

Carbon and Hydrogen Analysis By Semimicro Combustion

HEINZ HEINEMANN*

Carnegie Institute of Technology
Pittsburgh, Pa.

THE determination of carbon and hydrogen in the elementary analysis of organic compounds is usually carried out by macro (10) or micro (9) combustion methods, the relative advantages of which have been frequently discussed (5, 7, 11). Semimicro methods have been described (4, 6, 8) and compared with the other procedures. Semimicro methods combine the advantages of macro and micro methods. They permit the analysis of relatively small amounts of material in a short time without requiring the use of a micro balance. A normal analytical balance with a sensitivity of 0.1 mg. can be employed.

The method which, together with some recent improvements, will be described in this article has been worked out by E. Berl and coworkers (1, 2, 3) and is not very well known in this country. It has given very satisfactory results in several hundred analyses.

The amount of substance used for a determination should contain 10-15 mg. of carbon. The material is burned either in a porcelain or platinum boat, or mixed with oxidizing material like fine copper oxide in a stream of carbon dioxide-free, dried oxygen. When inorganic ash materials which retain carbon dioxide as carbonates are present, the combustion is carried out with lead chromate instead of copper oxide as the oxidizing material. In this case a blank run has to prove the absence of organic matter in the lead chromate.

Oxygen used for the combustion must be hydrogen-free. If electrolytic oxygen has to be used, the hydrogen must be burned over hot copper oxide. Carbon dioxide is removed from the oxygen with soda lime and, before entering the combustion tube, the oxygen is dried with the same agent which is later used to absorb the water of combustion. Suitable drying agents consist, e.g., of strong sulfuric acid, drierite, CaCl_2 , activated alumina or superphosphoric acid (a mixture of P_2O_5 and phosphoric acid) supported on porous porcelain chips.

The combustion tube, 40 cm. long and of 10 mm. diameter, rests in a split iron tube of 20 cm. length and 15 mm. diameter. It is heated in either a gas or an electric furnace. A very simple but satisfactory gas furnace consisting of a series of small bunsen burners placed under the split iron tube and a number of refractory shingles serving as baffles have been described by Berl and Burekhardt (1). Very

satisfactory results have also been obtained with a von Czoernig-Alber micro combustion furnace, the inside dimensions of which have been changed to accommodate the combustion tube. The furnace body is 20 cm. long, 6.25 cm. deep, and 5.6 cm. high. The hinged front is of transite. The furnace is mounted on an adjustable stand with leveling screws and adjustment for centering and dumping combustion tubes. It can be moved laterally on tracks and can also be moved forward and backward. With this furnace is used an electric sample heater, having a cylindrical chamber 75 mm. long and movable laterally on the tracks. The temperature of each heater is controlled by a voltage transformer.

The outlet of the combustion tube is connected to the absorption vessels with a ground glass joint (Figure 1). A piece of brass rod with a machined tip rests in the combustion tube and the ground glass joint. It heats up sufficiently during combustion to prevent condensation of water in the ground glass joint. When filling the combustion tube, a small plug of burned asbestos is tamped on the brass rod. Enough lead peroxide to give a layer of 2-3 cm. is then filled into the tube. The lead peroxide retains halogen compounds and nitric oxides and during combustion is kept at a temperature of 180°C . by means of an air bath (Figure 1) heated by gas or electrically. A 3 cm. long layer of lead chromate which acts to retain sulfur compounds is charged on top of the lead peroxide and is in turn superseded with a 16-20 cm. long layer of oxidizing material, either copper oxide or lead chromate. The length of this layer must be considerably increased when the substance to be burned shows a tendency to crack under the formation of methane.

During the combustion the temperature of the oxidizing layer is kept at $700\text{-}750^\circ\text{C}$. while the temperature of the sample heater depends on the character of the sample. The combustion should be carried out in such a manner that an easily combustible low temperature coke is formed which at higher temperatures and in the presence of sufficient oxygen and oxidizing oxides can be burned completely without the formation of graphite-like coke.

* Present Address: Attapulugus Clay Company, Philadelphia, Pa.

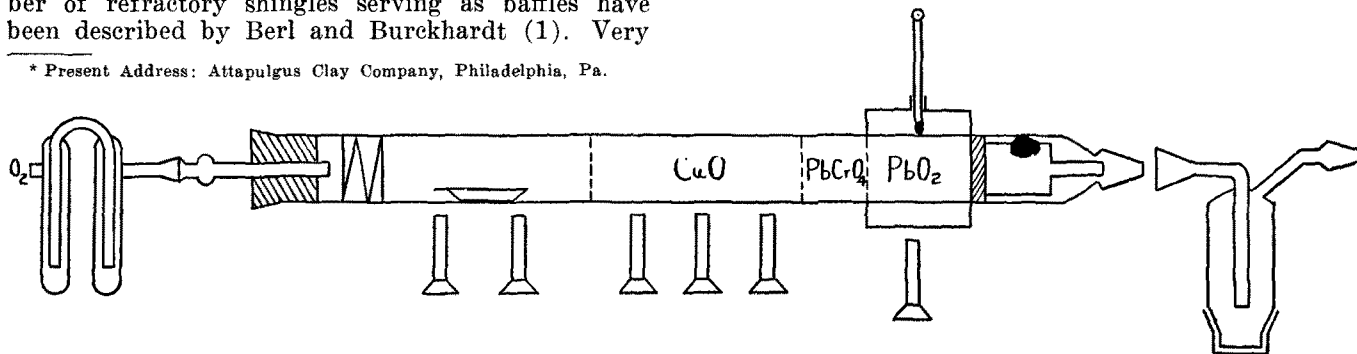


FIG. 1.

TABLE 1
 Analysis of Pure Compounds

	Trinitro Toluene			Cyclohexane			Oxalic Acid			Phthalic Acid			Acetone		
	Theoretical	I	II	Theoretical	I	II	Theoretical	I	II	Theoretical	I	II	Theoretical	I	II
Mg. sample.....	27.3	31.5	20.5	22.0	29.5	27.3	26.1	30.4	21.6	24.2
Mg. CO ₂ absorbed.....	34.4	39.1	64.2	69.0	27.9	26.6	54.5	64.1	49.2	54.9
Mg. H ₂ O absorbed.....	3.2	4.0	2.7	2.8	6.3	5.8	8.9	10.4	20.2	22.9
% C.....	33.7	34.2	33.8	85.7	85.4	85.6	26.7	25.8	26.6	57.8	56.9	57.5	62.1	62.1	61.9
% H.....	1.4	1.3	1.4	14.3	14.6	14.4	2.2	2.4	2.3	3.6	3.8	3.8	10.3	10.4	10.5

The absorption vessels used are illustrated in Figure 1. They have a removable base connected to the body by means of a ground glass joint. The absorption towers are interconnected by ground glass joints, and ground glass joint plugs and caps are provided to stopper the vessels before and after a determination and during weighing. To charge the absorption towers, they are inverted, the base is removed, and small glass wool plugs are inserted into inlet and outlet tubes. The carbon dioxide absorption vessel is filled first with a small amount of anhydrous CaCl₂ which absorbs water generated by the soda lime, followed by a main layer of soda lime. After replacing the base, the tower will stand on a balance pan without wire attachments. The water absorption vessel is charged with the same agent used to dry the oxygen stream.

The usual precautions have to be taken while charging the organic substance to be burned and during combustion. If the substance is liquid and very volatile, as in the case of diethyl ether or carbon tetrachloride, it is advantageously filled into a thin glass bulb which is sealed and inserted into the combustion tube. There the capillary bulb is crushed with a glass rod after the layer of oxidizing agent has been heated red hot. The combustion is carried out in a very slow oxygen stream, controlled by bubble counters at the beginning and end of the train. Depending on the type of compound to be analyzed, an oxygen rate of 0.5 to 2 liters per hour is maintained.

Substances which have a tendency to crack and form difficult-to-burn graphite are mixed in a finely pulverized state with an excess of the oxidizing agent (copper oxide or lead chromate) prior to charging them to the combustion tube. Liquids boiling above 120° C. are dropped on fine copper oxide in a pear-shaped weighing bottle, weighed and poured into the combustion tube. The weighing bottle is then repeatedly washed into the combustion tube with fine copper oxide.

The time consumed in carrying out one determination, including weighings, does not as a rule exceed 90 minutes. It can be reduced by operating several combustion units simultaneously. The chemicals in the combustion tube have to be renewed after about 20 determinations.

The method described was used in carbon and hydrogen determinations of organic substances varying in character from pure compounds to digested and hydrogenated plant products containing considerable inorganic impurities.

Table 1, representing check runs of five samples of pure compounds, indicates that dependable results can be obtained.

Table 2 compares results obtained by semimicro, micro, and macro combustion.

 TABLE 2
 Analysis of a Tar by Semimicro, Micro, and Macro Combustion

	Semimicro		Micro		Macro	
	I	II	I	II	I	II
Mg. sample.....	24.3	27.1	6.13	8.01	541.2	468.3
% C.....	86.2	85.6	86.0	86.7	85.9	86.0
% H.....	7.5	7.6	7.8	7.6	7.5	7.4
% O (by difference).....	6.3	6.8	6.2	5.7	6.4	6.4

Table 3 gives a number of results and checks for samples of different volatility, consistency, and ash content.

 Table 3
 Semimicro Analysis of Different Materials

	Sample 35 Tar		Sample 111 Plant Mat.		Sample 307 Liquid	
	I	II	I	II	I	II
Mg. sample.....	35.1	23.5	37.2	31.2	20.5	22.0
% C.....	76.1	75.9	88.0	87.6	85.4	85.6
% H.....	9.6	10.0	7.9	8.2	14.6	14.4
% O.....	13.7	14.1	4.1	4.2	0	0
% Ash.....	0	0	29.8	29.3	0	0

Summary

A semimicro method for the determination of carbon and hydrogen in organic substances of varying character, consistency, and volatility is discussed. An ordinary analytical balance is used for the weighings. Determinations of high accuracy are made on samples containing 15-20 mg. of carbon in less than 90 minutes.

REFERENCES

- Berl, E., and Burckhardt, H., *Ber.* 59, 890 (1926).
- Berl, E., and Schmidt, A., *Ber.* 65, 978 (1932).
- Berl, E., Schmidt, A., and Winnacker, K., *Ber.* 61, 83 (1928).
- Clark, E. P., *Semimicro Quantitative Organic Analysis*, New York, Academic Press, Inc., 1943.
- Fieser, L., and Fieser, M., *Organic Chemistry*, New York, D. C. Heath and Company, 1944.
- Natelson, S., Brodie, S. S., and Conner, E. B., *Ind. Eng. Chem., Anal. Ed.*, 10, 609 (1938).
- Niederl, J. B., and Niederl, V., *Micromethods of Quantitative Organic Analysis*, New York, John Wiley and Sons, 1942.
- Nieman, C., and Danford, V., *Ind. Eng. Chem., Anal. Ed.*, 12, 563 (1940).
- Pregl, F., *Quantitative Organic Microanalysis*, Philadelphia, P. Blakiston's Son and Company, 1937.
- Scott, W., *Standard Methods of Chemical Analysis*, Vol. 1, New York, D. Van Nostrand Company.
- Sucharda, E., and Bobranski, B., *Semimicro Methods for the Elementary Analysis of Organic Compounds*, London, E. C. 2, A. Gallenkampff and Company, Ltd.

CORRECTION

Legends for Figures 2 and 3 in the article, "Phase Investigations of Fats. I. Apparatus and Techniques for Fat-Solvent Systems at Low Temperatures (pp. 201-204) were transposed in the June issue of *Oil & Soap*. Figure 2 refers to the thermoregulator, and Figure 3 to the equilibration-filtration apparatus.