A Modification of Thorn and Shu's Method for Organic Carbon in Soils

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A modification of Thorn and Shu's method for determining organic carbon in soils is described. Results are presented for the determination of carbon in a number of pure compounds. The values for the carbon contents of eight soils have an average coefficient of variation of 0·9 per cent. and agree favourably with those found by a dry-combustion method.

For the determination of organic carbon in soils, several rapid methods are available,[1,2] all of which depend on oxidation. However, it is well known that the extent of oxidation can vary considerably and is complete for only a few soils. For example, during 1949, six New Zealand soils containing from 2 to 30 per cent. of carbon were analysed by either Allison's[1] or Schollenberger's[2] method in five laboratories, and the results were compared with those obtained by dry combustion.[3] As the carbon contents found by dry combustion were from 1·13 (brown granular clay) to 0·94 (skeletal soil) times those found by the rapid methods, Davies and his co-workers concluded that, although the rapid methods gave reproducible results, there was no correction factor of general application.

Most of the wet-combustion methods in which more drastic oxidation is used are less useful, as they are slower and do not achieve complete oxidation, or even a constant fraction of it. However, van Slyke and Folch[4] found that a mixture of sulphuric, orthophosphoric, chromic and iodic acids completely oxidised all the substances analysed, including cholesterol and stearic acid. Bremner[5] successfully applied this method to soils and soil extracts. Thorn and Shu[6] also used van Slyke and Folch's mixture to oxidise natural compounds, but instead of measuring manometrically the carbon dioxide evolved, they determined it by absorption in standard alkali under reduced pressure. Zinc turnings were used to remove acid vapours from the carbon dioxide, and iodine was removed by solid potassium iodide.

EXPERIMENTAL

When soils were analysed by Thorn and Shu's method, results were 5 to 10 per cent. low in the range 10 to 20 mg of carbon. This was attributed to slow diffusion of the carbon dioxide through the oxygen produced by the large excess of oxidant. The oxygen increased the pressure by more than 5 cm of mercury, but, when oxygen was removed by passing the gases through a roll of copper gauze heated in a silica tube, the initial pressure increased, after absorption of carbon dioxide was complete, by less than 1 cm of mercury. Replicate results were nearer to the correct values (as determined by dry combustion for soils and by calculation for pure compounds), but were extremely variable owing to uncontrollable amounts of acid vapours passing through the zinc trap. Attempts to prevent the acid vapours from passing into the standard alkali by lengthening the zinc trap and by inserting a trap containing sulphuric acid were unsuccessful. Little improvement was effected by passing the gases through a trap containing alkali and subsequently liberating carbon dioxide with lactic acid. The amount of alkali used had been calculated to react with the interfering gases and only a small proportion of the carbon dioxide, on the assumption that the stronger acids would be preferentially retained. However, the slightly longer procedure of quantitatively absorbing the carbon dioxide in an excess of sodium hydroxide also resulted in the quantitative absorption of the acid vapours. The traps containing zinc and potassium iodide were therefore discarded. Additional interference from halogens was then encountered and was not avoided when the trap containing potassium iodide was re-inserted or when hydrazine was added to the sodium hydroxide,[4] but was overcome by placing a spiral of silver wire immediately after the roll of copper gauze in the silica tube.

METHOD

APPARATUS—

The apparatus used is shown in Fig. 1 and is based on that described by Thorn and Shu.[6] The roll of copper gauze is wound on stiff resistance wire for ease of manipulation. Copper oxide is periodically removed by heating the roll of gauze in a bunsen flame, immersing it in the vapour above warmed methanol in a flask and leaving it there to cool. A clamp is inserted to control the gas flow from the combustion to the absorption flasks. This limits foaming of the reacting mixture and so permits more rapid heating than previously.

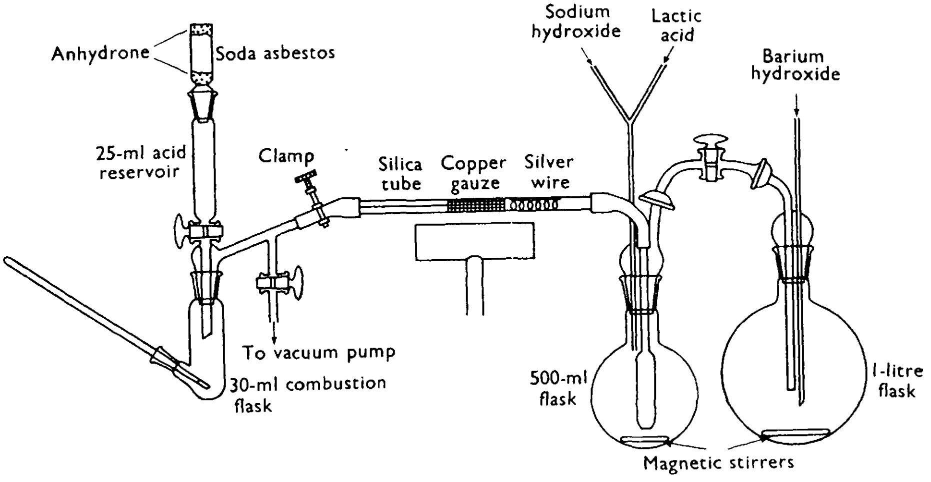

Fig. 1. Apparatus for determining carbon in soils by wet combustion

REAGENTS—

Iodate - dichromate mixture[7]—Grind together two parts by weight of potassium iodate and one of potassium dichromate.

Acid mixture[7]—Heat 67 ml of fuming sulphuric acid, 33 ml of syrupy phosphoric acid and 1 g of potassium iodate at 160° to 190° C until the iodate dissolves.

Sodium hydroxide, 0·5 N—Prepare free from carbonate.

Barium hydroxide, 0·2 N.

Lactic acid, 0·5 N.

Hydrochloric acid, 0·1 N.

Thymolphthalein indicator solution—Prepare a 0·1 per cent. w/v solution of thymolphthalein in 96 per cent. ethanol.

PROCEDURE—

Add 2 g of iodate - dichromate mixture to the finely ground sample, containing about 15 mg of carbon, in the combustion flask. Lubricate the ground-glass joints of the combustion flask and the stopcock from the acid reservoir with phosphoric acid. Evacuate the apparatus; during evacuation, allow 25 ml of 0·2 *N* barium hydroxide and 25 ml of 0·5 *N* carbonate-free sodium hydroxide to run into the 1-litre and 500-ml flasks, respectively, and heat the copper gauze in the silica tube to a dull red.

Close the stopcocks to the vacuum pump and to the second absorption flask, and allow 5 ml of the acid mixture in the acid reservoir to flow on to the sample. Heat the mixture carefully by means of a micro burner, and check any tendency to violent foaming by holding the flame at the base of the foam collar and by tightening the clamp between the combustion flask and the silica tube. When the temperature reaches about 150° C, close the clamp, heat to between 200° and 210° C, and then cautiously release the gases into the sodium hydroxide solution. After 5 minutes, remove the flame from beneath the copper gauze, close the clamp, run into the sodium hydroxide solution an amount of 0·5 *N* lactic acid calculated to give a final pH of 3 to 4, and open the tap leading to the flask containing the 0·2 *N* barium hydroxide. After a further 5 minutes, warm the first flask by means of a small flame until its contents boil. Absorption of the released carbon dioxide by the barium hydroxide is complete within 10 minutes. Restore the pressure in the apparatus to atmospheric by introducing air (free from carbon dioxide) through the pump line, and titrate the excess of 0·2 *N* barium hydroxide against 0·1 *N* hydrochloric acid to a faint blue end-point with thymolphthalein indicator solution. Note that the blank value can be taken as the trace amount of carbonate in the sodium hydroxide solution, but is best checked by oxidising an analytical standard, *e.g.*, hippuric acid.

TABLE I

CARBON CONTENTS OF VARIOUS PURE COMPOUNDS

Compound	Weight of sample, mg	Carbon content found, %	Theoretical carbon content, %
Hippuric acid	31·9 35·3 23·5 26·6	60·5 60·0 60·0 60·2	60·3
Potassium hydrogen tartrate	66·1 54·9	25·5 25·5	25·5
Sucrose	40·0 36·2	42·1 42·0	42·1
Glucose	39·3 47·6	39·9 40·0	40·0
Stearic acid	19·6 26·2	75·6 76·0	76·0
p-Chlorobenzoic acid	32·4 39·4	53·4 53·7	53·7
Cystine	52·9 60·9	30·0 29·9	30·0

Results

Some selected compounds were analysed, including some containing nitrogen, an alkali metal, sulphur or a halogen; the results are shown in Table I. The oxidation of sucrose produced far more iodine than did that of other compounds and, in absence of silver wire, caused results to be up to 2 per cent. higher than the theoretical value; results for chlorobenzoic acid were over 6 per cent. higher when the silver wire was omitted.

In Table II the results of analyses of eight soils by the proposed method are compared with those obtained by a micro dry-combustion method. For only one soil, a yellow-brown loam, did the carbon contents found by the two methods differ, the dry-combustion figure being, however, only 2·6 per cent. higher.

Table II

Carbon contents of various soils by the proposed and dry-combustion methods

Sample	Proposed method				Dry-combustion method	
	Number of determinations	Mean carbon content, %	Standard deviation, %	Coefficient of variation, %	Carbon content found, %	Mean carbon content, %
Brown granular clay loam	5	5·24	0·034	0·7	5·21, 5·27	5·24
Yellow-brown pumice soil	5	7·56	0·031	0·4	7·65, 7·57	7·61
Recent soil from alluvium	8	2·96	0·035	1·2	2·85, 2·96	2·91
Yellow-brown earth ..	5	3·45	0·037	1·1	3·40, 3·45	3·43
Yellow-brown loam	15	15·0	0·14	0·9	15·4, 15·3	15·4
	5	8·31	0·027	0·3	8·30, 8·27	8·29
Gley soil	5	4·82	0·043	0·9	4·72, 4·91	4·82
Well decomposed peat ..	6	16·3	0·24	1·5	16·2, 16·4	16·3

Conclusion

Although titrimetric methods for determining carbon dioxide are inherently less precise than the gravimetric method,[8] the proposed method for determining carbon in soils is much more rapid than the dry-combustion - gravimetric procedure and is sufficiently accurate for soils when uniformity of sample is likely to be a limiting factor.

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