THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY

THE USE OF COMPRESSED OXYGEN IN ELEMENTARY ORGANIC ANALYSIS AND OF SODA-LIME IN THE QUANTITATIVE DETERMINA- TION OF CARBON DIOXIDE.

BY FRANCIS G. BENEDICT AND OLIN F. TOWER.

THE ordinary method of elementary organic analysis in which use is made of air and oxygen contained in a gasometer, suffices where but few determinations are to be made. The manipulation is, however, too lengthy to permit of rapid work, and having occasion to make carbon and hydrogen determinations in a large number of foods used in connection with experiments with a respiration calorimeter in this laboratory, it was necessary to modify materially the method so as to increase its rapidity. The method formerly employed is essentially the same as that described in most text-books on organic analysis, and may be briefly outlined as follows :

Oxygen obtained by heating a mixture of potassium chlorate and manganese dioxide was collected over water in a Mitscherlich gasometer. It was then freed from carbon dioxide, and dried

as it entered the combustion tube. The substance was burned in the usual manner in a tube filled with granular copper oxide. The resulting water was collected in a tube containing glass wool drenched with sulphuric acid, and the carbon dioxide was absorbed in a potash bulb, which was followed by a small sulphuric-acid tube to collect the water coming over from the potash solution. On the end of a series of absorption tubes, a small ∪-tube was placed containing fused calcium chloride to absorb the moisture of the air in case of back suction. After the substance was completely burned and oxygen had been passed through, the tube was swept out with a current of air to remove all oxygen from the system.

There are several disadvantages in obtaining oxygen by the above method. The time consumed in generating and collecting the gas is considerable. Impurities present in manganese dioxide cause the formation of some carbon dioxide, which mixes with the oxygen and necessitates special care in purifying the gas before use. The oxygen standing in the gasometer over water becomes saturated with aqueous vapor. In order to remove all traces of carbon dioxide and water vapor it is necessary to pass the oxygen through the purifying apparatus very slowly. Furthermore, owing to the large quantities of these impurities present, the materials used in purification, *i. e.*, potassium hydroxide and sulphuric acid respectively, require frequent replenishing.

The use of Pepys or Mitscherlich gasometers for holding oxygen is an almost universal practice. These gasometers, if constructed of metal, soon leak owing to the attacks of acid fumes and vapors always present in a laboratory, and are constantly needing repairs. Glass gasometers do away with the large mass of metal, but rely on metallic pipes, cocks and connections to receive and deliver the gas. These connections are equally liable to the attack of acid, resulting in leakage and consequent loss of gas. The fragile nature of such gasometers and the necessity for transportation to the sink when being filled, make their handling difficult. Finally, the original cost of such an apparatus is not inconsiderable.

To overcome these disadvantages use is made of compressed oxygen in steel cylinders. Progress in the compressed air

industry has reached such a point that it is comparatively easy to secure a strong, thoroughly well-tested cylinder of highly compressed oxygen. These cylinders are made in all sizes, containing from a few gallons to 100 cubic feet of oxygen. For the laboratory, a cylinder containing ten cubic feet or seventy-five gallons is of convenient size. The oxygen thus compressed is of a high degree of purity. Formerly hydrocarbons were used to lubricate the machinery for compressing the gas, thereby causing contamination of the oxygen with volatile hydrocarbons, which introduced serious errors when the gas was used in elementary analysis. Manufacturers have, however, replaced the lubricating oils with graphite, thereby eliminating the undesirable impurities of gaseous hydrocarbons. In the several cylinders of oxygen tested in this laboratory, gaseous hydrocarbons, or at least any hydrocarbons, not completely absorbed by the sulphuric acid of the drying apparatus to be described beyond, were never detected.[1]

The oxygen in these steel cylinders is comparatively dry and free from carbon dioxide, so that its purification is easy to accomplish. The carbon dioxide is absorbed by soda-lime in a small U-tube.[2] Owing to the small quantity of carbon dioxide present, one tube of this sort will remove this impurity completely for over twenty-five combustions. The soda-lime tube is followed by the drying apparatus, consisting of a cylinder about twelve cm. high half filled with concentrated sulphuric acid, through which the oxygen bubbles, thereby indicating the rate of flow.

[1] Oxygen compressed in this form was first used in this laboratory for making combustions with an Atwater-Blakeslee bomb-calorimeter. These bomb-calorimeters have been introduced into several laboratories, all of which, consequently, have a supply of compressed oxygen. For those laboratories not possessing a cylinder the following is appended : The price of a ten-foot cylinder is about ten dollars. The so-called "commercial" oxygen, which differs from the "medical" only in so far as it has been, perhaps, a little less thoroughly washed and purified, costs at the rate of ten cents per foot; i. e., one dollar per ten cubic feet. This amount is not great compared with the cost of an ordinary Mitscherlich or Pepys gasometer. Inasmuch as the gasometers are used almost exclusively to hold oxygen, it will be seen that they are not indispensable to the ordinary laboratory supplied with a cylinder of oxygen. Ten cubic feet will last for a great many carbon and hydrogen combustions, while the advantage of using a cylinder of this gas in the lecture-room is obvious.

The writers would here express their obligations to Mr. A. K. Johnston of the S. S. White Dental Manufacturing Company, Princess Bay. N. Y.. who has furnished much valuable information.

[2] This and all other U-tubes here mentioned were five inches long and five-eighths inch outside diameter, as this was found to be the most convenient size.

Following this is a small ∪-tube containing pumice stone drenched with sulphuric acid to retain any moisture, which may escape absorption. The cylinder usually absorbs all the moisture, so that no gain in weight of the ∪-tube is observed. When the oxygen is run at an abnormally rapid rate, the ∪-tube shows a slight gain, as was proved by an experiment in which the ∪-tube gained one and eight-tenths milligrams after the oxygen had been passing rapidly through the system for thirty minutes.

Inasmuch as the oxygen contained in the steel cylinders is under great pressure, some method of regulating the flow of gas, as it enters the combustion tube, must be devised. The expensive precision and reduction valves used ordinarily with these cylinders can be replaced by the following simple arrangement : A rubber tube leading from the cylinder connects with a ⊤-tube, one end of which dips one inch under mercury in a small bottle fitted with a rubber stopper having two holes. The second hole is left open. A rubber tube connects the other end of the ⊤-tube with the purifying apparatus, which is in turn connected by rubber tubing to the combustion tube. This last rubber tube is supplied with a pinch-cock. When the valve on the oxygen cylinder is opened slightly, the gas will flow out, and passing through the driers produce a bubbling in the sulphuric-acid cylinders. As yet no gas escapes through the mercury. If now, as is often the case, one wishes to regulate the flow of gas, the pinch-cock is closed until the desired rate of flow is secured. Any excess of gas now escapes through the mercury trap. It is always possible to adjust the valve on the oxygen cylinder finally, so as to prevent any appreciable loss of oxygen through the mercury.

The furnaces used are of the ordinary Bunsen pattern, and have twenty-six burners. A hard glass combustion tube was filled in the usual manner with granular copper oxide. The oxidized copper spirals used to fill the entrance end of the tube after introducing the substance to be burned, were made by winding moderately stout copper wire in layers around a glass rod until the desired size was obtained. Such spirals were found to be more durable than those made from copper gauze. Red antimony rubber stoppers were found to possess a marked superiority in withstanding heat over those of ordinary rubber, and they were, accordingly, used

at each end of the combustion tube. All rubber connections were made with $\frac{5}{32}$-inch red antimony tubing.

The water formed during the process of combustion was absorbed as usual in a Volhard ∪-tube containing glass wool drenched with sulphuric acid. The absorption of the carbon dioxide was effected by passing the gas after leaving the sulphuric acid ∪-tube through a ∪-tube filled with specially prepared soda-lime, followed by a similar ∪-tube containing, in one limb, soda-lime, and in the other fused calcium chloride. This substitution of soda-lime for the usual absorbent of carbon dioxide, *i. e.*, potassium hydroxide, while by no means new,[1] has given such satisfactory results in our hands as to warrant publication.

Repeated tests of a most exacting nature have shown that soda-lime, prepared as described below, absorbs carbon dioxide more completely and rapidly than potassium hydroxide solution. Passing 150 liters of air containing three and five-tenths grams of carbon dioxide through a system of two soda-lime ∪-tubes and a final check ∪-tube containing glass beads drenched with barium hydroxide solution gave no turbidity in the last tube. The air was aspirated at the rate of 500 cc. per minute.[2] In another experiment[3] ordinary air from the room was drawn through one soda-lime ∪-tube, followed by a Drechsel gas-washing cylinder containing a strong barium hydroxide solution, at the rate of 2100 cc. per minute without noting any turbidity in the barium hydroxide solution. It is needless to add that these tests could in no way be duplicated, if potassium hydroxide solution were used. Obviously then, so far as the absorption of the carbon dioxide is concerned, there need be practically no limit to the rate at which the gas may be passed though the soda-lime tubes. As a matter of fact, in this method the rate of flow is regulated solely by the completeness of combustion. In case of back suction there was no liquid to look out for as when a potash solution was used. To prevent atmospheric moisture from being

[1] See *Ann. Chem.* (Liebig), **285**, 385.

[2] Preliminary Investigations on the Metabolism of Nitrogen and Carbon in the Human Organism, by W. O. Atwater. C. D. Woods, and F. G. Benedict. Bulletin 44, Office of Experiment Stations, U. S. Department of Agriculture, p. 28.

[3] This Journal, **20**, 299.

absorbed when back suction occurred, a small sulphuric-acid tube completed the series of tubes.

As dry air passes through the carbon dioxide absorbent in any system of tubes, it carries with it varying quantities of moisture, which must be collected and weighed to secure the true weight of the absorbed carbon dioxide. Actual experiments show this amount of water lost from a soda-lime tube during a combustion to be on the average about one-fourth of that lost from an ordinary Geissler potash bulb. To collect this water from the soda-lime tube, one limb of a second ∪-tube is filled with calcium chloride, while the other is filled with soda-lime. The limb filled with soda-lime is connected with the first ∪-tube. Both tubes are weighed. In ordinary combustions the second tube rarely gains as much as two milligrams, while a sulphuric-acid tube following a potash bulb ordinarily gains from six to ten milligrams. To prove the complete retention of water by the calcium chloride, a sulphuric-acid ∪-tube was placed immediately following, and weighed before and after a combustion, and in no case was any gain in weight observed. An additional advantage of this second ∪-tube lay in the fact that the first tube could be completely used up without the fear that carbon dioxide might escape absorption. When the second tube gained much more than two milligrams, it was an indication that the first tube was exhausted, and it was accordingly replaced by a fresh tube. A fresh soda-lime tube can be used ordinarily for six combustions before becoming exhausted, while it is hardly safe to use a potash bulb more than twice.

The progress of the absorption of carbon dioxide by the soda-lime is also indicated by a marked change in color. The fresh soda-lime has a slightly yellowish tinge, while the portion converted to carbonate is pure white. With a potash solution no such indication is present, and one must rely solely on the increase in weight of the potash bulb. As the carbon dioxide is absorbed in one limb of the tube, a very marked line of advancement is noticed where the color change occurs. This line advances as the absorption proceeds, and the efficiency of any tube can be immediately ascertained by noting this change in color.

A not inconsiderable item in considering the relative merits of

soda-lime and potassium hydroxide solution is the question of the expense of the potash bulbs. Compared with the ⊔-tubes they are very expensive, and their fragile nature is a decided disadvantage. Where a large number of combustions are to be made, it has been found advantageous to have a number of these soda-lime ⊔-tubes filled in advance, and fitted with one-holed rubber stoppers carrying small bent glass tubes plugged at the ends with short bits of rubber tubing and a piece of glass rod. These tubes can be weighed to the second decimal place and, when wanted, checked up accurately on the balance.

In order to still further shorten the time of making a combustion, sweeping out the oxygen with air after combustion was omitted. As the tubes were weighed originally filled with air, the oxygen filling them after combustion, should be replaced by air. This is accomplished after the tubes have been disconnected in the following manner : Air, purified by passing through a soda-lime ⊔-tube and a sulphuric-acid ⊔-tube, is drawn by gentle suction with the mouth through the tubes to be weighed. These air-purifying tubes are kept in readiness, so that very little time is consumed in the process. If the tubes were weighed filled with oxygen, the error would be almost inappreciable, since the empty space in the ⊔-tubes is small, particularly as compared with the empty space in a potash bulb. Before each weighing, the tubes were wiped off lightly with a piece of cheese-cloth. Weighings were in each case made with a counterpoise. The ease with which a ⊔-tube can be wiped, as compared with a potash bulb, is apparent.

It was found that time could be saved by using two furnaces. One person then gave all his time to watching the furnaces, while another person made the weighings and kept the tubes replenished. By thus utilizing about one-third of the time of a second man, an average of two combustions an hour could be made. The furnaces were both connected with the same oxygen cylinder by inserting a Τ-tube just beyond the mercury safety trap previously described. Each furnace was supplied with an independent set of drying and purifying tubes. This was necessary in order to observe the rate of flow of each current of gas. To test the efficiency of the apparatus and method, substances of known composition and purity, *i. e.*, cane-sugar

and benzoic acid, were analyzed and the results are given in the following table:

| Substance.	Amount used. Gram.	Carbon di-oxide found. Gram.	Carbon		Water found. Gram.	Hydrogen	
			Found. Per cent.	Theor. Per cent.		Found. Per cent.	Theor. Per cent.
Cane-sugar..	0.2000	0.3075	41.94	42.10	0.1145	6.41	6.43
" " ..	0.2018	0.3111	42.05	....	0.1158	6.42	....
Benzoic acid	0.2058	0.5193	68.83	68.85	0.0911	4.95	4.92
" "	0.1738	0.4388	68.87	....	0.0780	5.02	....

The cane-sugar was obtained as rock-candy. This was dried, powdered, and dried again until there was no loss in weight. The benzoic acid was a chemically pure preparation of the market. It was melted and recrystallized twice before being used. No traces of moisture could then be found.

The above results, fair samples of many others, seemed to justify the use of this method for determining carbon and hydrogen in organic substances. As a direct application of this method, it will suffice to say that over eighty samples of foods have been burned, and the agreement of duplicates is, to say the least, remarkable. Agreement as close as 0.03 or 0.04 per cent. was often obtained. Obviously this agreement substantiates in no way the absolute determination of carbon and hydrogen, but it does imply that the method is easy and regular, presenting no great difficulties in manipulation.

One essential feature is the soda-lime. As ordinarily prepared and sold in the market, it is a mixture of sodium and calcium hydroxides fused and granulated. Its chief use has been as a drier for gases and for determining organic nitrogen. Such soda-lime has very little absorptive power for carbon dioxide. To absorb carbon dioxide readily the soda-lime must be moist. This moisture is best obtained by modifying the method of preparation. One kilogram of commercial caustic soda, "Greenbank Lye," is treated with 500–600 cc. water in an iron kettle forming a strong solution, or more properly a thin paste. While still hot, one kilogram of quicklime, coarsely powdered, is rapidly added, stirring constantly with an iron rod or piece of gas pipe. The lime is slaked by the water of the caustic soda solution, and soon the whole mass heats and steams up. While in this stage, it is advisable to keep the mass stirred and the lumps broken up. No outside heat is necessary, and as soon as

cool the product may be placed in wide-mouthed bottles, and the corks sealed in with paraffin or wax. When cool, it should not be moist enough to show water as such, *i. e.*, no particle should glisten in strong light. If too dry, a small quantity of water can be readily added after the soda-lime is made, though the great danger lies in adding too much water, thereby making the lime too pasty for the most efficient absorption. We have made over fifty kilograms of such soda-lime in the past three years, and invariably secure a good product when using the above formula.

While moisture is essential in securing the complete absorption of carbon dioxide, the amount of moisture carried away from a soda-lime ∪-tube by an air current is, as has before been stated, much less than that brought away from a potash bulb. Assuming that the soda-lime here used is a mixture of the hydroxides of sodium and calcium, and that the normal carbonates are formed when carbon dioxide is absorbed, we could properly have two equations; *viz.*,

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O,$$
$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$
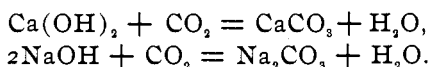
Thus one molecule of carbon dioxide absorbed liberates one molecule of water from the hydroxides. Accordingly, for every gram of carbon dioxide absorbed about four-tenths gram of water is liberated. In actual experimenting, however, but a very small portion of this water leaves the soda-lime ∪-tube. In one tube 2.7467 grams of carbon dioxide were absorbed and only 0.1378 gram of water left the soda-lime tube. The sodium carbonate formed appears to retain the major portion of the water hygroscopically. While the deca-hydrated sodium carbonate loses its water of crystallization readily, the anhydrous salt takes up water with great avidity, and it is to this that we must attribute the retention of so much water in the soda-lime tube. Were it possible to form the acid carbonates of sodium and calcium under these conditions, the water would be retained chemically, and in fact not liberated. To disprove this high improbability some of the white spent soda-lime was heated in a long tube to low redness with provision for absorbing any carbon dioxide given off, exactly similar to the absorbing ap-

paratus used above in the case of combustions. The first soda-lime ⊔-tube lost one and eight-tenths milligrams, while the second containing also calcium chloride gained one and six-tenths milligrams, which shows that no carbon dioxide was driven out of the spent soda-lime. A large amount of water was, however, given off, indicating that the white seemingly dry carbonate had really absorbed considerable water hygroscopically. The whitening in a tube is not, therefore, due to drying out. Experiment has also shown that moistening white, spent soda-lime does not increase its absorbent power for carbon dioxide.

Soda-lime prepared as outlined above is recommended as a general reagent for freeing gases from carbon dioxide, such as normal air in determining gas densities. As a reagent for the quantitative determination of carbon dioxide, both in elementary organic analysis and in air analyses, it has given excellent satisfaction. The air analyses were made in connection with the respiration calorimeter above referred to. It appears to be an excellent general substitute for potassium hydroxide solution in all cases where the solid form of reagent is not proscribed.

CHEMICAL LABORATORY, WESLEYAN UNIVERSITY,
MIDDLETOWN, CONN.

THE DETERMINATION OF CARBON MONOXIDE, METHANE, AND HYDROGEN BY COMBUSTION.

BY L. M. DENNIS AND C. G. HOPKINS.

IN the development of technical gas analysis the researches of Winkler, Hempel, Lunge, and others have given us many methods which are both rapid and exact and which yield results quite as satisfactory as those obtained by the classical methods of Bunsen. But for the determination of hydrogen and methane modern methods have been found to be far from satisfactory. The combustion of hydrogen and hydrocarbons by means of copper oxide is no longer used because of its inconvenience. The combustion of hydrogen by means of palladium asbestos is open to the error which may result from the partial burning of the methane present. The fractional combustion of hydrogen by palladium sponge and the absorption of hydrogen by palladium