A COMPARISON OF METHODS OF DETERMINING CARBON IN SOILS

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INTRODUCTION

For the determination of organic carbon in soils various methods have been proposed and they may be classified as followows:

1. Dry combustion:
    (a) Furnace combution.
    (b) Bomb combution or Parr's method. An oxidation with sodium peroxide in which sodium carbonate is formed.
2. Wet combustion: In which the material to be analyzed is treated with a mixture of chromic and sulfuric acids. Various modifications of this method have been proposed.

It has been shown experimentally that the dry combustion methods give higher results than the wet combution, but the former have certain disadvantages which may be summarized in the following way. The dry combustion methods require a rather complicated and expensive equipment and it is somewhat more difficult to manipulate. In some cases (especially in the furnace dry combustion) the determination is very long and tedious. The wet oxidation methods are adaptable for the estimation of carbon, both in solutions and in dry substances, while the dry combustion methods are only adaptable for the estimation of carbon in dry substances.

Naturally, the aim of many investigators had been to obtain a wet oxidation method, capable of determining the total carbon in amounts that would compare with the dry combustion methods.

White and Holben (**14**) claim that they have found the ideal method: a wet oxidation process which is capable of determining amounts of carbon identical with those obtained by the dry combustion methods.

This work was undertaken with the purpose of comparing the relative efficiency of the chromic acid method as given by White and Holben (**14**) and the official method as given by the Official and Tentative Methods of Analysis of the Association of Agricultural Chemists (**7**), with the Parr's dry combustion process.

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REVIEW OF LITERATURE

In 1848 Rogers and Rogers (**9**) devised a wet oxidation method for the determination of carbon in native and artificial graphites. The oxidizing agent employed in this process was a mixture of bichromate of potassium and sulfuric acid, which the authors claimed, that when applied to graphite, under the conditions given, converted the carbon rapidly and completely into carbon dioxide. The process was gravimetric.

In 1880 Warington and Peake (**12**) furnished data which led to the conclusion that oxidation of carbon in soils by means of a mixture of chromic and sulfuric acids gave results lower than those obtained by the furnace combustion in a current of oxygen. The mode of procedure was quite similar to that recommended by E. Wolff in his "Anleitung zur Chemischen Untersuchung Landwirthschaftlich Wichtiger Stoffe". The materials were kept below their boiling point by heating in a water bath. They stated, however, that the complete destruction of the humic material in the soil does not necessarily imply that the carbon has been entirely converted to carbon dioxide. They used a gravimetric method. The oxidation with the permanganate method, as used by the authors indicated higher result than with chromic acid; but even the permanganate method failed to convert the whole of the carbon to carbon dioxide, the product with the permanganate being, on an average of 4 soils, 92.4 per cent of that yielded by the combustion in oxygen.

In 1904 Cameron and Breazeale (**4**) confirmed the ideas of Warington and Peake (**12**) by stating that the oxidation of carbon in soils by the mixture of chromic and sulfuric acids gave results lower than those obtained by the furnace combustion. But they concluded that the combustion of a soil by the wet method with chromic acid mixture, as described in their paper, would give a more accurate idea of the organic matter in the soil, than the furnace combustion method. Beside the method was more rapid.

n this same year Parr (**8**) published his new method of determining carbon. The combustion of the organic material is affected by means of sodium peroxide, the charge being contained in a closed bomb or cartridge surrounded by water. He claims that the method is much more accurate than the various forms of alkalimeters, which were tried for comparison, and that its ease of manipulation renders it preferable to the absorption method, especially for technical work.

Hall and Miller (**6**) in 1906 reexamined the chromic acid method and concluded that the error was due to incomplete oxidation, other substances than carbon dioxide being produced. They found that by passing the products of combustion over heated copper oxide all the carbon would be obtained as carbon dioxide.

Ames and Geither (**1**) in 1914 concluded that if boiled for 30 minutes a mixture of 3.3 grams chromic acid in 10 cc. water to 50 cc. of sulfuric acid (sp. gr. 1.84) will oxidize all the organic carbon and liberate carbon dioxide chemically or mechanically held in soils, provided the soil is ground to pass thru a 60 mesh sieve. One to three grams of soil were used for each 60 cc. of mixture. They made no attempt to prevent the acid fumes passing into the carbon dioxide absorption tower. They used a wet combustion volumetric method.

Schollenberger (**10**) in 1916 suggested certain improvements in the method described by Ames and Gaither (**1**). The changes referred to, consist of the use of a mixture of phosphoric and sulfuric acids, instead of sulfuric acid alone, with chromic anhydride as the oxidizing agent. Also the substitution of barium hydroxide for sodium hydroxide as the alkaline absorbent for carbon dioxide. He also suggested the replacement of the modified Camp absorption by the Meyer absorption apparatus or Truog's bead tower, together with changes in procedure made necessary by the changes in the reagents employed. The partial substitution of phosphoric for sulfuric acid reduces to a negligible quantity the fuming noticed when sulfuric acid is used alone. Phosphoric acid alone gave invariably lower results.

Gortner (**5**) in 1916 kept the digestion mixture below the boiling point for 2.5 hours and passed the products of combustion thru a heated combustion tube.

Finally in 1925 White and Holben (**14**), published their new method entitled, "Perfection of Chromic Acid Method for Determining Organic Carbon". The authors claim that their method has the following advantages. (**1**) The sulfur-trioxide absorption tube, used for the first time in this study greatly simplifies the usual analytical procedure. (**2**) Eliminates the use of a combustion tube. (**3**) The proposed method has the advantage over the dry combustion method in that it eliminates the possibility of leaving behind the residue of undecomposed carbonates. (**4**) It may be used for the estimation of carbon both in solution and in dry substances. (**5**) The use of the proposed sulfur trioxide absorption tube eliminates the necessity of secondary combustion. (**7**) The results compare with the furnace comustion with CuO and with th bomb combustion.

EXPERIMENTAL

The plan of the investigation included the analysis of 25 soil samples, of high and low carbon content, representative of the type found in the State of New York. The analysis included determinations of organic carbon by the Official Wet Oxidation Method and the chromic acid method of White and Holben (**14**). The results were compared with those obtained by Waterman (**13**) following the Parr combustion procedure.

Soils Used: The samples were taken by the Department of Agronomy (Cornel University) some years ago, and accurate records were taken of the location so that at any future time duplicate samples might be taken at exactly the same place.

Preparation of Sample: In general, soil samples were taken at a depth of eight inches by the method described in the Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists (**7**) .When received in the laboratory the samples were spread out and allowed to air-dry. The original air-dry samples were thoroughly mixed and a subsample taken for analysis. The subsamples were rubbed in a porcelain mortar, using a rubber tipped pestle, and then passed thru a sieve having circular perforation 1 mm. in diameter. The material not passing the sieve was discarded. The sifted subsamples were then ground in an agate mortar until they passed entirely thru a sieve having 100 meshes to the linear inch.

Organic Carbon: Was determined by analyzing for total carbon and then substracting the inorganic carbon obtained.

DESCRIPTION OF METHODS

I. The Official Wet Oxidation Method.

Detailed Procedure: With slight changes the procedure listed in page 25 of the Official Methods (**7**) was followed.

Having the apparatus set as in Figures 1 and the solutions prepared as given in the Official Methods (**7**) the order of procedure was as follows:

Two grams of the 100 mesh soil were placed in the evolution flash (Fig. 1). The apparatus was freed of atmospheric carbon dioxide by suction and then 30 cc. of 0.5 N NaOH were introduced into the absorption tower. Gentle suction was applied and 10 cc. of the oxidizing solution were run into the evolution flask. Twenty-five cc. of the acid mixture were then added, the contents gently agitated and a low flame placed under the flask. The heating was continued for 30 minutes after the mixture began to boil.

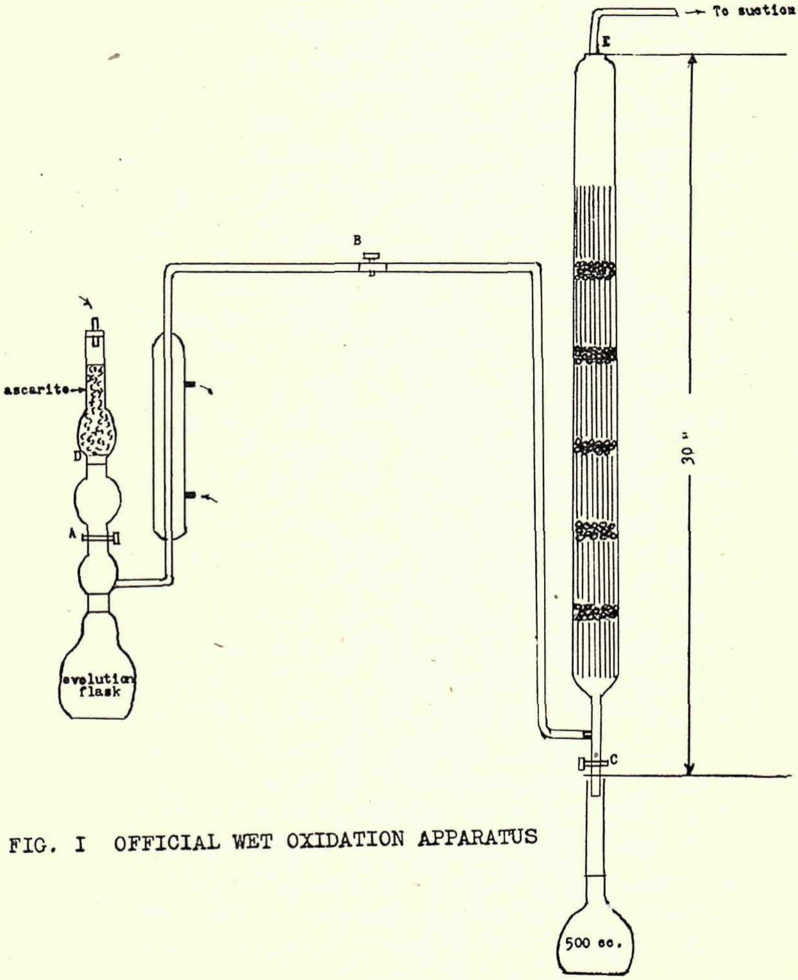

FIG. I OFFICIAL WET OXIDATION APPARATUS

The suction was released at the end of the agitation and aspiration and the absorbent was washed into a 500 cc. volumetric flask. *By the addition of 10 cc. of a neutral aqueous solution of barium* chloride (250 grams of $BaCl_2 . 2H_2O$ per liter) the sodium carbonate in the volumetric flask was precipitated. Then it was diluted to volume and the precipitate of barium carbonate was allowed to settle. A 200 cc. aliquot was pipeted and the residual hydroxide was titrated against 0.5 N hydrochloric acid, using phenolphthalein indicator.

The difference between the residual hydroxide in terms of 0.5 N alkali and the 0.5 N sodium hydroxide originally used is equivalent to the carbon dioxide formed by oxidation of the organic carbon plus the inorganic carbon dioxide present in the sample.

For the determination of inorganic carbon the procedure as described above was followed using the fololwing modifications: (1) 10 grams of soil were used, (2) oxidizing solution was omitted, (3) 60 cc. HCl (1 : 9) were substituted for the acid solution. (4) The flask was agitated but not heated.

When the apparatus is set as described previously, that is: using 2 grams of soil and 30 cc. of 0.5 N sodium hydroxide in the absorption tower, it cannot determine soils which are higher than 4.498 per cent of total carbon. Soil which are higher in total carbon than the above mentioned figure need that only one gram sample should be used or else use 45 cc. of 0.5 N sodium hydroxide in the absorption tower.

Suction troubles and leakages in the rubber tubing were the principal troubles which I encountered in dealing with this apparatus. The suction must be slow and uniform otherwise the gas liberated in the reaction would pass thru the absorption tower with imperfect absorption of the gas. This may be incidental to loss of carbon dioxide and the spoiling of the determination. The suction should be arranged so that bubbling thru the absorption tower should be as constant as possible. About 30 to 50 bubbles per minute are sufficient.

When emptying the contents of the absorption tower into the 500 cc. volumetric the tower was washed 3 or 4 times with pure distilled water. After completing to volume the tower was drained thoroughly.

A strong flame while boiling was very undesirable as it forced the acid fumes in the evolution flask to pass uncondensed to the absorption tower.

The painting of rubber connections with white shellac (Devoe and Reynolds Co., Inc., N. Y.) was found to be very desirable.

Thick rubber connections were more efficient because they lasted longer in good working order than the thin-walled rubber connections.

Another precaution that was followed was to avoid the use of grease in the glass connections of the Knorr carbon dioxide apparatus.

Notwithstanding the many precautions taken to obtain the 0.5 N sodium hydroxide absolutely free of CO_2, it was found to be absolutely impossible. The presence of carbon dioxide was noticed when barium chloride was added to the alkali, in which case a very faint white precipitate was noticed. In order to see the effect of the CO_2 on the titration of the absorbent solution the following test was performed.

The 30 cc. of 0.5 N NaOH, quantity which was used for absorbing the CO_2 in the Official Method apparatus, were placed in the absorption tower. Then drained, completed to volume in the volumetric flask and finally aliquots were taken and titrated against 0.5 N HC1.

Results obtained:

Aliquot	*Titration with 0.5 N. HC1*
No. 1—200 cc.	12. cc.
100 cc.	5. 95 cc.
No. 2—200 cc.	12. 05 cc.

We might conclude then that the effect of the carbon dioxide dissolved in the alkali was negligible as far as the accuracy of the method is concerned.

II. Method of White and Holben (**14**).

The procedure as described by White and Holben (**14**) was followed as carefully as possible. The apparatus is shown in Fig. 2.

Two grams of soil were placed in the generating flask, M. Tubes F and I were connected by means of a glass tube and air was pulled through for several minutes Valve C was closed and the aspirating continued for a short time to test the apparatus and at the same time to create a partial vacuum at M. F and I were closed and the weighed tubes G and H were attached. K is detached from L and 4 grams chronic acid (CrO_3) dissolved in 10 cc. water were placed in the bulb L. K was conected to L and the solution run into flask M. Fifty cc. H_2SO_4 (sp. gr. 1.83 — 1.84) were then run into M in a similar manner leaving open valve C. Air was then pulled again thru the apparatus and the solution brought to boil. The solution was then boiled for 30 minutes during which time air was pulled through at the usual rate. Then tubes G and H. were removed, wiped, and weight after an interval of 15 minutes.

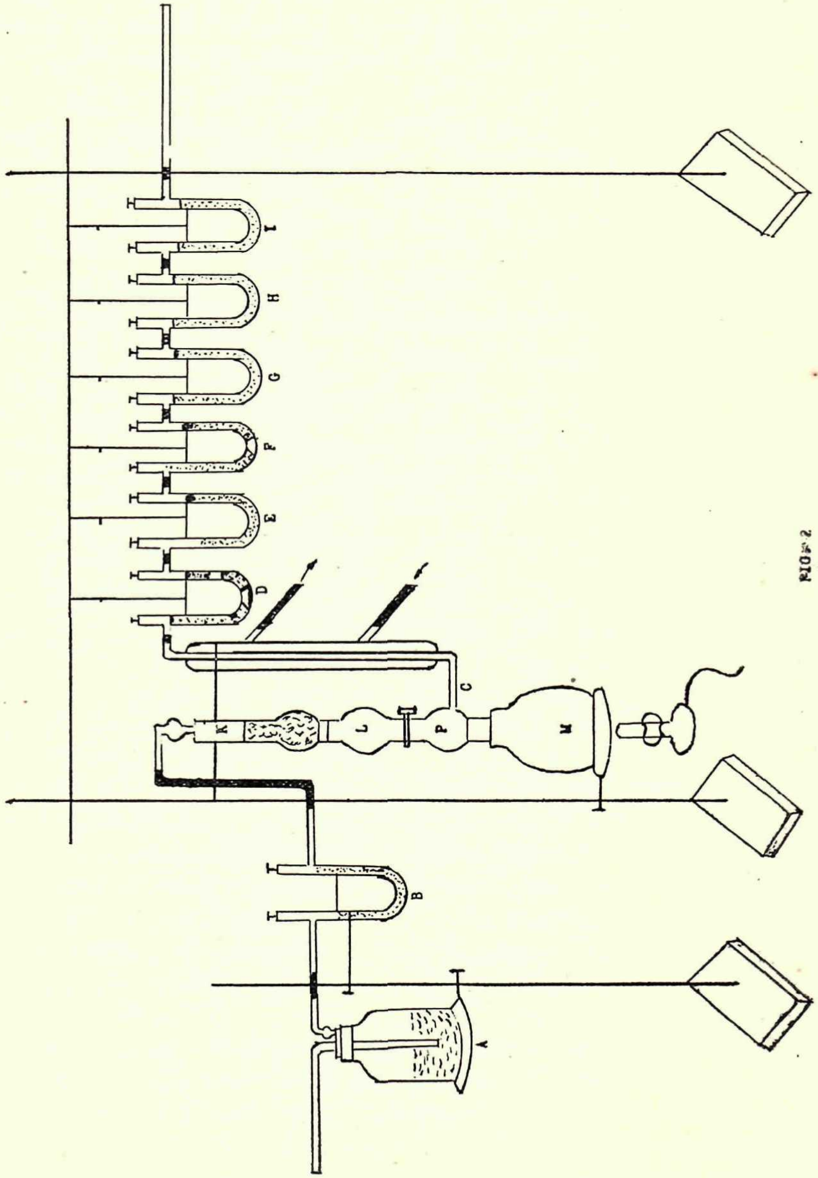

FIG. 2

Weighing of the soda-lime and acid-drying tubes required certain precautions. It was necessary to wipe the tubes and weigh them after 15 minutes in order to get equilibrium of the electrical effect created by the wiping. Tubes G and H were weighed against a common counterpoise tube of the same size made up to weight with 3 grams of the soda lime and acid-pumice tubes. Just before weighing each tube the valves were opened for an instant to equalize the inside and outside atmospheric pressures. Certain modifications of this method were tried. One of them was the substitution of ascarite absorbent for the soda-lime carbon dioxide colelcting tube. The other was the substitution of the Allihn gas-washing bottle containing 1 : 1 potassium hydroxide for ascarite in an ascarite bottle.

The results may be summarized as follows:

No. 1—Using ascarite as gas absorbent + ascarite air purifier.

Soil No.	*% Organic Carbon*
11A	1.4075
11A	1.3775

No. 2—Using soda-lime as absorbent + KOH air purifier.

Soil No.	*% Organic Carbon*
11A	1.3498

No. 3—With ascarite as CO_2 absorbent + KOH air purifier.

Soil No.	*% Organic Carbon*
3A	2.9150

No. 4—With apparatus as designed by the authors.

Soil No.	*% Organic Carbon*
3A	2.9161

From these figures we might conclude that ascarite is as good an absorbent as soda-lime and that it can be freely substituted for the soda-lime in this determination. Also a nascarite bottle is as efficient a purifier of the air as is the Allihn gas-washing bottle containing 1:1 potassium hydroxide.

After the preliminary tests the experiments were carried out in exactly the same way as described by the authors. A slight variation was made in the suctioning process in which suction from a faucet was used instead of the aspirator used by the authors. But it is supposed that this change did not affect the results of the experiments.

This gravimetric method as given by White and Holben (**14**) has certain sources of error which can only be overcome by a very careful techinque. In fact any gravimetric process for the determination of carbon has decided disadvantages attending to the use of the absorption tubes. Some of the sources of error which may alter the results of this gravimetric process and which may be incident to loss of time are:

(1) It requires very elaborate precautions to prevent changes of weight of the tube due to gain or loss of moisture, necessitating complications in the purifying train and the use throughout the apparatus of drying agent of the same hygroscopic power.

(2) Difficulties in weighing large glass vessels caused by electrical effects in wiping, by buoyancy, and by changes in temperature between the balance room and laboratory.

(3) The liability to error from access of gases containing sulfur and chlorine, which may be formed during combustion of the metal or of the carbonaceous residue therefrom. The difficulty had been avoided in the chromic acid method by the use of an U tube fitted with glass beads and a saturated solution of silver sulfate in 5 per cent sulfuric acid.

(4) The difficulty of determining whether the increase in weight of the tube is due solely to the carbon dioxide.

(5) The time lost in waiting for the absorption tubes to reach equilibrium before weighing.

If the complicated purifying train gets out of order or if the tube itself introduces errors in some way, it may often be difficult to locate and correct the trouble. In actual practice with this method this last experience unfortunately occurred and it was after much working that the source of error was located in one of the U tubes whose stopper was not air tight and was thus leaking.

III. Parr's Dry Combustion Method.

The following description of the method is taken from Waterman's (3) thesis.

1. Place 1 gram soil, 5 gm. Na_2O_2, .75 gms. magnesium powder in the bomb, close, screw tight and explode by holding in a gas flame. Cool under tap.

2. Unscrew cap and wash charge into the 150 cc. flask, using boiling water in wash bottle. Boil the solution to remove excess oxygen and to fill the flask with water vapor.

3. While boiling the solution, raise the levelling tube till the burette is filled with mercury. Then shut stopcock. Close stopcock into acid funnel.

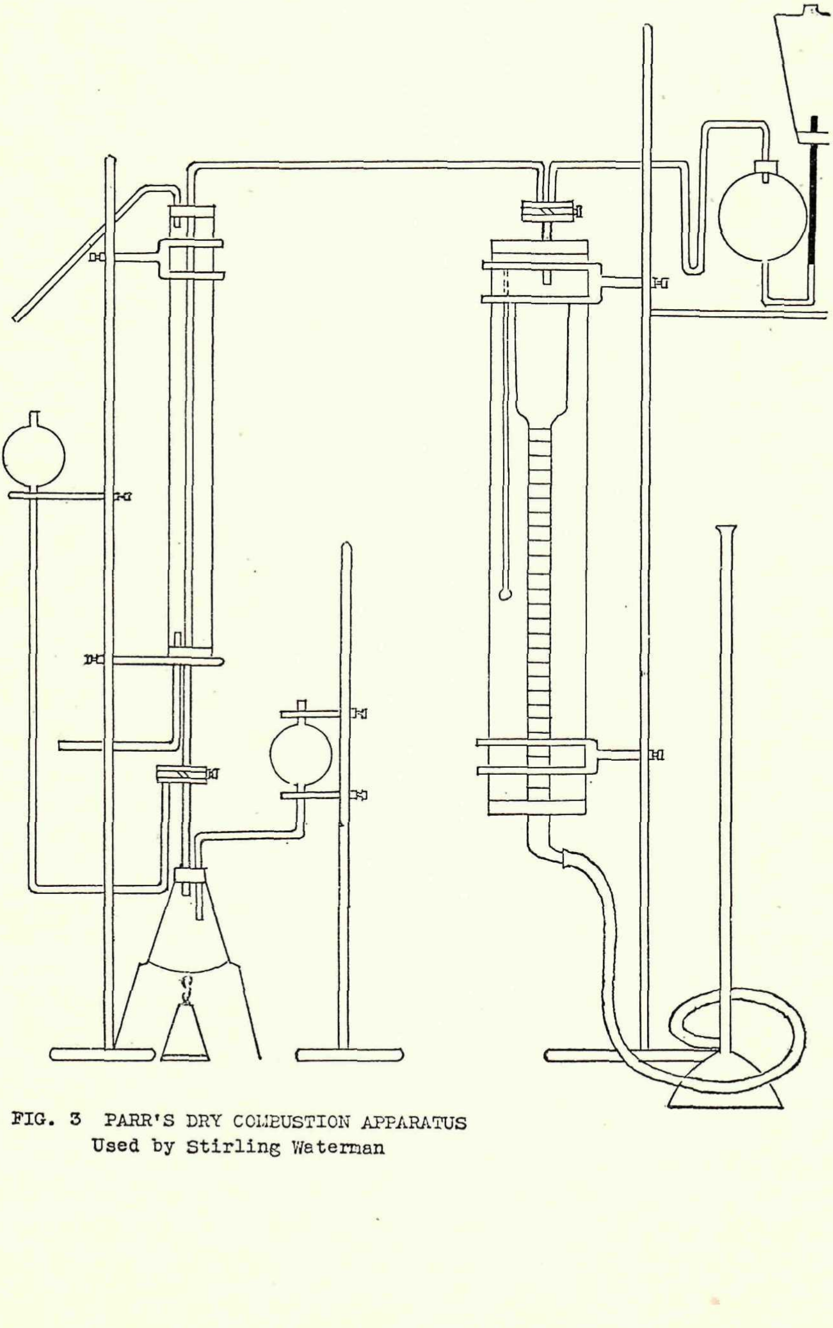

FIG. 3 PARR'S DRY COMBUSTION APPARATUS
Used by Stirling Waterman

4. Place the 150 cc. flask in place and gradually open the cock connecting the condenser with the burette. (Caution). If opened too quickly solution will boil up and pass over into burette.

5. Place 50 cc. 1:1 H_2SO_4 in acid funnel and allow to run *slowly* into flask.

6. When all H_2SO_4 is run in, close stopcock and boil solution for ten minutes controlling heat so that water will not pass into the burette.

7. Fill acid funnel with cold, recently boiled, CO_2 free, water. Allow it to run into flask until the water rises to the first stopcock. Then shut it off and connect with mercury funnel. By raising it, fill the tube right to the burette with mercury. All the gas is now in the burette.

8. Close the stopcock at the top of the burette, lower levelling tube to a convenient level and draw in air through the pipette. Then close the stopcock, raise levelling tube until both columns are level and read. The level of the KOH in the pipette should be noted.

9. Then open cock, pass gas up to 100 cc. mark into the pipette, close cock and shake to absorb the CO_2. Return the unabsorbed gas to the burette so that level of KOH is the same as in 8. Close stopcock, level the mercury and read. Difference is CO_2.

10. Again lower levelling tube as before, allow air to enter and repeat the operation. The CO_2 envolved by one gram generally requires two to five such operations—more from two grams.

11. Note temperature of gas, and barometric pressure and calculate the volume of CO_2 present at 0°C and 760 mm. pressure. Then calculate the per cent total carbon.

12. The carbonate CO_2 is measured in the same way, adding 10 gms. of soil to 50 cc. water in the flask and boiling before placing on the apparatus. The rest of the operation is the same as above described.

A comparison of the Official Method and the Parr dry combustion shows the fact 14 out of 24 samples agreed within a difference of 0.2 per cent, the majority of them much more closely, and the differences being in either direction. The agreement is fairly good when we consider that the analyses were made by different individuals, using different methods. Furthermore, the samples that do not agree within a 0.2 per cent difference are pretty close to it, with the possible exception of soil 3A. The analysis of this sample by the Parr method shows a very low figure, but there is some reason to believe that something might be wrong with that figure since the other methods agreed with the expected difference.

RESULTS

COMPARISON OF 3 METHODS OF DETERMINING CARBON IN SOILS

Sample No.	Soil Type	Per cent organic carbon air-dry sample		
		Official Wet Combustion Method	Method of White & Holben	Parr's Combustion Method
16A	Ontario Loam	1.78	1.47	2.14
14A	Ontario Loam	1.85	1.67	1.69
27A	Ontario Loam	3.09	2.85	3.21
48A	Ontario Loam	1.50	1.28	1.60
57A	Ontario Loam	2.35	1.77	1.98
61A	Ontario Loam	1.65	1.38	1.65
56A	Ontario Loam	1.59	1.30	1.66
58A	Ontario Loam	1.91	1.89	2.17
7A	Volusia stony silt loam	2.55	2.27	2.86
54A	Volusia stony silt loam	5.41	4.54	5.32
34A	Volusia stony silt loam	2.79	2.45	2.32
3A	Volusia stony silt loam	3.15	2.97	2.26
49A	Volusia silt loam	1.65	1.47	1.58
12A	Volusia silty clay loam	2.67	2.45	2.74
66A	Vergennes clay	2.50	2.28	2.58
67A	Vergennes clay	2.82	2.45	2.75
65A	Vergennes clay	2.23	1.98	1.91
55A	Wooster gravelly silt loam	2.64	2.40	3.01
53A	Wooster silt loam	3.22	3.27	3.55
22A	Honeoye silt loam	2.14	1.96	2.24
32A	Dutchess silt loam	2.82	2.46	2.54
28A	Gloucester loam	2.56	2.32	2.53
11A	Dunkirk silt & clay loam	1.81	1.38	1.86
8A	Lordstown stony silt loam	3.71	3.42	3.67
63A	Worth loam	2.66	2.39	(1)

(1) Figures not available for this sample by the Parr dry combustion method.

The agreement between the methods of White and Holben (**14**) and the Parr Combustion (**13**) is not very satisfactory, the former giving uniformly low results which represent approximately 90 per cent of the total carbon obtained by the Parr method.

It would appear from these results that the official wet oxidation method is more accurate than that described by White and Holben (**14**). It appears also that the latter has the disadvantage of more complicated equipment and requires more care and time in the manipulation.

SUMMARY

1. Total carbon was determined in 25 samples of soil using the Official wet oxidation method and the chromic acid method of White and Holben (14). The results were compared with those obtained by Waterman (**13**) with the Parr dry combustion method.

2. The Official wet combustion method compared favorably with the absolute method of Parr.

The method of White and Holben (**14**) gave consistently low results.

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