An Adaptation of Pregl's Microcombustion to a Semi-microcombustion Method for the Determination of Carbon and Hydrogen.

By **Walter M. Lauer** and **Frank J. Dobrovolny.**

(Contribution from the School of Chemistry of the University of Minnesota.)

The methods of quantitative organic microanalysis as developed by FRITZ PREGL[1]) constitute one of the most valuable contributions to the field of organic analysis. In spite of this fact they have not received the attention in the United States which they deserve. This is perhaps largely due to the necessity of using a microbalance, if one wishes to use the amounts recommended by PREGL. For example, this investigator carries out a determination of carbon and hydrogen on a sample which weighs two milligrams. In order to avoid the use of a balance of this accuracy, WISE[2]) has developed a simple and neat modification of PREGL'S[3]) earlier procedure for the determination of carbon and hydrogen. He has shown that if the analyst is content to use 12 to 22 milligrams samples for analysis, the weighings may be performed on a sensitive analytical balance.

During the prosecution of recent work[4]) several groups of substances were obtained which were exceedingly difficult to analyze by the ordinary methods of macrocombustion. The authors have accordingly devised a semimicrocombustion method which is a combination of the method of WISE and of the more recent method of PREGL, together with some modifications. It has been found to possess a number of advantages and has been used with considerable success in several laboratories.

---

[1]) Quantitative Organic Microanalysis. — PREGL. Translated by FYLEMAN; J. & A. Churchill, London.

[2]) J. A. C. S. *39*. 2055—68 (1917).

[3]) F. PREGL, in E. ABDERHALDEN'S Handbuch der Biochemischen Arbeitsmethoden. (i. i.) Vol. 5, 1307—56.

[4]) SMITH and DOBROVOLNY. J. A. C. S. *48*. 1693 (1926).

Description of Apparatus.

Drying Train and Pressure Regulator (A. B. and C in Fig.).

Oxygen from a high pressure tank fitted with a reducing valve is passed through A, an ordinary calcium chloride tube, which contains pieces of solid potassium hydroxide about the size of a pea. These are held in place by plugs of fine glass wool. A is connected to B, the pressure regulator, by means of a piece of "artificially-aged" rubber tubing[5]).

The pressure regulator, B, consists of a tube, about 20 cm. in length and 2 cm. in diameter with a small side-arm. A small tube (5—7 mm. outside diameter) is sealed through this larger tube in the manner indicated in the figure. This is then inserted into a large test-tube (about 16 cm. in length and 4 cm. in diameter) which contains sulfuric acid. The regulator is mounted in such a manner as to allow raising or lowering of this outer test-tube.

The bubble counter, which contains a small of sulfuric acid, together with the phosphorus pentoxide tube, is designated C in the figure. The bubble counter is about 1,5 cm. in diameter and the size of the opening in the inner tube is approximately 1 mm. in diameter. It is connected to the pressure regulator, B, with artificially aged rubber tubing and to the phosphorus pentoxide tube by means of a ground glass joint. The body of the phosphorus pentoxide tube is 1,5 cm. in diameter (outside) and the length avaible for filling with drying agent and glass wool is about 11 cms. This tube may be filled by first inserting a plug of fine glass wool, then alternating with layers of phosphorus pentoxide and thin layers of fine glass wool.

The drying train here described can be used for a large number of determination when ordinary tank oxygen is used. For example, the authors have used one drying train for about one hundred and fifty determinations without refilling.

The Combustion Tube (D and E in Figure).

The tube in which the combustion is carried out is Pyrex glass, 1,5 cm. in diameter (1,2 cm. inside diameter) and 40 cm. long.

---

[5]) All rubber tubing, which is referred to as being artificially aged, was heated at 100° C. in a drying oven for a period of several hours while air was aspirated through it with a water-pump. (See PREGL, Quantitative Organic Microanalysis, p. 17—18.)

The tip is 2 cm. in length with an outside diameter of 5 mm. (3 mm. inside diameter). It is filled according to the following method, which is due to WISE: "First, a pledget of fine glass wool, loosely packed into the constricted portion of the tube; second, a 2,5 cm. layer of asbestos treated with cupric oxide (prepared by impregnating acidwashed asbestos with a concentrated cupric nitrate solution, drying and carefully igniting), containing a few short lengths of cupric oxide wire; third, a 0,5 cm. layer of plain asbestos; fourth, a 1,5 cm. layer of platinized asbestos (prepared by immersing purified asbestos in 10% hydrochloroplatinic acid solution, drying and igniting): fifth, a 0,5 cm. layer of plain asbestos; sixth, a 3,5 cm. layer of asbestos treated with cupric oxide and mixed with cupric oxide wire; seventh, a 0,5 cm. layer of plain asbestos; eighth, a 1,5 cm. layer of platinized asbestos; and finally a 0,5 cm. layer of plain asbestos."

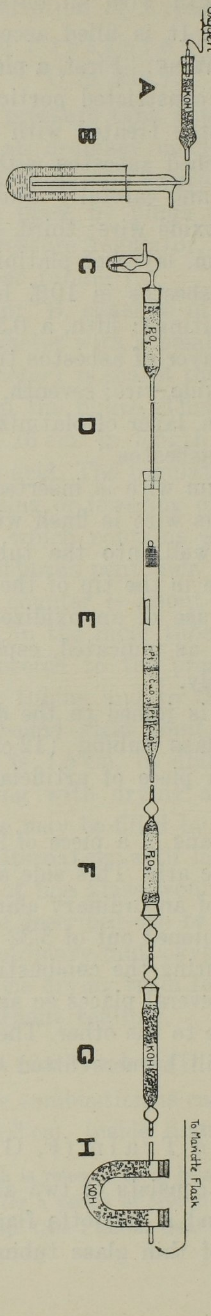
A fairly stout platinum wire is inserted into the small end of the tube. One end of this wire is flush with the tip of the tube, the other end extends well into the tube filling. In this way condensation of moisture in the tip of the tube is prevented. The authors also favor the use of an oxidized copper spiral (about 2 cm. in length), placed as indicated, especially with compounds which sublime very readily.

The combustion tube is joined to the drying train C through a piece of capillary glass tubing (12 cm. long with 0,5 mm. opening) by means of a piece of artificially aged rubber tubing and a rubber stopper.

It is supported by means of a piece of 90° angle iron, provided with a 3/8 inch iron side arm. This side arm is then attached to a ring stand by means of an ordinary clamp holder. Small covers about 2 inches long, fashioned out of 3/32 inch sheet iron, furnish covering for the tube during the combustion. This piece of angle iron may be slotted at several places so as to lessen heat transfer from one end of the tube to the other. The stand is lined with asbestos paper. Two Tirrill burners fitted with wing tops furnish heat for the combustion.

The Absorption Train (F, G and H in Figure).

The absorption train consists of two absorption tubes (F and G), a guard tube, H and a Mariotte flask. The two absorption tubes are constructed of thin glass tubing with an outside dia-


oxygen
KOH
A
B
C
P_2O_5
D
E
Pt
CuO
Pt
CuO
F
P_2O_5
G
KOH
H
KOH
To Mariotte Flask

meter of 12 mm. The one end is provided with a small bulb about 12 mm. in diameter. This bulb connects with the body of the tube through a constriction with a 1 mm. opening. (The outside diameter of this constriction is approximately 5 mm.) The tip of the tube which is joined to this bulb consists of a piece of glass tubing 2,5 cm. in length with an opening of 3 mm. (5 mm. outside diameter). This tip is provided with two constrictions (1 mm. opening) placed about 1 cm. apart and as indicated in the figure.

The other end of the absorption tube is fitted with a well- constructed ground-glass joint. This ground-glass joint serves to connect the body of the tube with a 12 mm. bulb provided with a 2,5 cm. tip. The construction of this bulb and tip is the same at that specified for the end which is farthest removed from the ground-glass joint.

The two absorption tubes, (F and G) differ only in the length of the barrell. The phosphorus pentoxide tube, F, has a barrel 10 cm. in length, and the potassium hydroxide tube, G, is provided with a 13 cm. barrel.

The phosphorus pentoxide tube is filled in the following manner. A plug of fine glass wool is first inserted and pushed into place by means of a glass rod. Alternating thin layers of phosphorus pentoxide and glass wool are then introduced until the tube is filled. The last layer introduced should be glass wool and care must be taken to remove bits of glass wool from the ground surface of the tube. A minimum amount of a heavy stop-cock grease is used on this joint. All ground glass connections must be examined very carefuly and any grease which protrudes should, of course, be removed.

The potassium hydroxide tube, G, is filled in the following manner. A plug of fine glass wool is first introduced and pushed into place. Small pieces of potassium hydroxide about the size of flax-seed are then placed into the end of the tube. The tube is then filled with pieces of potassium hydroxide, the pieces gradually becoming larger and larger until finally, the last three or four centimeters of the barrel are filled with pieces about the size of a pea or even a trifle larger. Finally a piece of fine glass wool is introduced to hold the potassium hydroxide in place. The ground surface of the glass joint is cleaned. A heavy stop-cock grease is also used on this joint.

Phosphorus pentoxide and potassium hydroxide tubes prepared in this manner can be used for about twenty determinations without recharging. Care must be exercised in the filling of the potassium hydroxide tube or else the tube will become clogged after a small amount of carbon dioxide has been absorbed. For this reason it is important that relatively coarse pieces of the absorbent be used in the end of the tube which is directed towards the combustion tube. After the analyst has once learned how to fill these tubes, this difficulty will disappear.

The guard tube, H, is a small U-tube filled with pieces of potassium hydroxide about the size of a pea. This filling is held in place with glass wool. Ordinary rubber stoppers close the ends of the U-tube.

The Mariotte flask consists of a large aspirating bottle of about 2 l. capacity. The neck of the top of this bottle is fitted with a two-holed rubber stopper. This stopper carries an ordinary stop-cock extending a short distance through the stopper and a glass tube extending to within about one inch of the bottom of the aspirating bottle. This glass tube is connected to the one side of the guard tube H by means of a piece of rubber tubing. The outlet of the aspirating bottle is fitted with a well-fitting cork stopper, which carries a piece of glass tubing. This glass tubing extends several inches into the aspirating bottle and after passing through the cork stopper bends at 90° and passes up along side of the aspirating bottle to the top.

The rubber connections.

The rubber tubing for the connections between (a) the combustion tube, E and the phosphorus pentoxide tube F, (b) the phosphorus pentoxide tube, F and the potassium hydroxide tube, G and (c) the potassium hydroxide tube, G and the guard tube, H, is impregnated. For connection (a) the impregnating material is paraffin, while in the cases of (b) and (c) vaseline is used. This simple operation is carried out as follows: The tubing (thick-walled) is cut into lengths of 2—2,5 cm. These are placed in a suitable flask and covered with molten vaseline or paraffin, as the case may be. The flask is then connected with a vacuum pump. After about 20 minutes no more bubbles will arise from the pieces of rubber tubing. They are then brought to atmospheric pressure. After most of the impregnating material has been allowed to drain off, the openings in the pieces of tubing are cleaned out with a small cloth moistened with glycerine, and finally with a dry cloth.

The rubber tubing which is used to cap the absorption tubes is cleaned with a glass rod moistened with glycerine and then wiped dry with a cloth.

Detailed Procedure.

"Burning out" the Combustion Tube. The combustion tube is heated by means of two Tirrill burners, which have been provided with fish-tails, while a slow stream of oxygen is passed through the tube. The analyst should satisfy himself that the tube has been completely "burned out" by running a blank determination. The details of the procedure for a blank determination are similar to those of an actual determination and therefore are not enumerated separately.

Weighing Absorption Tubes and Sample. During the time required for "burning out" the combustion tube, the absorption tubes and the sample are weighed. These weighings are performed as follows: The capped absorptions tubes are wiped with a cloth moistened with water until they are perfectly clean. They are then wiped with a dry cloth and allowed to stand near the balance for a period of about twenty minutes. A rack fashioned out of aluminum wire serves as a convenient method of support for the absorption tubes. After twenty minutes have elapsed, the caps are removed and the tubes are carefully transferred to the balance pan. A small cradle constructed of aluminum wire supports the tube on the balance pan. The tube is then weighed to the nearest 0,05 mgm.

The sample is weighed into a small boat. (The authors have used a boat constructed of platinum foil. In the case of some substances, e. g. ozonides, a porcelain boat was prefered on account if its lower thermal conductivity). A sample of about twenty milligrams is used. Here again, the weighings are made to the nearest 0,05 mgm.

The Combustion Proper. During the latter part of the procedure described under the weighings the burner nearest the bubble counter is turned off. After the end of the tube has cooled sufficiently the absorption train is connected to the combustion tube, the drying train is disconnected from the combustion tube, the oxidized copper spiral is removed by means of a suitable hook and the boat containing the sample is introduced. The oxidized copper spiral is replaced, the drying train is connected to the combustion tube, and the water is started to flow drop-wise from the Mariotte flask into a graduate. The operations are carried out in this order and without delay. The burner which was turned off is now lighted, after removing fish-tail, and placed under the copper spiral. The burner nearest the absorption train has been allowed to burn continuously during these operations. The heating of the sample is carried out in such a manner as to require about 15 minutes for its oxidation. The fish-tail is then placed on the burner nearest the drying train and the heating continued until the boat has been burned clean, at which time this burner is turned off. Experience soon enables the operator to control the rate of combustion. Any moisture which may have collected in the end of the phosphorus pentoxide tube is removed by grasping this end between the warm prongs of a pair of crucible tongs. About 100 cc. of oxygen is then aspirated through the apparatus to sweep out the last amounts of carbon dioxide and water. The flow of water from the Mariotte flask is then discontinued, and the absorption train is disconnected from the combustion tube.

The experienced analyst will have a second pair of weighed absorption tubes and a second sample available at this time, for the apparatus is now ready for another combustion.

The absorption tubes which were used for the first sample are then attached to a second potassium hydroxide guard tube and Mariotte flask. Air which has been passed through a purfying train containing phosphorus pentoxide and potassium hydroxide is then aspirated through the absorption tubes in order to displace the oxygen. About one hundred cc. of air suffices for this purpose. Instead of this procedure the analyst may find it preferable to fill the absorption tubes with oxygen before their first weight is taken. The tubes are then capped, wiped and finally after standing for about twenty minutes are weighed in the manner previously described.

With a little experience, it is possible to carry out seven or eight analyses in an eight hour day. Furthermore, the results obtained by students, who were unfamiliar with both this method and that of macro-combustion, have convinced the authors that the technique of the method here described is acquired more easily than that of the macro-combustion. This is most probably due to the accurate control of the combustion which is afforded by the use of the oxygen pressure regulator and the Mariotte flask. The adaption of these two devises for this purpose is due to the excellent work of PREGL.

Results.

The following typical analyses were carried out using the above procedure. The substances analyzed, which contained only carbon, hydrogen and oxygen, were materials obtained from different sources and no attempt at further purification was made.

This method can be extended to include compounds which contain other elements, by making suitable changes in the tube filling.

Table I.

Substance analyzed	Found %H	Found %C	Calc. %H	Calc. %C
Vanillin	5,3	63,2	5,30	63,13
	5,4	63,5		
	5,3	63.2		
Salicylic Acid	4,6	60,7	4,38	60,86
	4,5	60,7		
Benzoic Acid	5,0	68,8	4,95	68,82
	5,0	68,7		
Anthraquinone . . .	4,0	80,4	3,88	80,75
	3,9	80,5		
	3,8	80,5		
Duroquinone	7,4	73,1	7,37	73,12
	7,5	73,2		
	7,5	73,2		
	7,5	72,9		
Resorcinol	5,6	65,2	5,50	65,42
Mannitol	7,6	39,7	7,75	39,54
	7,8	39,7		
Anisic Acid	5,3	62,8	5,30	63,13
	5,4	62,8		
Benzalacetophenone .	5,9	86,7	5,81	86,50
	5,8	86,5		
Hydroduroquinone . .	8,6	72,2	8,50	72,25

Summary.

1. A semi-microcombustion method for the determination of carbon and hydrogen, which is a combination of the method of Wise, of the more recent method of Pregl, together with some modifications, has been described.

2. The results obtained by its use in the case of compounds containing only carbon, hydrogen and oxgen are as satisfactory as those obtained by the methods of micro-combustion, and they are more conveniently obtained.