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MODIFIED DRY COMBUSTION METHOD FOR THE DETERMINATION OF ORGANIC CARBON IN SOILS.

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The estimation of organic matter in the course of a soil study is of fundamental importance since this soil component affects markedly the physical, chemical and biological properties of the soil. Just like clay, it possesses many of the properties of colloids: it modifies greatly the readiness with which mineral plant food is rendered available to the crop and it is the medium in which the micro-organisms in the soil live and perform their functions.

The loss-on-ignition method was probably the first to be employed for the estimation of soil organic matter. But this gives very unreliable results especially when the soil—contains clay and carbonates. As a striking example could be mentioned the analysis of a sample of black soil from Hagari. This gives a loss on ignition (exclusive of moisture lost at 100°) of about 7%. Out of this there is only 0.9% of organic matter, the rest of the loss being due to carbonates and combined water. Methods employing sodium hydroxide, ammonia or hydrogen peroxide are probably useful for the estimation of particular parts of organic matter present in the soil and not for the whole of it. (1)

The majority of the methods now commonly employed are based on the determination of organic carbon by a wet or dry combustion method and then calculating the organic matter by using a conventional factor, 1.724. Allowance is made for the presence of carbonates which are estimated separately. Among wet combustion methods, the rapid volumetric procedure of—Schollenberger (2) and its modifications give at best only a rough idea depending upon the nature of the soil components and upon the state of oxidation of the organic matter. Soil organic matter is, extremely complex and exists in different states of oxidation. The presence of reducing and oxidising—substances greatly modify the validity of the results. Robinson's new method (3) using the Kjeldahl procedure suffers from the same drawbacks. Even in the simplest cases of sugars having the formula $C(H_2O)_n$, he did not get complete recovery. With such varied classes of substances as acids, fats, waxes, proteins and other nitrogen compounds the equation $C + 2H_2SO_4 = CO_2 + 2H_2O + 2SO_2$, does not find a uniformly approximate application. Under the circumstances only the direct absorption and weighing of the carbon dioxide evolved may be expected to give reliable results for the organic carbon content. Even here, wet methods using solutions of chromic acid or permanganate, give low results evidently due to incomplete oxidation, and these are only slightly less laborious than the dry combustion method which is universally recognised as the standard. Owing to the wide applicability of this dry combustion method, modifications to make it more rapid and free from any possible source of error will be very valuable and this has been the aim of the work described in this paper.

Before embarking on the estimation of organic carbon in soils, it was proposed first to work out a modification using pure organic substances of various types whose compositions have been established beyond doubt. The chief difficulties in the Liebig's combustion method are (i) slow and sometimes incomplete combustion of some complex refractory bodies, and (ii) the errors introduced by the presence of nitrogen, halogen and sulphur in the substances analysed. The first has been greatly minimised by the use of oxygen for the combustion instead of air and by using platinum boats instead of porcelain ones. Nitrogenous compounds give rise to oxides of nitrogen which get absorbed along with carbon dioxide and thus high values are obtained. Fresh, reduced copper coil placed at the exit end of the combustion tube, removes this error by reducing the oxides to nitrogen, but its use is cumbersome and tedious. Halogen compounds give rise to halogens which have been attempted to be trapped by using a U tube of potassium ferrocyanide or a similiar reagent, but the best procedure seems to be the use of red hot silver gauze or wool. Oxides of sulphur from the sulphur compounds have been attempted to be removed by using sodium chromate solution or pumice soaked in

concentrated sulphuric acid. But these are not found to be effective. The most perfect solution of all these difficulties is that of Pregl (4) in what is known as the Universal filling of the combustion tube for micro-estimations. He uses a mixture of copper oxide wire and lead chromate (hempseed size) or copper oxide impregnated with the chromate for filling the combustion tube in the place of the usual copper oxide. The lead chromate at red heat retains all oxides of sulphur effectively. Short lengths of silver wool kept at red heat remove the halogens and the nitrous fumes are absorbed by pure lead peroxide kept at the boiling point of decalene. This has been adapted for macro-combustions also by Davies (5). In this procedure lead peroxide is the chief source of trouble. It requires to be specially pure and made into a particular state of subdivision. Variations from the optimum conditions of temperature means failure of analysis. On a macro scale it is rather cumbersome to use and the constant temperature arrangement is not easily fitted up. The chief characteristics of the modification adopted in this paper and found suitable for soils in ordinary laboratories are as below:—

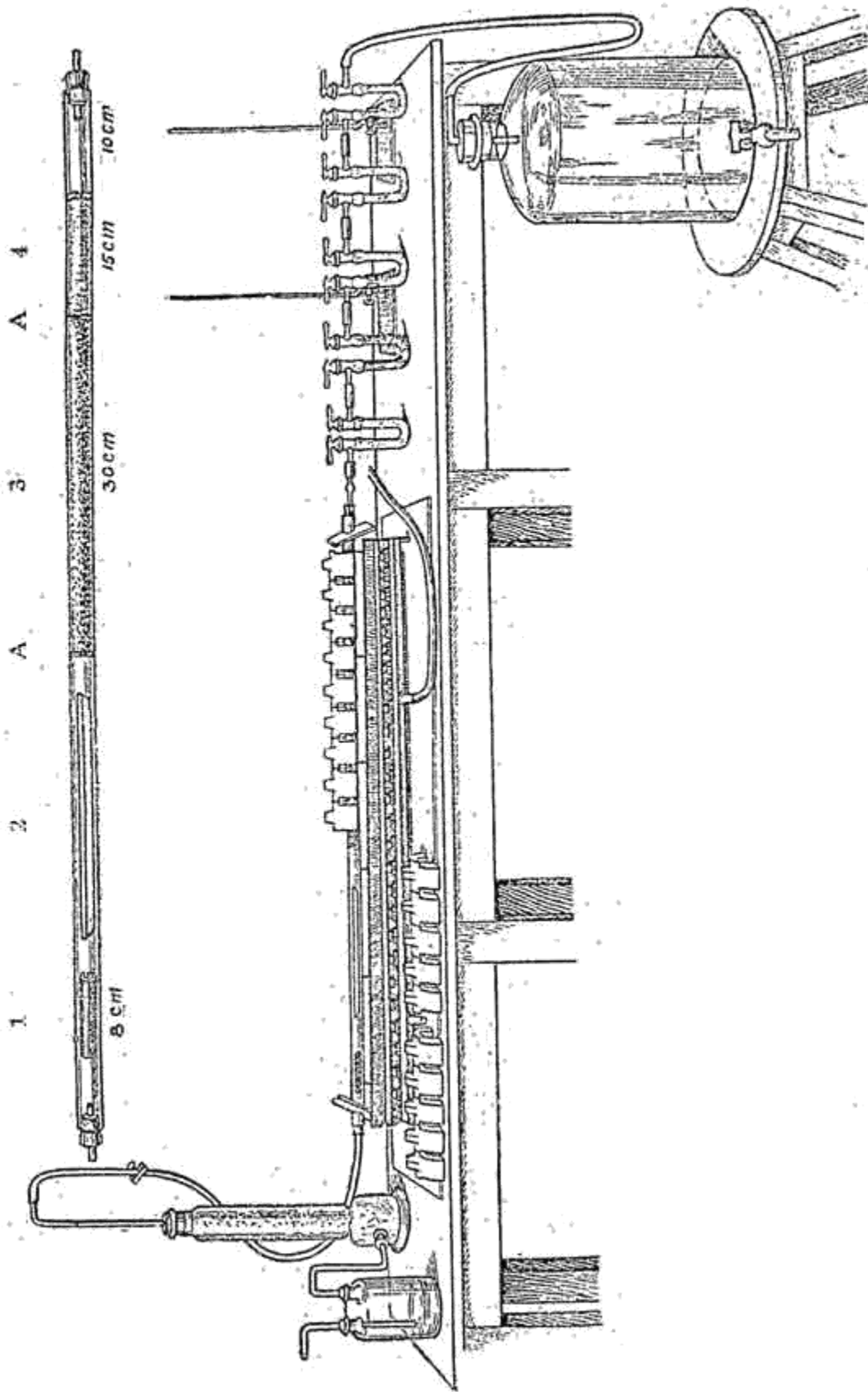
(i) the substance is mixed up with powdered copper oxide and burnt at red heat in a current of air. Under the circumstances there is rapid and complete oxidation of carbon; oxygen is not necessary for the combustion.

(ii) a mixture of well ignited wire form copper oxide and lead chromate (hempseed size) is employed for filling the tube. Oxides of sulphur are thus retained.

(iii) a length of about 15 c. m. of closely packed fine silver wire or wool at red heat serves to remove all halogens.

(iv) instead of lead peroxide and the decalene bath, a U tube containing pumice soaked in concentrated sulphuric acid has been found to be quite effective in retaining nitrous fumes. Probably the combined action of silver and sulphuric acid gives the arrangement its merit.

Materials for filling the combustion tube. A good hard glass combustion tube about 1 metre in length and 8 to 10 m. m. in diameter is chosen, the ends are softened in a flame or smoothed with a grinding stone or file and finally cleaned and dried. Pure precipitated lead chromate is moistened with water formed into a thin slab on a glass plate and cut into small pieces. This is first dried in the steam oven, transferred to a nickel basin and ignited over a bunsen burner for about one hour. At this stage the substance is in the form of irregular pieces of hempseed size. Wire form copper oxide also is ignited for half an hour in a nickel crucible over a bunsen burner. The silver



1. Oxidised Copper Coil. 2. Silver Boat. 3. Copper Oxide Lead Chromate Mixture. 4. Silver Wire. A, A, Asbestos Plugs. 4. Silver Wire.

wire was the thinnest that could be made out of pure silver by a local silver smith. Asbestos used for the filling was pure gooch asbestos which was well ignited in a platinum basin over a strong bunsen flame.

Filling the combustion tube. A, A are asbestos plugs about 1 c. m. in thickness. About 10 c. m. length is left empty at the exit end. The silver wire is cut into small lengths and packed closely into the tube. Used up samples are ignited in a current of hydrogen and then they are fit for use again. When the copper oxide and lead chromate are prepared as stated above, they do not require igniting in the combustion tube very long. There is then ample space in the tube for introducing the boat and an oxidised copper coil 8 c. m. in length. The boat was made locally out of pure silver. It just went into the tube easily and it was about 1 m. m. in thickness. The length was between 6 and 8 inches to suit circumstances so that it easily took in the copper oxide soil mixture. It is not seriously affected during the combustion. The inside alone gets a little brown after considerable use.

The purifying and absorption trains. Before entering the combustion tube the air that is aspirated bubbles through 50 per cent. potassium hydroxide kept in a Wolfe's bottle, and subsequently through a big soda lime tower. The absorption train consists of the following:—

(i) *U tube containing coarse granules of calcium chloride for removing water*:—It was found essential to provide this with a bulb at the inlet so as to condense most of the water produced. With some clayey soils containing large quantity of water of chemical combination this was found to prolong the life of the calcium chloride considerably. Since calcium chloride is likely to contain some lime it was first saturated with carbon dioxide by connecting the U tube to a Kipp's apparatus provided with a gas washing bottle containing concentrated sulphuric acid. After passing the gas for a few minutes the outlet tap was closed and the tube left with the other end connected with the Kipp for 12 hours. The U tube was then disconnected and about 200 c. c. of air passed through in about 10 minutes so that the excess of carbon dioxide was completely removed.

(ii) *U tube containing pumice (hempseed size) soaked in concentrated sulphuric acid*:—This should contain some excess of sulphuric acid so that a little of it collects at the bottom bend and serves as a bubble counter. Since the gases coming in here are dry, the acid does not get diluted and hence is more effective in absorbing nitrous fumes.

(iii) *Two soda lime U tubes for absorbing carbon-di-oxide*:—These tubes have a few centimeteres of calcium chloride at the exit ends so as to prevent the escape of moisture from the moist soda lime. For good absorption it is essential to ensure that the soda lime is sufficiently moistened. For this purpose the substance is spread on a large

piece of paper, and water sprayed from a wash bottle provided with a narrow jet. Too much of water rendering the granules sticky should be avoided. The first U tube is usually refilled when the second shows an increase of over 1 m. g. in weight during an estimation. The quantity of moisture in the soda lime limits the number of estimations for which it could be used. With one sample containing sufficient moisture the first tube was effective for more than 20 estimations and the second did not show any appreciable increase during each estimation. Whereas in another case with less moisture it could not be used for more than 6 estimations. During the combustion it is essential to wrap the soda lime absorption tubes with wet cotton, as otherwise considerable heat is generated and the soda lime loses moisture and its absorptive power is lessened.

(iv) *A U tube containing soda lime in one limb and calcium chloride in the other to serve as a guard tube. Blank test:*—Since the wire from copper oxide and lead chromate had been ignited prior to filling, the tube required only a preliminary heating of about 2 hours at dull red hot during which time about 1500 c. c. of air was aspirated. It was then ready for a combustion. Commercial copper oxide powder gives a fairly high blank even after ignition in a nickel crucible for one hour over a strong bunsen flame. This could be eliminated by keeping it at red heat in a hard glass tube for one hour and aspirating 700 c. c. of air through. Large quantities (100–150 grams) could be treated at one time and stored up for use. A blank using this copper oxide gave practically no increase in the weight of the soda lime absorption tubes.

Analysis of pure organic substances:—*Carrying out a combustion.* The combustion tube which has been filled and ignited as above is now connected to the calcium chloride and sulphuric acid U tubes and the front part containing the copper oxide lead chromate mixture raised to dull red heat. Meanwhile the substance (about 0.1 gram) is weighed into a small clean porcelain basin mixed with 10 grams of specially ignited copper oxide and transferred to the silver boat. The basin is washed twice with small quantities of copper oxide and the washings added to the boat. The weighed soda lime U tubes and the guard tube are now connected in the front and after all the taps have been opened, the boat and the oxidised copper gauze are introduced into the combustion tube and the rubber stopper is pushed in tight. The aspirator is then connected and a very gentle stream of air is aspirated by adjusting the air inlet in the purifying train. The oxidised copper coil is first raised to dull red heat and next the boat itself heated very slowly so as to avoid too rapid a combustion. About half an hour is an optimum time for the complete combustion. When the gas evolution has slackened considerably as judged from the bubbling in the sulphuric acid tube the air inlet is opened wider and about 350 c. c. of air aspirated. At the beginning the rate is kept slow, but later on

it could be increased so that 20 c. c. is aspirated in a minute. This does not take more than one half hour so that the combustion and absorption takes just less than one hour.

Before starting another combustion the burners in the back part of the furnace containing the boat and copper gauze are turned out, the tiles removed and this portion allowed to cool as the absorption tubes are being weighed and a fresh sample got ready. It was found advisable to turn out 1 or 2 burners under the copper oxide lead chromate mixture also in order to avoid cracking of the tube when the cold boat was introduced. This precaution is specially necessary in the case of soils containing high percentage of chemically combined water. The side arms of the U tubes are cleaned inside with a little cotton, the stoppers opened for a moment closed again and then weighed.

The whole analysis takes less than 1½ hours and 5 to 6 estimations could be done in a day. The method was tested by using a number of pure organic substances belonging to typical groups. Even very refractory bodies burnt very smoothly and rapidly. Amongst nitrogen compounds, the aromatic nitro-compounds have been shown by Pregl to offer the crucial test of the efficiency of a method since they give rise to large quantities of nitrous fumes. With this method these have given quite correct values for carbon. The highly resistant sulphur compound, sulphonal offered no difficulty. The results of several repetitions with each compound were found usually to be about 0.2 to 0.4 per cent high.

Sample analytical results.

	Found.	Required.
	%	%
Cane sugar	42.3, 42.1	42.1
Cholesterol	84.2, 83.8	83.8
Acetanilide	71.3, 71.2	71.1
Strychnine	75.8, 75.4	75.5
Uric acid	36.1, 35.9, 35.7	35.7
Metadinitro benzene	43.1, 42.9, 43.0	42.8
Sulphonal	36.9, 36.7, 36.9	36.8
Bromoethylphthalimide	47.6, 47.4	47.3

It may be suggested that for a macro method for C and H the same apparatus could be used with only this modification that instead of the admixture of the substance with fine copper oxide it has to be burnt in a current oxygen.

For the determination of organic carbon in soils the amount of the sample to be taken for analysis will depend upon the nature of the

specimen. Usually enough soil is taken so as to yield about 0.1 g. of carbon dioxide. A sample passing a—100 mesh sieve is found to be convenient as thereby errors due to sampling of small quantities could be minimised. Otherwise the decomposition is equally good even with 1 m. m. mesh samples. It is mixed with 10 grams of the specially ignited copper oxide and the combustion carried out as above.

The chief difference between the analyses of pure substances and of soils lies in the length of time for which the heating is to be done. This is due to the presence of carbonates in the soils in more or less quantities. They may require longer heating and greater volume of air to be aspirated in order to complete the decomposition. Since calcium carbonate is the one most common in soils and probably the most difficult to decompose, experiments were made to find out the conditions of complete decomposition of calcium carbonate when mixed with copper oxide and ignited in the combustion tube at red heat. The progress of the decomposition was followed by stopping the aspiration of air and disconnecting the soda lime tubes at different intervals and weighing them. It was thus found that by keeping at red heat for about 45 minutes and passing 700 c. c. of air only 75% of the carbonate underwent decomposition, whereas after just more than one hour and passing 1000 c. c. of air though, the decomposition was complete.

On the other hand sodium carbonate decomposed to about 20% only under the same conditions within 1½ hours. Further decomposition was exceedingly slow. Hence this combustion method may not give quite correct results with soils which contain sodium carbonate, since the correction for the presence of carbonate in evaluating the organic carbon cannot be found out exactly.

It should be mentioned here that with all the soils mentioned below it was found that the oxidation of the organic matter and the decomposition of the carbonates could be completed by carrying out the combustion within one hour which involves keeping the boat at red heat for about 30 minutes and aspirating 350 c. c. of air only. The actual burning of the organic matter takes about 30 minutes and the carrying over of carbon dioxide into the soda lime tubes takes 20–30 minutes. The rapidity of the decomposition of soil carbonates may probably be due to their existence as a mixture of various metallic carbonates. This considerably shortened the time of analysis so that about 5 to 6 analysis could be done in day.

The following soils from typical localities in South India were analysed for organic carbon. The results indicate values obtained after allowing for the carbonates which are here expressed as Calcium carbonate.

Serial Number.	Soil description.	Carbon. %	CaCO ₃ %	Remarks.
Dryland Soils.				
1	Coimbatore, Central Farm. (New Permanent Manurials) Cattle manure plots.	0.74, 0.74	2.27	Pale red soil.
2	Do. No manure plots.	0.59, 0.59	2.75	"
3	Hagari (Bellary district) Soil Moisture Plots. 1st foot	0.53, 0.52	5.95	Heavy black soil.
	" 2nd "	0.52, 0.54	6.55	"
	" 3rd "	0.50, 0.50	6.84	"
	" 4th "	0.52, 0.52	7.34	"
	" 5th "	0.59, 0.58	8.27	"
	" 6th "	0.49, 0.46	8.59	"
4	Koilkuntla (Kurnool district).	0.53, 0.51	3.32	Black soil.
5	Palakkuppam.	0.35, 0.35	0.39	Red loamy soil.
Wet Land Paddy Soils.				
6	Coimbatore, Central Farm. Green manure plot.	0.74, 0.74	0.41	Puddled with green manure. Heavy soil.
7	Vedapatty, Paddy Breeding Station, Coimbatore.	0.73, 0.73	0.93	"
Estate Soils.				
8	Upper Parlai Estate, Valparai.	2.66, 2.69	0.32	Pale red soil.
9	Arnakal Estate.	2.00, 1.96	0.14	"

This work was done in the Chemistry Section of the Agricultural Research Institute, Coimbatore and the author expresses his thanks to the Govt. Agricultural Chemist for facilities offered.

References.

- (1) Soil Science, 30, 97.
- (2) " 24, 65.
- " 31, 483.
- " 29, 239.
- (3) Journal of Agricultural Science. 19, 315.
- (4) Pregl. Quantitative Organic Micro-analysis. (translated by Fyfe).
- (5) Journal of the Chemical Society. 1927, 3161.

SUGARCANE INSECTS AND PROBLEMS CONNECTED WITH THEM IN SOUTH INDIA*.

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Introduction. In the Madras Presidency, sugarcane is cultivated in all the important agricultural tracts, and at present, the area under this crop occupies somewhere about 126,000 acres.

The latest available crop statistics show the following distribution of cane area in the Presidency.—N. Circars 48,750 acres; Central districts 44,500; Carnatic including Nellore, Chingleput and S. Arcot 12,850; the Ceded Districts 11,700; the Southern districts 3,800; West Coast and Hills 3,620. For the whole of India the area under cane during 1931—32 has been noted to be 2,886,000 acres; over 50% of the sugar products is from the U. P.

* Note prepared as a member of the Committee for preparing a Sugarcane Pests Research Scheme, which met at Simla on 7th August 1933.