Determination of Carbon in Organic Compounds by the Iodic Acid Decomposition Method

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In the previous papers the author and his co-workers have already reported that by using a mixture of potassium iodate and strong phosphoric acid, elementary carbons[1], oxidation values of organic compounds[2], and nitrogen in organic compounds[3,4] can be simply and rapidly determined. Among these methods the determinations of carbon contents in elementary carbons, such as graphite, active carbon and so on, containing some inorganic substances, and those of oxidation values of organic compounds composed of carbon, hydrogen, and oxygen are based on the following reactions, respectively,

$$5C+4HIO_3=5CO_2+2H_2O+2I_2$$

$$\begin{aligned}5C_kH_mO_n+2(2k+m/2-n)HIO_3\\=5kCO_2+(2k+3m-n)H_2O\\+(2k+m/2-n)I_2.\end{aligned}$$

Carbon contents in elementary carbons as well as oxidation values of organic compounds can be indirectly determined by titrating the liberated iodine in the above reactions.

If it is possible to estimate the liberated carbon dioxide by any suitable method in the above-mentioned reactions, it may be possible to determine directly the carbon contents in elementary carbons and in organic compounds.

The present investigation has aimed at establishing a new direct method for the determination of carbon in organic compounds by means of iodic acid decomposition followed by titrimetric estimation of the liberated carbon dioxide. The investigation on the direct determination of carbon in elementary carbons is now undertaken in this laboratory and will be reported later.

For the present study the investigation of direct semimicrodetermination of oxygen in organic substances achieved by R. D. Hinkel and R. Raymond[5] serves as a good reference. They described the fact that carbon monoxide formed in the pyrolysis of an organic compound is oxidized with iodine pentoxide, the resulting carbon dioxide is absorbed in a measured excess of 0.05 N alkali, and the excess is back-titrated with 0.025 N acid after precipitation of the carbonate formed with barium chloride.

In the present investigation, using a carbon dioxide absorber of a special type and an anhydrous sodium thiosulfate-filled iodine absorber, which were devised by Hinkel and Raymond, satisfactory results have been obtained. In this paper the recommended apparatus, reagents, and procedure for this method, the analytical results of several organic compounds, and the discussion concerning them are described.

Apparatus

The apparatus used in this study is illustrated in Fig. 1. It is mainly composed of three parts, a reaction vessel A, a carbon dioxide absorber B, and an iodine absorber K.

Into the reaction vessel A a gas-introducing tube H and a thermometer F, which is covered with a thermometer-protecting tube G, are inserted. These tubes are attached to the vessel A with rubber tubes. After passing through a concentrated solution of sodium hydroxide, a soda lime-filled tube, and concentrated sulfuric acid in turn, the air free from carbon dioxide is introduced by means of a suction pump into the vessel A through the three-way stopcock D of a water-addition funnel C, which is used to add water to the vessel A after the decomposition of a sample. The vessel A is heated at the bottom with a samll electric heater J, the temperature of which can be regulated with a transformer. The left arm of the vessel A is connected to the absorber B through the iodine absorber K filled with anhydrous sodium thiosulfate and a stopcock L.

The carbon dioxide absorber B is the same one that was used by Hinkel and Raymond. The tube B is closed at the top by means of a rubber stopper, through which the capillary tips of two burets, Q and N, containing standard solutions of hydrochloric acid and sodium hydroxide, respectively, and the tip of a reagent-addition tube R are inserted. The standard solution of sodium hydroxide is introduced from its reservoir to the buret by the compressed air. At the top of the buret N and the left side arm of the absorber B there are soda lime-filled guard tubes, P and S.

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[1] T. Kiba, S. Ohashi, T. Takagi, and Y. Hirose, *Japan Analyst*, **2**, 446 (1953).

[2] S. Ohashi, This Bulletin, **28**, 171 (1955).

[3] S. Ohashi, ibid., **28**, 177 (1955).

[4] S. Ohashi, ibid., **28**, 537 (1955).

[5] R.D. Hinkel and R. Raymond, *Anal. Chem.*, **25**, 470 (1953).

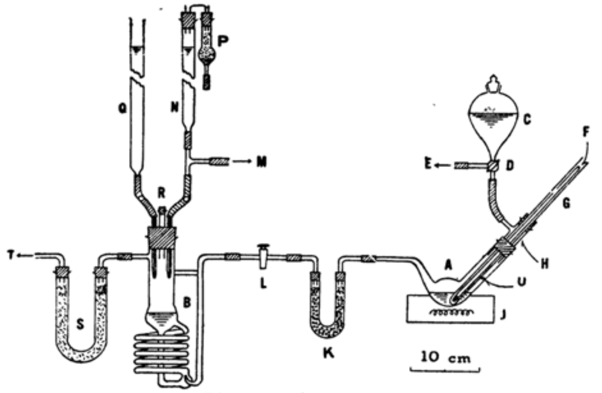

Fig. 1. Apparatus

A: Reaction Vessel
B: Carbon Dioxide Absorber
C: Water-Addition Funnel
D: Three-Way Stopcock
E: To an Apparatus Preparing the Carbon Dioxide-Free Air
F: Thermometer
G: Thermometer-Protecting Tube
H: Gas-Introducing Tube
J: Electric Heater
K: Iodine Absorber
L: Stopcock
M: To a Sodium Hydroxide Reservoir
N: Buret of Sodium Hydroxide
P: Soda Lime-Filled Guard Tube
Q: Buret of Hydrochloric Acid
R: Reagent-Addition Funnel
S: Soda Lime-Filled Guard Tube
T: To a Suction Pump
U: Small Glass Hook

Reagents

Potassium Iodate.—Extra pure grade potassium iodate was used.

Strong Phosphoric Acid.—About 400 g. of extra pure grade 89% orthophosphoric acid was dehydrated by heating until the temperature of the liquid reached 320°C. Its specific gravity was 1.96.

Anhydrous Sodium Thiosulfate.—Sodium thiosulfate having 5 mol. of water of crystallization was dehydrated in vacuo at 40°C on a water bath. The resulting white anhydrous salt was crushed and its coarse fraction was used.

Standard Solution of Hydrochloric Acid.—A 0.1 N hydrochloric acid solution standardized against pure anhydrous sodium carbonate was used.

Standard Solution of Sodium Hydroxide.—A 0.1 N sodium hydroxide solution standardized against 0.1 N hydrochloric acid described above was used. According to Hinkel and Raymond, the sodium hydroxide pellets used must contain at least 2.5% by weight of sodium carbonate. If this quantity is not present, an appropriate amount should be added to the solution. The standardization was carried out by means of the method described in the section of procedure.

Barium Chloride.—A 10% solution of extra pure grade barium chloride was used.

Thymol Blue.—A 0.1 % solution of thymol blue was used.

Procedure

Weigh accurately a 10 to 60 mg. of sample, depending upon its carbon content, into a small weighing tube; choose the sample weight so that the liberated carbon dioxide will consume about 50% of the sodium hydroxide used. Add 4 to 5 ml. of strong phosphoric acid and two or three times as much of the theoretically required amount of potassium iodate into the vessel A. Into the carbon dioxide absorber, and 3 drops of the indicator solution of thymol blue. Hang the weighing tube containing the sample on the small glass hook U of the thermometer-protecting tube G. Connect all of the apparatus and make sure that it is tight. Sending carbon dioxide-free air from E through the apparatus by a suction pump, expel all the air containing carbon dioxide, present in it. Then add 25 ml. of 0.1 N sodium hydroxide to the absorber B from the buret N.

Stop the suction, close the stopcock D, and open the stopcock L a little. Let the weighing tube containing the sample fall in the reaction medium by rotating the thermometer-protecting tube G. Then, gently heat the bottom of the vessel A with a small electric heater J. During the decomposition reaction keep the temperature of the reactants between 180° and 230°C, and regulate the stopcock L so that 2 bubbles of gas per second pass through the inlet of the absorber B. The greater part of the liberated iodine is sublimed and condensed on the inside wall of the vessel A. The small part of it is sent to the tube K and absorbed on anhydrous sodium thiosulfate. After the end of the decomposition reaction, stand the vessel A aloof from the heater until the temperature of the reaction medium falls to about 140°C. Apply gentle suction and open the stopcock D to introduce about 10 ml. of carbon dioxide-free water into the vessel A. Then heat once more the aqueous solution in the vessel A on the heater to expel the remaining carbon dioxide in the reaction medium. Then take away the heater and continue drawing air through the apparatus, at the rate of 2–3 bubbles per second for about fifteen minutes, in order to get all the carbon dioxide into the absorber B.

From the reagent-addition tube R quickly add 10 ml. of 10% barium chloride to the absorber solution and close the top of the tube R. Then, applying rapid suction, titrate the remaining sodium hydroxide with 0.1 N hydrochloric acid until the blue color of thymol blue is changed to the light yellow one.

From the volumes of 0.1 N sodium hydroxide and 0.1 N hydrochloric acid used in the experiment the carbon content of the sample is calculated.

The standardization of 0.1 N sodium hydroxide is carried out as follows. After removing the air containing carbon dioxide from the apparatus, 25 ml. of 0.1 N sodium hydroxide, 3 drops of the indicator solution, and 10 ml. of 10% barium chloride are added to the absorber B and this solution is titrated with 0.1 N hydrochloric acid, stirring the contents of the absorber B by letting the carbon dioxide-free air flow rapidly.

Results and Discussion

At first, in order to examine the purity of the carbon dioxide-free air used in this study, after passing the air through a measured amount of 0.1 N sodium hydroxide in the absorber B for twenty to forty minutes, it was titrated with 0.1 N hydrochloric acid in the same manner as in the standardization of sodium hydroxide described above. As shown in Table I the ratios of the volumes of 0.1 N sodium hydroxide and 0.1 N hydrochloric acid were almost equal to that in the case without aeration.

TABLE I

EXAMINATION OF THE PURITY OF THE CARBON DIOXIDE-FREE AIR USED

Aeration min.	$\frac{0.1\text{ N HCl ml.}}{0.1\text{ N NaOH ml.}}$
0	1.000
20	0.999_8
30	0.996_7
30	1.002_4
40	1.000_4

If the vapor of phosphoric acid is expelled from the reaction medium by heating and if it is absorbed in sodium hydroxide solution, it causes a serious error. In order to examine this point, two kinds of strong phosphoric acid having the specific gravity 1.93 and 1.96 were used. To the vessel A 5 ml. of the strong phosphoric acid was added and heated at various temperatures for fifteen minutes, while the vapor expelled from the medium was sent by the air stream into a definite amount of 0.1 N sodium hydroxide. From the results shown in Table II it was found that the strong phosphoric acid of the specific gravity 1.93 can not be used for the present purpose and that of the specific gravity 1.96 should be used.

TABLE II

EFFECT OF THE VAPORIZATION OF STRONG PHOSPHORIC ACID

Specific Gravity of Strong Phosphoric Acid	Temp. °C	$\frac{0.1\text{ N HCl ml.}}{0.1\text{ N NaOH ml.}}$
1.93	Room Temp.	1.000
〃	167	0.989_8
〃	181	0.998_6
〃	200	0.987_9
1.96	Room Temp.	1.000
〃	230	1.000_6
〃	235	1.000_9

Next, using sodium carbonate as a sample, preliminary experiments were undertaken to examine some conditions. The results obtained are shown in Table III. These experiments indicated that after the decomposition reaction, the reaction medium should be diluted with water and heated once more to expel the carbon dioxde dissolved in strong phosphoric acid. Also the time required to expel the carbon dioxide present in the apparatus is within fifteen minutes.

TABLE III

DETERMINATION OF CARBON IN SODIUM CARBONATE

Carbon Content Calculated: 11.33%

Sample Weight mg.	Carbon Content Found %	Carbon Content Deviation %	Expelling Time min.	Remarks
52.5	10.5	−0.8	15	Without additon of water
55.6	10.6	−0.7	30	
74.7	10.6	−0.7	15	
77.0	11.1	−0.2	30	
52.8	11.2	−0.1	15	With addition of water
55.5	11.3	0.0	15	
57.4	11.3	0.0	13	
66.4	11.4	+0.1	15	
70.5	11.2	−0.1	15	
72.5	11.3	0.0	15	

Analyses of various known organic compounds, oxalic acid, sodium oxalate, tartaric acid, dulcitol, arabinose, alanine, urea, and methylred were carried out by this method. Thess results are summarized in Table IV. The accuracy of the data is within ±2%. The time required for one analysis is about fifty minutes.

The absorption tube used in this method is very advantageous for the determination of carbon dioxide, because the addition of alkali solution as well as the titration with acid solution can be done under the condition in which carbon dioxide present in the

TABLE IV
DETERMINATION OF CARBON IN ORGANIC COMPOUNDS

Substance	Carbon Content	Sample Weight	Carbon Content	
			Found	Deviation
	%	mg.	%	%
Oxalic Adid $C_2H_2O_4 \cdot 2H_2O$	19.05	40.2	19.2	+0.1
		41.5	19.2	+0.1
		51.1	19.5	+0.4
		57.4	19.1	0.0
		44.2	18.8	−0.3
Sodium Oxalate $Na_2C_2O_4$	17.93	40.3	18.0	+0.1
		44.0	18.0	+0.1
		46.9	18.0	+0.1
		54.2	17.9	0.0
Tartaric Acid $C_4H_4O_6$	32.01	23.1	32.1	+0.1
		25.3	32.1	+0.1
		27.1	32.4	+0.4
		28.2	31.9	−0.1
Dulcitol $C_6H_{14}O_6$	39.56	20.4	39.6	0.0
		21.5	39.6	−0.6
		27.5	39.4	−0.2
		27.5	39.4	−0.2
Arabinose $C_5H_{10}O_5$	40.00	23.5	39.6	−0.4
		24.5	40.0	0.0
		27.3	39.7	−0.3
		32.1	39.6	−0.4
Alanine $C_3H_7O_2N$	38.70	11.7	39.1	+0.4
		15.7	38.5	−0.2
		18.9	38.9	+0.2
		25.6	38.7	0.0
Urea CH_4ON_2	20.00	33.8	20.0	0.0
		35.9	19.8	−0.2
		36.6	20.4	+0.4
		40.8	19.9	−0.1
		47.7	19.9	−0.1
Methylred $C_{15}H_{15}O_2N_3$	66.90	13.4	65.9	−1.0
		14.2	66.4	−0.5
		15.0	66.0	−0.9

atmosphere is excluded perfectly from the titrating system.

For the determination of carbon in organic substances Pregl's dry combustion method has so far been commonly used. However various wet combustion methods have been recently developed to overcome the defects of Pregl's method. Among others the investigations of D. D. Van Slyke and his coworkers[6] are very remarkable. The present method reported by the author is also one of the wet combustion methods for the determination of carbon in organic compounds. As regards the time required for analysis and the accuracy of data the author's method is inferior to that of Van Slyke, but as regards the inexpensiveness of the apparatus and the simplicity of the analytical techniques the former is superior to the latter. The present method can not be applied to volatile compounds. The applicability of the author's method should be further investigated and the improvement of the apparatus is also a problem remaining for the future.

Summary

(1) A new wet combustion method for the determination of carbon in organic compounds has been developed.

(2) A sample is decomposed by heating with a mixture of potassium iodate and strong phosphoric acid. The liberated carbon dioxide is absorbed in 0.1 N sodium hydroxide, using a spiral type absorber. After adding barium chloride solution the excess sodium hydroxide is titrated with 0.1 N hydrochloric acid, using thymol blue as indicator, in the absorber.

(3) A part of the liberated iodine is absorbed into the tube filled with anhydrous sodium thiosulfate in order to avoid the absorption of the iodine in the alkali solution in the absorber.

(4) Analyses for several organic compounds gave satisfactory results. Using 10 to 60 mg. of samples, the accuracy was within ±2%. Analysis time for one sample is about fifty minutes.

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[6] e.g., D.D. Van Slyke, *Anal. Chem.*, 26, 1706 (1954).