0

B7L 1543

UNCLASSIFIED

W-2512

The Wet Carbon Combustion and Some of Its Applications

(1953 Fisher Award Lecture)

by

Donald D. Van Slyke

Brookhaven National Laboratory, Upton, N. Y.

This report has been photostated to fill your request as our supply of copies was exhausted. If you should find that you do not need to retain this copy permanently in your files, we would greatly appreciate your returning it to TIS so that it may be used to fill future requests from other AEC installations.

(This research was done under the auspices of
the Atomic Energy Commission)

This document is

PUBLICLY RELEASABLE

Larry C. Williams
Authorizing Official

Date: 08/03/2007

6623 01

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The dry combustion of carbon has been developed to such precision and convenience that one may well ask what need there is for an alternative wet combustion. There are, however, some conditions under which the dry combustion offers difficulties, and other conditions where the wet combustion offers advantages in speed and convenience, or accuracy. For some substances, the dry combustion requires modification. Explosive materials require special handling. If alkali or alkali-earth metals are present, the procedure must be modified, or CO_2 will be held back as alkali carbonate. Arsenic, antimony, bismuth and mercury, if present in the sample, become volatilized and ruin the filling of the combustion tube. Boron and thallium have also been reported to interfere. For combustion of biological material, it is often inconvenient to get the sample into a boat for the dry combustion. Occasionally substances have been found to defy accurate analysis by dry combustion; the ease with which complete combustion to CO_2 is attained can vary greatly. I recall an encounter with this variability when I was doing combustions in P. A. Levene's laboratory with the method of Dennstedt, in which platinum is used

to catalyze the dry combustion. I had been using this method for amino acids, with which the combustion part of the analysis was easily completed in 15 minutes. But when I attempted to burn lipids, extreme caution and two hours were required to avoid low results from escape of carbon monoxide.

Attempts to devise satisfactory wet combustions, usually with oxidation by chromic acid, go back nearly a hundred years. But the first that appears to have been accepted as accurate by the standards of the organic chemist appears to be that published by Messinger in 1890 (1). Messinger oxidized with a mixture of sulfuric and chromic acids, and then led the gases over heated copper oxide to burn any carbon monoxide that might escape the chromic acid. The method was really a combination of the dry and wet combustions. It was exact, but it was complicated, and took 2 hours for completion.

Klüster and Stallberg (2) in 1893, encountering a trimethyl aromatic compound that gave results about 9 per cent too low by dry combustion, applied Messinger's combined dry-and-wet combustion and simplified it in detail so that the combustion could be

finished in shorter time. Klüster and Stallberg's procedure is given in Hans Meyer's "Organic Analyses," 1938 edition, as still the standard wet combustion method for precise results.

For carbon determination in biological material, the Messinger-Klüster-Stallberg method is too complicated to be convenient when numerous analyses are required. The wet combustion has consequently been applied to biological problems by many investigators in simplified forms, with omission of the cupric oxide-charged combustion tube. With such procedures, using chromic acid in most cases, it has been possible to obtain quantitative results with many substances and approximate results with others, but the wet combustion thus simplified did not attain use for precise organic analysis.

The basic problem that had to be solved to make the wet combustion both convenient and precise was the development of an oxidation mixture that would by itself give theoretical yields of CO₂ with organic substances in general.

During work on the isolation of hydroxylysine from protein hydrolysates, it became desirable in our laboratory to obtain accurate ratios of total nitrogen, amino nitrogen and carbon in solutions of amino acids during the process of repeated fractionation, and the desirability of a quick and accurate wet combustion led to the attempt to devise an oxidizing mixture which would reliably convert organic carbon completely to carbon dioxide. It was finally found (3) that when iodic and chromic acids together were used in an approximately anhydrous medium made by mixing fuming sulfuric with phosphoric acid, combustion was complete in one or two minutes with a wide variety of compounds, including fatty acids, cholesterol, and acetylated sugars. This combustion mixture was attained after many discouraging trials, which at one time led us to revert to the accessory tube with heated copper oxide. For convenience we will call the above combustion mixture of Van Slyke and Folch the "anhydrous" mixture. Per 100 ml., it originally (3) consisted of 67 ml. of fuming sulfuric acid ("20 per cent SO_3 "), 33 ml. of phosphoric acid of specific gravity 1.72, 5 gm. of CrO_3 ,

and 5 gm. of KIO_3 . At room temperature the mixture was supersaturated with respect to HIO_3 , but a solution prepared with heat would hold its iodic acid for a working day. For most substances it sufficed to use a stock solution of CrO_3 in the acid mixture, and add pulverized KIO_3 with the organic sample in the combustion tube; the iodate dissolved as soon as the chromic acid mixture was heated. Carbohydrates, however, appear to require the presence of iodic acid from the start of the reaction in order to avoid escape of slight amounts of carbon monoxide.

Eventually (4), the oxidizing mixture was modified to the two forms given in Table I. For a combustion the sample and solid reagent are placed in the combustion vessel and the latter is connected with apparatus to absorb or freeze (liquid N_2) the CO_2 evolved. The liquid reagent is then added and the mixture is heated for about 1.5 minutes after the initial CO_2 evolution is finished and apparent boiling has begun. The "apparent boiling" is in fact evolution of O_2 from the CrO_3 . The acid mixture does not reach its own boiling point. For the reagent for carbohydrates,

which is 90 per cent iodate, the 1:1 mixture of ordinary concentrated sulfuric and phosphoric acids is a medium preferable to the anhydrous acid mixture, because reaction in the former occurs without decomposition of iodate to I_2 . Such I_2 as is formed is due to reaction of HIO_3 and organic matter.

As long as Cr^{VI} is present, any free iodine formed is oxidized back to iodic acid. It is undesirable and unnecessary to continue heating the "anhydrous" reagent until all Cr^{VI} has lost O_2 and changed to Cr^{III} , and evolution of I_2 has begun.

The above outlined combustion mixtures have been used in different laboratories with various procedures, gravimetric, titrimetric, and gasometric, to measure the CO_2 evolved.

The first procedure (3) employed with the new reagents was absorption of the CO_2 by NaOH in the manometric apparatus of Van Slyke and Neill, and manometric measurement of the CO_2 gas subsequently set free by addition of acid. This is still routine in our laboratory. A similar procedure with this apparatus, but with chromic acid oxidizing mixtures of more limited application, was

first employed by Backlin (5) in 1930 in Sweden, and by the writer, Page, and Kirk (6). It has been modified with regard to construction as well as reagents (3,4).

The combustion is carried out in a test tube of about 15 ml. capacity (or 25 ml. for semi-micro analyses with 4-15 mg. carbon (see Table I)) attached to the chamber of the manometric apparatus. The evolved CO_2 is absorbed in the manometric chamber by alkali solution which contains hydrazine to reduce any halogens set free by the combustion. The absorbed CO_2 is set free from the alkali solution by addition of acid, the CO_2 gas is brought to a definite volume, either 2, 10, or 46 ml., depending on the size of the carbon sample (see Table I), and the pressure exerted by the liberated CO_2 gas is measured on the manometer. Combustion and manometric measurement can be completed in 15 minutes. With the same apparatus one can do an "ultra-micro" analysis with 0.2 to 0.7 mg. of carbon, a "micro" analysis with 1 to 3 mg. as in the usual dry micro combustion, or a "semi-micro" analysis with 5 to 15 mg. of carbon, putting the gas at different volume marks in the manometric chamber

for the pressure measurements. The details were developed in their final form with Dr. Jordi Folch and John Plazin (3,4).

Completeness of the combustion and accuracy of the manometric measurement are almost automatic. The step that requires some attention is the transfer of CO_2 from the combustion tube to the alkali in the manometric chamber. This is accomplished by raising and lowering the mercury and alkali solution in the chamber after the combustion is completed and while the combustion tube is still attached to the chamber. Twenty excursions made in the course of 3 minutes absorb all the CO_2 . To obtain absorption in this time it is necessary to limit the amount of gases other than CO_2 in the system. Presence of much oxygen or nitrogen gas retards the passage of CO_2 into the alkali. Hence, after the apparatus has been connected as shown in Fig. 1, and before either the alkali solution has been added to the manometric chamber or acid to the combustion tube, about 90 per cent of the air is evacuated from the combustion tube by drawing the air twice in succession from the combustion tube over into the 50 ml. chamber and ejecting it, the chamber

and its mercury serving as an air pump. Also, in order to avoid evolution of an excess of oxygen gas from the chromic acid, the combustion fluid is boiled gently without unnecessary heat and only for 1.5 minutes. With these conditions, the transfer is complete and results such as those in Table II are uniformly obtainable.

For weighing dry samples of 3 to 8 mg., used for "micro" combustions, the aluminum scoop shown in Fig. 2 is used. It can be made in a few minutes from a sheet of aluminum. Being metallic, it is not subject to the electrostatic trouble that afflicts glass weighing vessels in dry winter weather. For the wet combustion, it is made of such length that it deposits the sample in the bottom of the combustion tube. The scoop is weighed before and after discharging the sample.

When the sample is in solution, either in water or in a volatile organic solvent, an aliquot is evaporated to dryness in the combustion tube, and the analysis performed on the residue.

As indicated by Table II, the error is usually less than 0.3 per cent of the amount of carbon determined when the analysis is made on samples containing 2-3 mg. of carbon, the CO_2 being measured by the pressure that it exerts at 10 ml. volume. When submicro analyses are done with samples of 0.3 to 0.7 mg. of carbon and measurement of the CO_2 pressure at 2 ml. volume; the usual limit of error is about ± 0.5 per cent.

It is desirable to have the accuracy of a procedure checked in more than one way. McCready and Hassid (7) have provided such control by applying the Van Slyke-Folch combustion mixture and measuring gravimetrically the CO_2 evolved. Their apparatus is shown in Fig. 3. The gases from the combustion tube are passed through zinc to remove acid, through a drying tube to remove water, and the CO_2 is then absorbed by soda lime as in dry combustions. (The reflux condenser is really not necessary.) The results shown in Table III are of such accuracy that these investigators state that the method is as accurate as the classical dry combustion.

In Fig. 4 is shown an arrangement, extreme in its simplicity, used by Lindenbaum, Schubert, and Armstrong (8) for gravimetric measurement of CO_2 yielded by the "anhydrous" combustion mixture. The CO_2 in this case is absorbed in barium hydroxide solution. The two chambers are evacuated before the acid of the combustion mixture is added. The O_2 evolved from the mixture by continuing the heating after the combustion proper is over serves to drive the last portions of CO_2 over into the barium hydroxide solution. The BaCO_3 precipitate is weighed. With semi-micro samples of 10 to 15 mg. of carbon, results similar in accuracy to those of McCready and Hassid were obtained.

Titration of the CO_2 liberated by the "anhydrous" wet combustion has also yielded theoretical results accurate within the limits of the titration procedure. In a procedure developed by Farrington, Niemann, and Swift (9), the CO_2 is absorbed in sodium hydroxide from which it is then precipitated as barium carbonate. Adherent alkali on the centrifuged BaCO_3 is neutralized, and the BaCO_3 is determined by dissolving in excess 0.05 N hydrochloric

acid, boil off the CO_2 , and titrating the excess HCl with 0.05 N alkali. Some of the results obtained are shown in Table III.

We now pass to some applications of the wet combustion.

It affords the most precise micro method for the total fats of blood serum. The procedure now used at Brookhaven (10) is as follows: Proteins and fats are precipitated together by zinc hydroxide after diluting the serum with 25 volumes of water in a centrifuge tube. The precipitate is washed with water in the centrifuge tube to complete the removal of water-soluble extractives.

The washed residue is then mixed with enough 2 to 1 chloroform-methyl alcohol lipid solvent, introduced by Folch (11), to make the total volume 25 times that of the serum sample, and the protein precipitate is centrifuged down. Aliquots of the supernatant lipid solution are measured into combustion tubes, dried, and the carbon is determined in the residue. The 0.5 mg. of fat from 0.1 ml. of normal serum suffices for an analysis precise within 1 part in 200. The determination of lipid carbon is analogous to that of protein nitrogen.

Another micro determination is that of serum proteins, introduced by Hoagland (12), who preferred it to the micro-Kjeldahl. Proteins in a sample of 0.02 ml. of serum are precipitated in the centrifuge-combustion tube (Fig. 5) with alcohol-ether, and are washed with the same solvent to remove lipids. The protein precipitate is then dried and the carbon is determined.

The manometric wet combustion has been used in micro determination of several elements which form precipitates with organic reagents. The precipitations are made in a combustion tube tapered at the bottom as shown in Fig. 5, so that it can be used to wash the precipitates by centrifugation. The precipitate is then subjected to combustion without removing it from the tube. Table V indicates a number of analyses that have been made by this procedure.

During the past few years the "anhydrous" wet combustion mixture has attained fairly general use in determining the radioactivity of organic mixtures containing carbon-14. In most cases the CO₂ has been precipitated as barium carbonate, and the activity of the latter measured with a Geiger counter. Counting C¹⁴ as barium

carbonate has the advantage of simplicity, but is not adaptable to measurement of weak activities, because only a small percentage of the disintegrations are counted; a large part of the beta rays is absorbed before they escape the barium carbonate, and another part is lost by the geometry of the counter. Ten per cent may get counted. A more efficient way of measuring weak activities is provided by transferring the carbon dioxide in the gaseous form to either a proportional counter or an ionization chamber. In the gas counters there is practically no loss from either self-absorption or geometry.

The manometric wet combustion of total carbon has been combined, at the Brookhaven National Laboratory (18), with counting either as BaCO_3 or CO_2 gas, to yield simultaneous determination of total carbon and its C^{14} specific activity. After the carbon dioxide is measured in the manometric apparatus, it is transferred either to a barium hydroxide solution or directly to a gas counter. For the BaCO_3 method a test tube containing 2.5 ml. of barium hydroxide of approximately 0.25 N concentration is attached to

the manometric chamber as shown in Fig. 6. The air in the tube and in the connections is evacuated, and the CO_2 from the chamber is passed into the tube and absorbed by the barium hydroxide. The carbonate is then filtered on a porous glass disk and used for counting.

For transfer of CO_2 gas directly from the manometric chamber to a gas counter, the arrangement is shown in Fig. 7. The gas counter, E, from Bernstein and Ballentine (19), is a cylinder of approximately 100 ml. volume with a wire anode in the center; a silver coating about the interior wall serves as cathode. The glass coil, D, in the connecting tube is immersed in a cooling liquid of dry ice and alcohol to intercept moisture. The counter tube is immersed in liquid nitrogen to condense carbon dioxide. After the CO_2 obtained in a combustion has been measured manometrically, the manometric chamber and the counter are attached as shown in the figure, except that the cock of the chamber is closed instead of being open as shown. The counter and connections are evacuated with a "High-vac" pump in the course of a

minute to less than 0.3 mm. of mercury pressure, and the cock of the chamber is opened as shown. The carbon dioxide passes rapidly over into the counter tube and the transfer is completed in two to three minutes. The counter is then detached and filled to atmospheric pressure with dry methane. The counting is done with a current of 3600 volts and is estimated to include 98 per cent of the disintegrations of C^{14} . With this procedure it is possible to measure specific C^{14} activities as little as one per cent of those that can be measured in the same counting time with the same accuracy in a barium carbonate counter. In our laboratory, men who have used both types of counter have preferred the gas counter, for its convenience in eliminating the handling of $BaCO_3$, even when specific activities were sufficient to be measured by either type of counter.

D. L. Buchanan (20) at the Argonne National Laboratory has employed another combination of the "anhydrous" wet combustion and manometric measurement for combined total carbon and C^{14} activity. His apparatus is shown in Fig. 7. He does not absorb

the CO_2 in alkali before the manometric measurement, but passes it through a tube heated to 1000°C . to decompose N_2O to N_2 and O_2 , then through a tube containing metallic silver heated to 400° to remove halogens, and through a coil cooled with dry ice and alcohol to remove H_2O and SO_2 . The CO_2 is then condensed in a tube cooled with liquid nitrogen. The CO_2 tube and manometer being connected and completely evacuated, the CO_2 is brought to room temperature and its pressure measured on the manometer, indicating the amount of carbon in the sample. The CO_2 is then transferred to an ionization chamber and its activity measured with a vibrating reed electrometer. For extremely weak specific activities Buchanan's arrangement has over that of Van Slyke, Steele, and Plazin (18) an advantage in that the size of sample that can be employed in Buchanan's apparatus can be several times greater, permitting measurement of correspondingly weaker specific activities. The Brookhaven arrangement (18) has the advantage that it can be set up in a few minutes on an ordinary laboratory bench in connection with the Van Slyke-Neill manometric apparatus,

which is used for various other analyses when not employed for C^{14} . In our laboratory, there are four different manometric apparatuses that are at times used for C^{14} and at other times for the various other manometric analyses.

At the Oak Ridge Laboratory, the completeness of the combustion of organic substances by the "anhydrous" wet combustion mixture is taken for granted in the technique that is used for measuring the C^{14} activity of pure substances. The substance is burned in the "anhydrous" combustion mixture and the CO_2 gas is transferred without measurement directly to a previously evacuated ionization chamber where the activity is measured. The total carbon is assumed to be that theoretically yielded by the substance burned. This procedure was introduced in 1948 by Neville (21) and data have recently been published from the same laboratory by Raaen and Ropp (22) confirming its precision. This stripped-down procedure can, of course, be used only with material free from elements that would upset the ionization counter. For such, since the combustion itself requires only a few minutes,

the procedure makes combustion of many samples per day possible.

The standard error of 0.2 to 0.3 per cent in specific C^{14} activities determined by Raaen and Ropp indicates the reproducibility of both the counting procedure and the combustion.

Summary

Results from different laboratories during the past 12 years indicate that wet combustion with the present iodic-chromic acid oxidation mixtures provides for a wide variety of organic compounds a rapid carbon determination comparable in accuracy to that of the dry combustion, free from interference by elements that require modification of the dry combustion, convenient for analysis of organic precipitates and thereby for micro determination of other elements, and suitable for combustions in which carbon determination is combined with measurement of C^{14} activity by counting as either $BaC^{14}O_3$ or $C^{14}O_2$.

References

20

1. Messinger, J., Ber. d. d. sch. Ges., 23, 2756 (1890).
2. Küster, F. W., and Stallberg, A., Ann. d. Ch., 278, 215 (1893).
3. Van Slyke, D. D., and Folch, J., J. Biol. Chem., 136, 509 (1940).
4. Van Slyke, D. D., Plazin, J., and Weisiger, J. R., J. Biol. Chem.,
191, 299 (1951).
5. Backlin, E., Biochem. Z., 217, 483 (1930).
6. Van Slyke, D. D., Page, I. H., and Kirk, E., J. Biol. Chem.,
102, 635 (1933).
7. McCready, R. M., and Hassid, W. Z., Anal. Chem., 14, 526 (1942).
8. Lindenbaum, A., Schubert, J., and Armstrong, W. D., Anal. Chem.,
20, 1120 (1948).
9. Farrington, P. S., Niemann, C., and Swift, E. H., Anal. Chem.,
21, 1423 (1949).
10. Van Slyke, D. D., and Plazin, J. P., unpublished.
11. Folch, J., Ascoli, I., Lees, M., Meath, J. A., and LeBaron, F. N.,
J. Biol. Chem., 191, 833 (1951).

6623 21

References - 2

12. Hoagland, C. L., and Fischer, D. J., Proc. Soc. Exp. Biol. Med.,
40, 581 (1939).
13. Hoagland, C. L., J. Biol. Chem., 136, 543 (1940).
14. Thompson, W. B., N. Y. State Dept. Health Reports, p. 21 (1945).
15. Hoagland, C. L., J. Biol. Chem., 136, 533 (1940).
16. Van Slyke, D. D., and Kreysa, F., J. Biol. Chem., 142, 765 (1945).
17. Kirk, E., J. Biol. Chem., 106, 191 (1934).
18. Van Slyke, D. D., Steele, R., and Plazin, J. P., J. Biol. Chem.,
192, 769 (1951).
19. Bernstein, W., and Ballentine, R., Rev. Scient. Instr., 20,
347 (1949).
20. Buchanan, D. I., J. Am. Chem. Soc., 74, 2389 (1952).
21. Neville, O. K., J. Am. Chem. Soc., 70, 3499 (1948).
22. Raaen, V. F., and Ropp, G. A., Anal. Chem., 25, 174 (1953).

Reagents for Wet Carbon Combustion (4)

Reagent	Amount of carbon in sample	Liquid reagents		Solid reagents		Volume at which CO ₂ pressure is measured in manometric analysis
		"Anhydrous" mixture 2 vols. fuming H ₂ SO ₄ (20p.c. SO ₃) 1 vol. H ₃ PO ₄ (1.72 sp.g.) 1 gm. KIO ₃ per 100 ml.	Special Mixture 1 vol. H ₂ SO ₄ (1.84 sp.g.) 1 vol. H ₃ PO ₄ (1.72 sp.g.) 1.5 gm. KIO ₃ per 100 ml.	KIO ₃ - K ₂ Cr ₂ O ₇ 2:1	KIO ₃ - K ₂ Cr ₂ O ₇ 10:1	
	<u>mg.</u>	<u>ml.</u>	<u>ml.</u>	<u>gm.</u>	<u>gm.</u>	<u>ml.</u>
"Anhydrous" general combustion mixture	0.2 - 0.7	2	-	0.15	-	2.0
	1.0 - 3.5	2	-	0.30	-	10.0
	4 - 15	5	-	1.00	-	46.0
Mixture for carbohydrates	0.2 - 0.7	-	2	-	0.15	2.0
	1.0 - 3.5	-	2	-	0.30	10.0
	4 - 15	-	5	-	1.00	46.0

One of the pulverized solid reagents is placed in combustion tube with the dry sample, connection is made with vessel to absorb or freeze evolved CO₂, then the appropriate liquid reagent is added and heat applied.

TABLE II

23

Results, Manometric Micro Analyses (3)

Substance	Mg. sample	Minutes boiled	Per cent carbon	
			Found	Theoretical
Stearic acid	4.131	1	75.98	76.00
	4.461	1	75.80	
	4.132	2	75.86	
	3.975	2	76.13	
	4.218	3	75.87	
Cholesterol	3.539	1	83.98	83.87
	3.236	1	83.87	
	3.474	2	84.02	
	3.663	2	83.91	
	3.370	3	83.93	
	3.769	3	83.99	
Silver acetate	19.050	1	14.35	14.37
	18.703	2	14.39	
	18.227	3	14.40	
Penta-acetyl glucose	4.983	1	49.25	49.23
	4.834	2	49.53	
	4.885	3	49.33	

TABLE III

24

Results of McCready and Hassid (7). Combustion with the "Anhydrous" Mixture followed by Absorption and Weighing of CO₂ in Soda Lime Tube.

Substance	Sample mg.	CO ₂ mg.	Carbon	
			Found %	Calculated %
Glucose	22.82	33.40	39.91	40.00
	11.22	16.50	40.11	
2,3,4,6-Tetramethyl- β -methyl glucoside	15.30	29.47	52.53	52.78
	10.65	20.50	52.49	
Starch acetate	24.00	44.20	50.22	50.00
	6.48	11.85	49.87	
Palmitic acid	7.87	21.61	74.88	74.94
	14.40	49.58	74.95	
Phenylhydrazine hydrochloride	27.34	49.76	49.63	49.82
	12.90	23.48	49.65	
Benzoic acid	13.30	33.40	68.51	68.85
	11.18	28.20	68.78	

25

TABLE IV

Results of Farrington, Niemann, and Swift (9). Combustion with the "Anhydrous" Mixture followed by Absorption of CO₂ in NaOH. Precipitation as BaCO₃, and Measurement of the BaCO₃ by Titration between pH 8 and 4.

	Milligrams of carbon	
	Present	Found
Sodium oxalate	2.92	2.95
	2.15	2.16
	1.87	1.84
	1.86	1.88
	1.69	1.68
	1.88	1.92
Potassium hydrophthalate	4.51	4.54
	6.29	6.26
	5.33	5.33
	5.61	5.61
β, β' -Dichloroethyl sulfide	2.73	2.76
Adipic acid	5.84	5.85
	5.38	5.43
	5.20	5.20
	5.47	5.51

TABLE V

26

Micro Mineral Analyses by Combustion of Organic Precipitates

Element	Phosphorus	Magnesium	Sulfur	Calcium	Sodium
Precipitate	Strychnine phospho-molybdate	Hydroxy-quinolate	Benzidine sulfate	Picrolonate	Uranyl zinc acetate
No. of carbon atoms for 1 atom of element	73	18	12	20	20
Mg. of element required for an analysis	0.01	0.03	0.03	0.02	0.02
Authors	Kirk (17) Hoagland (13)	Hoagland (15)	Hoagland (13)	Van Slyke and Kreysa (16)	W. B. Thompson (14)

6023

21

Fig. 1 - Arrangement of Van Slyke and Polch (3) for combustion with absorption of CO_2 by alkali solution in the manometric apparatus of Van Slyke and Neill. The absorbed CO_2 is subsequently freed by acid and measured by the pressure exerted at 2, 10, or 46 ml. volume for amounts of carbon in the ranges 0.2 to 0.7, 1 to 3.5, and 5 to 15 mg., respectively.

Fig. 2 - Aluminum scoop for weighing samples.

Fig. 3 - Apparatus of McCready and Hassid (7) for absorbing CO_2 in soda lime in gravimetric wet combustion.

Fig. 4 - Apparatus of Lindenbaum, Schubert, and Armstrong (8) for wet combustion with collection of CO_2 for gravimetric determination as BaCO_3 . H is charged with $\text{Ba}(\text{OH})_2$ solution. Dry sample and KIO_3 are placed in E. E and H are evacuated. CrO_3 in $\text{H}_3\text{PO}_4 - \text{H}_2\text{SO}_4$ admitted through C.

Fig. 5 - Combustion tube for washing and combustion of small precipitates (15).

Fig. 6 - Manometric chamber arranged for transfer of CO_2 to $\text{Ba}(\text{OH})_2$ solution preliminary to $\text{BaC}^{14}\text{O}_3$ counting (18).

Fig. 7 - Manometric chamber arranged for transfer of CO_2 to proportional counter tube for counting as C^{14}O_2 (18).

Fig. 8 - Partial diagram of apparatus used by Buchanan (20) for combined determination of total C and its C^{14} content. Combustion is with the "anhydrous" mixture in flask a. Nitric oxide is decomposed by heating the gases to 900°C . in a quartz tube f, halogens by silver at 450° in tube g, H_2O and SO_2 by condensing in h. The CO_2 is condensed in coil i, eventually measured by the pressure on manometer r, and transferred to s for counting.

30

31

6623

32

Refer 3-177-3

34

6623 35

35

6623 36

36

6625

36