A. NOYES AND A. W. HOMBERGER.

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Terpenes, camphor and their derivatives often undergo molecular rearrangements which render conclusions drawn with regard to their structure fallacious. Very little is known with regard to the laws governing such rearrangements and it seems possible that a careful study of some of these changes may throw additional light upon the nature of the forces which exist in molecules containing carbon. The first step in such a study must consist in establishing the structure of compounds which result from such rearrangements. From the nature of the case this is often extremely difficult as we have very little to guide us in deciding whether a rearrangement has taken place in a given reaction or not. In the end, one is dependent on that sort of cumulative evidence which is so characteristic of many of the most difficult problems of organic chemistry and which is so trying to minds which desire an absolute proof for everything that is to be accepted as scientific.

The work described in this paper has, of course, made very little progress toward the study of the larger question and is quite incomplete. As it must be discontinued for some time, however, it seems desirable to record, briefly, the results obtained.

α-Camphoramidic acid, $C_8H_{14}(CO_2H)CONH_2$, gives with sodium hypo-