

LIII.—*On the Determination of Carbon in Soils.*

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It has been long recognised that the amount of organic matter present in soils cannot be accurately determined from the loss on ignition. The hydrated silicates contained in soil retain water even when dried at a temperature far exceeding 100° , but part with this water at a red heat. The loss on ignition is thus always in excess of the carbonaceous matter really present. It consequently becomes necessary to determine directly the amount of carbon in a soil whenever an exact measurement is required of the organic matter present.

A series of determinations of carbon in arable soils from the experimental fields at Rothamsted was made some years ago by Mr. F. A. Manning. The methods he employed were oxidation with chromic acid, and combustion with chromate of lead. These methods gave on the whole nearly agreeing results, the combustion process

generally yielding a slightly higher proportion of carbon. More recently a considerable number of carbon determinations by the chromic acid method have been made in the Rothamsted Laboratory, chiefly by Mr. P. H. Cathcart. We have ourselves lately examined three methods for the determination of carbon in soil, and propose in the present paper to describe the mode of proceeding adopted, and to give examples of the results.

1. *Oxidation with Chromic Acid.*

This method is recommended by E. Wolff in his admirable "*Anleitung zur chemischen Untersuchung landwirthschaftlich wichtiger Stoffe.*" It consists in treating the soil with sulphuric acid and bichromate of potassium, or by preference with a mixture of sulphuric and chromic acids, the carbonic acid evolved being estimated in the usual way. This method is recommended by Fresenius as an alternative to a combustion of the soil with oxide of copper or chromate of lead. It is apparently the method which has been most generally employed in agricultural investigations.

The mode of proceeding employed in the present case has been quite similar to that directed by Wolff. 10 grams of the finely powdered soil are placed in a flask of about 250 c.c. capacity, provided with a caoutchouc stopper, through which pass two tubes, one for the supply of liquids, the other for the delivery of gas. The soil is treated with 20 c.c. of water and 30 c.c. of oil of vitriol; and the whole, after being thoroughly mixed, is heated for a short time in a water-bath, the object in view being the decomposition of any carbonates existing in the soil. Air is next drawn through the flask to remove any carbonic acid which has been evolved. The stopper is next removed, and coarsely powdered bichromate of potassium introduced. In the case of a pasture soil containing 3 per cent. of carbon, 6 grams of bichromate will be found sufficient, a portion remaining undissolved at the end of the experiment. The stopper is then replaced, its supply tube closed by a clamp, and the delivery tube connected with a series of absorbents contained in U-tubes. The first of these tubes contains solid chloride of calcium; the second, fragments of glass moistened with oil of vitriol; the third and fourth are nearly filled with soda-lime, a little chloride of calcium being placed on the top of the soda-lime at each extremity. The last-named tubes are for the absorption of carbonic acid, and have been previously weighed. The series is closed by a guard tube containing soda-lime, with chloride of calcium at the two ends.

The flask containing the soil and bichromate is now gradually heated in a water-bath, the contents of the flask being from time to time mixed by agitation. A brisk reaction occurs, carbonic acid

being evolved in proportion as the soil is rich in organic matter. The temperature of the water-bath is slowly raised to boiling as the action becomes weaker, and is maintained at that point till all action ceases. As bubbles of gas are slowly evolved for some time, it has been usual in these experiments to prolong the digestion for four or five hours. When the operation is concluded the source of heat is removed, an aspirator is attached to the guard tube at the end of the absorbent vessels, and air freed from carbonic acid is drawn through the flask and through the whole series of **U**-tubes. The **U**-tubes filled with soda-lime are finally weighed, the increase in weight showing the amount of carbonic acid produced. The object of the chloride of calcium placed on the surface of the soda-lime is to retain the water which is freely given up when the soda-lime absorbs carbonic acid. The second **U**-tube filled with soda-lime does not gain in weight till the first is nearly saturated; it thus serves to indicate when the first tube requires refilling. The same tubes may be used several times in succession.

It was found in some preliminary experiments that no increase in the carbonic acid evolved was obtained by substituting chromic acid for bichromate of potassium.

The organic matter of the soil appears to the eye to be completely destroyed by the digestion with sulphuric acid and bichromate of potassium; the residue of soil remaining in the flask when washed with water is perfectly white, or the dark particles, if any, are found to be unaltered by ignition, and therefore to be inorganic in their nature. Under these circumstances considerable confidence has naturally been felt in this method. The complete destruction of the humic matter of the soil does not, however, necessarily imply that the carbon has been entirely converted into carbonic acid. The first doubt on this head we owe to an observation made to one of us by Professor Wanklyn. He pointed out that in other known cases of the action of chromic acid on organic matter the oxidation frequently stopped short of the production of carbonic acid, and that while oxidation with chromic acid apparently led to a complete reaction when the carbon was in the form of graphite, it would probably yield other products than carbonic acid when the carbon existed as a carbohydrate. The doubt thus raised as to the correctness of the results yielded by the chromate method made it desirable to check the work already done by the use of other methods for the determination of carbon.

2. *Oxidation with Permanganate of Potassium.*

In the trials with this method 10 grams of soil were digested in a closed flask with a measured quantity of solution of caustic potash

and crystals of permanganate of potassium. The quantity of potash solution finally adopted was 20 c.c., containing 5 grams of potash. 7 grams of the permanganate were found to be sufficient for a soil containing 3.3 per cent. of carbon. Trials were made with various modes of digestion. The plan which answered best was to heat the flask for half an hour in boiling water, and then for one hour in a salt-bath. The flask during this digestion was connected with a small receiver containing a little potash solution, to preserve an atmosphere free from carbonic acid; distillation to a limited extent was allowed during the digestion in the salt-bath. In some experiments the contents of the flask was distilled to dryness in a chloride of calcium bath, but the results obtained by this plan were frequently low and irregular, the caustic potash forming with clay soils a hard mass, which was afterwards attacked with difficulty by dilute acid.

The first part of the operation being completed a caoutchouc stopper carrying a delivery and supply tube was fitted to the flask, which was then connected with the system of U-tubes already described. Dilute sulphuric acid was then poured down the supply tube, a water-bath surrounding the flask was brought to boiling, and maintained thus for one hour, after which air free from carbonic acid was drawn through the apparatus, the U-tubes containing soda-lime being finally disconnected and weighed.

In the first stage of this method the carbon of the organic matter is converted into carbonate, and probably also into oxalate of potassium (Wanklyn, *Phil. Mag.* [5], 5, 466); in the second stage the oxalate is decomposed by the sulphuric acid and permanganate, and the carbon existing, both as oxalate and carbonate, is evolved as carbonic acid, and absorbed by the weighed soda-lime tubes. Both F. Schulze and Wanklyn have employed permanganate of potassium for the determination of organic carbon, but they have preferred to calculate the amount of carbon from the quantity of permanganate consumed; as, however, by so doing everything oxidisable by permanganate is reckoned as carbon, it seems better to make a direct determination of the carbonic acid formed.

From the amount of carbonic acid found we have to subtract that existing as carbonates in the soil, and in the solution of potash used. For this purpose an experiment is made with the same quantities of soil and potash previously employed, but without permanganate, and the carbonic acid obtained is deducted from that yielded in the experiment with permanganate. If the potash used contains organic matter two blank experiments will be necessary, one with potash and permanganate, and one with soil alone.

A further difficulty arises from the presence of chlorides in the materials, which occasions an evolution of free chlorine when the

permanganate solution is heated with sulphuric acid. This error occurs also with the chromic acid method, but in that case the quantity of chloride is merely that contained in the soil, which is usually very small; in the permanganate method we have also the chloride present in the caustic potash, and this is often considerable. Corrections for chlorine by blank experiments are unsatisfactory, the amount of chlorine which reaches the soda-lime tubes depending in part on the degree to which the chloride of calcium tube has become saturated with chlorine. It is better therefore to remove the chlorine in every experiment by the plan which Perkin has suggested (*Trans. Chem. Soc.*, 1880, 121), by inserting a tube containing silver foil, maintained at a low red heat, between the flask and the absorbent **U**-tubes.

The amount of carbonic acid yielded by oxidation with permanganate of potassium was found to be considerably in excess of that obtained by oxidation with chromic acid; to ascertain whether these higher results really represented the whole of the carbon present in the soil trials were next made by actual combustion of the soil in oxygen.

3. *Combustion in Oxygen.*

It appeared that the most convenient mode of carrying out the combustion of soil would be to place the soil in a platinum boat, and ignite it in a current of oxygen in a combustion-tube partly filled with cupric oxide. This plan has proved very successful. A wide combustion-tube is employed, about 20 inches long, and drawn out at one end; the front of the tube is filled for 8 inches with coarse cupric oxide, the hind part is left empty to receive the platinum boat. The drawn out end of the combustion-tube is connected with a series of absorbent **U**-tubes, quite similar to those employed for the estimation of carbonic acid in the chromic acid method. Between these absorbent vessels and the combustion-tube we at first inserted a tube filled with 7 inches of the chromate-pumice recommended by Perkin (*Trans. Chem. Soc.*, 1880, 121, 457) for the absorption of nitrous fumes, this tube being kept just sufficiently hot during a combustion to prevent the deposition of water. Latterly we have abandoned the chromate tube, and substituted for the chloride of calcium tube employed to dry the gas a three-bulbed Geissler tube filled with oil of vitriol. The oil of vitriol has proved quite effective in retaining nitrous fumes, combustions of nitrogenous soils made with and without the chromate tube giving closely agreeing results. The wide end of the combustion-tube is connected with a gasholder of oxygen; the oxygen gas is made to pass through a **U**-tube of soda-lime before entering the combustion-tube, to remove any possible contamination of carbonic acid.

In starting a combustion the part of the combustion-tube containing the cupric oxide is brought to a red heat, and oxygen is passed for some time through the apparatus. 10 grams of soil, previously dried, are placed in a large platinum boat, which is next introduced at the wide end of the combustion-tube. The combustion is conducted in the usual manner, a current of oxygen being maintained throughout the whole operation. It is very useful to terminate the whole series of absorbent vessels with a glass tube dipping into water; the rate at which the gas is seen to bubble serves as a guide to the supply of oxygen from the gasholder, the consumption of oxygen varying of course with different soils, and at different stages of the combustion. At the close of the combustion oxygen, or air freed from carbonic acid, is passed for some time through the apparatus to drive all carbonic acid into the absorbent vessels. One experiment can be followed by another as soon as the hind part of the combustion-tube has cooled sufficiently to admit a second platinum boat. The same combustion-tube can be employed for several days, if packed in the usual manner in asbestos.

The presence of carbonates in the soil occasions some difficulty in working the combustion method, as a part of this carbonic acid will, of course, be given up on ignition, and be reckoned as carbon. The simplest mode of meeting this difficulty is to expel the carbonic acid belonging to the carbonates before the combustion commences. We have had but little experience with soils rich in carbonates, the Rothamsted soils containing at most but a very small proportion of chalk. With such soils we have employed the method already made use of by Mr. Manning in his earlier work on the same subject, namely treatment with a strong solution of sulphurous acid. The 10 grams of soil taken for combustion are placed in a flat-bottomed basin, covered with a thin layer of sulphurous acid, and frequently stirred. After a time the action is assisted by a gentle heat. When the carbonates have been completely decomposed the contents of the basin is evaporated to dryness on a water-bath, the dry mass is then pulverised, and removed to the platinum boat for combustion in oxygen. For the action of the sulphurous acid to be complete it is essential that the carbonates should be in very fine powder, even chalk is but imperfectly attacked when present in coarse particles.

A few experiments were made to test the efficacy of this process. Carbon was first determined in the usual way in three soils naturally free from carbonates; chalk, previously ignited at a low heat to destroy organic matter, was then added in quantity equal to 5 per cent. of the original soil. The soil containing the chalk was next reduced to a very fine powder, a quantity of the mixture corresponding to 10 grams of the original soil was treated with sulphurous acid, and

the carbon again determined. The percentages of carbon found were as follows:—

| Kind of soil. | In original soil. | | | After addition of chalk and treatment with sulphurous acid. | | |
|--------------------|-------------------|---------|-------|---|---------|-------|
| | Exp. 1. | Exp. 2. | Mean. | Exp. 1. | Exp. 2. | Mean. |
| Old pasture | 3·21 | 3·25 | 3·23 | 3·24 | 3·33 | 3·29 |
| New pasture | 2·33 | 2·32 | 2·33 | 2·32 | — | 2·32 |
| Clay subsoil | 0·29 | 0·29 | 0·29 | 0·31 | 0·30 | 0·31 |

Having thus described the methods which we have examined, we will next submit some numerical results obtained by their use.

Comparison of Methods.

A considerable number of soils analysed by the chromic acid method have been lately re-analysed by the combustion method; the results compare as follows:—

Percentage of Carbon found by two methods in Soils dried at 100°.

| No. | Kind of soil. | Chromic acid method. | | | Combustion method. | | | Yielded by chromic acid if carbon by combustion 100. |
|-----|------------------|----------------------|---------|-------|--------------------|---------|-------|--|
| | | Exp. 1. | Exp. 2. | Mean. | Exp. 1. | Exp. 2. | Mean. | |
| 1 | Old pasture | 2·85 | 2·79 | 2·82 | 3·58 | 3·55 | 3·57 | 79·0 |
| 2 | „ | 2·83 | 2·79 | 2·81 | 3·57 | 3·53 | 3·55 | 79·1 |
| 3 | „ | 2·76 | 2·76 | 2·76 | 3·46 | 3·46 | 3·46 | 79·7 |
| 4 | „ | 2·74 | 2·76 | 2·75 | 3·37 | 3·38 | 3·38 | 81·4 |
| 5 | „ | 2·64 | 2·54 | 2·59 | 3·31 | 3·36 | 3·34 | 77·5 |
| 6 | „ | 2·51 | 2·43 | 2·47 | 3·15 | 3·15 | 3·15 | 78·4 |
| 7 | „ | 2·40 | 2·44 | 2·42 | 3·09 | 3·13 | 3·11 | 77·8 |
| 8 | New pasture | 1·92 | 1·93 | 1·93 | 2·41 | 2·40 | 2·41 | 80·1 |
| 9 | „ | 1·66 | 1·81 | 1·74 | 2·39 | 2·43 | 2·41 | 72·2 |
| 10 | Arable soil | 1·78 | 1·78 | 1·78 | 2·14 | 2·13 | 2·14 | 83·2 |
| 11 | „ | 1·21 | 1·14 | 1·18 | 1·40 | 1·43 | 1·42 | 83·1 |
| 12 | Subsoil | 0·28 | 0·27 | 0·28 | 0·37 | 0·38 | 0·38 | 73·7 |

Of the above soils the arable soils, Nos. 10 and 11, were the only ones containing carbonates in any quantity exceeding a minute trace. The two soils in question were treated with sulphurous acid before combustion, the others not.

All the determinations by the chromic acid method were made by Mr. P. H. Cathcart, with the exception of Nos. 9 and 12, which were

executed by another experimenter, and are seen to give distinctly lower results. Excluding these two analyses the relation of the carbon found by the two methods is tolerably constant, the average being 79·9 of carbon found by oxidation with chromic acid for 100 yielded by combustion in oxygen. The results obtained by the chromic acid method thus appear to be very considerably below the truth.

Four typical soils have been analysed by the permanganate, as well as by the chromic acid and combustion methods. The results obtained were as follows:—

Percentage of Carbon found by Three Methods in Soils dried at 100°.

| No. | Kind of soil. | Combustion method. | Chromic acid method. | Permanganate method. | | | Yielded by permanganate if carbon by combustion 100. |
|-----|-----------------------|--------------------|----------------------|----------------------|---------|-------|--|
| | | Mean. | Mean. | Exp. 1. | Exp. 2. | Mean. | |
| 2 | Old pasture | 3·55 | 2·81 | 3·26 | 3·30 | 3·28 | 92·4 |
| 8 | New pasture | 2·41 | 1·93 | 2·29 | 2·30 | 2·30 | 95·4 |
| 11 | Arable soil | 1·42 | 1·18 | 1·28 | 1·33 | 1·31 | 92·3 |
| 12 | Subsoil | 0·38 | 0·28 | 0·34 | 0·34 | 0·34 | 89·5 |

Oxidation by permanganate thus gives a much higher result than oxidation with chromic acid; but even the permanganate fails to convert the whole of the carbon into carbonic acid, the product with permanganate being on an average of the four soils 92·4 per cent. of that yielded by combustion in oxygen.

Wanklyn states (*Phil. Mag.* [5], 7, 138) that a temperature of 160—180° is necessary in some cases to effect complete oxidation with permanganate and caustic potash. Such a temperature was found impracticable when dealing with soil, from the action of the potash on the silicates present: hence possibly the low results obtained.

Combustion in oxygen appears from these experiments to be the most satisfactory method for determining carbon in soil, nor is this method on the whole longer or more troublesome than the other methods investigated.

We have further determined the loss on ignition of the four soils mentioned above, with the view of comparing this loss with the amount of organic matter calculated from the carbon actually present. In making this calculation we have taken as the amount of carbon in the soil that found by combustion in oxygen, and have assumed with Schulze, Wolff, and Fresenius that 58 per cent. of carbon will be present in the organic matter of soils. The four soils were heated suc-

cessively at 100°, 120°, and 150°, till they ceased to lose weight; the loss on ignition in each of these stages of dryness is shown in the following table:—

Percentage Loss on Ignition compared with Organic Matter calculated from Carbon.

| No. | Kind of soil. | Loss on soil dried at 100°. | | | Organic matter at 58 per cent. carbon. |
|-----|--------------------|-----------------------------|----------------------------|----------------------------|--|
| | | Between 100° and ignition. | Between 120° and ignition. | Between 150° and ignition. | |
| 2 | Old pasture | 9·27 | 9·06 | 8·50 | 6·12 |
| 8 | New pasture..... | 7·07 | 6·88 | 6·55 | 4·16 |
| 11 | Arable soil..... | 5·95 | 5·70 | 5·61 | 2·44 |
| 12 | Clay subsoil | 5·82 | 5·39 | 4·76 | 0·65 |

The loss on ignition is seen to be in all cases very considerably in excess of the organic matter calculated from the carbon, even when the soil has been dried at as high a temperature as 150°. The error of the ignition method is least in soils rich in organic matter, as, for instance, the old pasture soil in the above table. The error reaches its maximum in the case of the clay subsoil, which contains very little carbonaceous matter, but is naturally rich in hydrated silicates, which part with their water only at a very high temperature.
