# FURTHER APPLICATION OF POTASSIUM FERRICYANIDE METHOD* IN THE ESTIMATION OF ORGANIC CARBON IN SOILS

By K. L. Khanna and S. C. Sen

*(Central Sugarcane Research Station, Pusa, Bihar)*

Received June 17, 1946

## 1. Introduction

The complex nature of humus which depends largely on its origin and mode of formation leads to considerable difficulties in the estimation of organic carbon in soil. Further, in view of the fact that the standard dry combustion method is complicated, laborious and time-consuming, resort is being had almost entirely to the wet combustion methods by workers on soil. Of these, the acid permanganate method modified by Nostitsz (1936), the alkaline permanganate method by Puri (1937) and Potassium dichromate method by Walkley and Black (1934) are in common use. During the course of their work, the authors have experienced much difficulty in the application of these methods for the estimation of organic carbon in calcareous soils, which in North Bihar may contain sometimes as high as 25–30 per cent. of $CaCO_3$. Under these conditions, potassium permanganate in acid medium is found to decompose on heating and thus straight away lead to erroneous results. Walkley and Black's method which perhaps surpasses all the methods referred to above in regard to simplicity and rapidity, gives invariably higher values in calcareous soils compared to the dry combustion method while Puri's alkaline permanganate method although it is the nearest approach in aggregate of the soil samples examined, gives generally lower values and its end-point is not too well-defined. With the success already achieved by the authors with the alkaline potassium ferricyanide solution in the estimation of reducing sugars in cane juice (1938) and carbohydrate in cane leaves extract (1942), this solution was further tried to estimate organic carbon in soils. The results obtained during the last two seasons have compared very favourably with those obtained by the standard dry combustion method.

*The previous papers relate to the use of this method for the estimation of: (i) Reducing sugars in cane juice and (ii) Carbohydrate in cane leaves.

## 2. Experimental

Potassium permanganate in acid medium decomposes on heating (Nostitsz, *loc. cit.*) and the authors find that the rate of decomposition increases with the period of boiling (Table I). Both potassium permanganate and potassium ferricyanide in alkaline medium, however, remain quite stable for the brief period of boiling which is usually not more than five minutes and is quite ample to oxidise the organic matter.

TABLE I

*Rate of decomposition of oxidising agents with the period of boiling*

| Period of boiling | (A) Acid potasium permanganate | | (B) Alkaline potassium permanganate | | (C) Alkaline potassium ferricyanide | | Remarks |
|---|---|---|---|---|---|---|---|
| | Vol. N/10 $KMnO_4$ taken | Vol. N/10 $KMnO_4$ found | Vol. N/10 $KMnO_4$ taken | Vol. N/10 $KMnO_4$ found | Vol. $K_3Fe(CN_6$ taken | Vol. $K_3Fe(CN)_6$ found | |
| Just boiling | 20·0 | 18·5 | 10·0 | 10·0 | 20·0 | 20·0 | The methods used for A & B were exactly those recommended by the authors and for C as follows— 20 c.c. of 5% $K_3Fe(CN)_6$ sol. are boiled with 20 c.c. of 2·5% KOH and titrated against 0·5% extra pure dextrose sol. using one drop of 1% methyline blue as an internal indicator |
| | 20·0 | 18·0 | do | do | do | do | |
| 1 minute boiling | 20·0 | 15·1 | do | do | do | do | |
| | 20·0 | 14·9 | do | do | do | do | |
| 2 do do | 20·0 | 14·8 | do | do | do | do | |
| | 20·0 | 14·5 | do | do | do | do | |
| 3 do do | 20·0 | 14·0 | do | do | do | do | |
| | 20·0 | 13·8 | do | do | do | do | |
| 4 do do | 20·0 | 13·6 | do | do | do | do | |
| | 20·0 | 13·5 | do | do | do | do | |
| 5 do do | 20·0 | 13·0 | do | do | do | do | |
| | 20·0 | 12·7 | do | do | do | do | |

The alkaline potassium ferricyanide solution is a well-known oxidising agent and it has been observed that its rate of oxidation increases with the increased concentration of the solution. From the experimental results obtained with the various concentrations of the potassium ferricyanide as well as the KOH solutions, the following procedure has emerged as giving the best results in so far as the estimation of organic carbon in soils is concerned. This consists in boiling 2 grammes of soil (finely powdered and seived through 100 mesh wire-gauze) with 20 c.c. of 2·5% KOH solution for one minute, then adding 20 c.c. of 5% potassium ferricyanide solution from a graduated burette, and further boiling on an electric heater for 3–4 minutes for complete oxidation. The excess of ferricyanide solution is titrated back against 0·5% extra-pure glucose solution, the glucose and ferricyanide

solution being standardised such that 20 c.c. of 5% ferricyanide solution exactly neutralises 20 c.c. of 0·5% extra-pure glucose solution.

Walkley and Black (*loc. cit.*) while comparing their results with those from the standard dry combustion method found that only 60–85 per cent. of carbon reacted with Potassium dichromate and therefore they multiplied their results by 1·32. Puri (*loc. cit.*) similarly worked out a constant factor of 3·9 to go with his method. This factor so far as the method outlined above is concerned is 0·2 for 2 grammes of soil, the percentage of organic carbon in soil being calculated by multiplying the volume of 5 per cent. potassium ferricyanide solution consumed by 2 grammes of soil by 0·2 (Table II). Liebig's standard method of combustion was used as the standard for comparing the results. The soil was heated in a stream of oxygen, the products of oxidation passing over glowing copper oxide to ensure complete oxidation and then overheated lead chromate to remove oxides of nitrogen, sulphur and halogens. The carbon dioxide produced was determined gravimetrically. Over a dozen soil samples in the series given in Table II contain inorganic carbon (as $CaCO_3$) and, therefore, this $CaCO_3$ was removed from the soils before actual combustion by evaporating the

TABLE II

*Comparative results of organic carbon estimation by the four methods*

| Soil No. | Particulars | Percentage of organic corbon in soils | | | |
|---|---|---|---|---|---|
| | | Alkaline pot. permanganate method (Puri) | Pot. dichrote method (Walkley and Black) | Standard dry cumbustion method(Liebig) | Alkaline pot. ferricyanide method |
| 1 | 2 | 3 | 4 | 5 | 6 |
| 1 | Sepaya .. | 0·43 | 0·64 | 0·64 | 0·64 |
| 2 | Musheri .. | 0·37 | 0·64 | 0·53 | 0·42 |
| 3 | Motipur .. | 0·29 | 0·64 | 0·47 | 0·48 |
| 4 | Pusa .. | 0·35 | 0·62 | 0·54 | 0·56 |
| 5 | Majhaulia .. | 0·41 | 0·47 | 0·39 | 0·30 |
| 6 | Sabour .. | 0·59 | 0·78 | 0·65 | 0·75 |
| 7 | Monghyr .. | 0·53 | 0·68 | 0·55 | 0·56 |
| 8 | Harinagar .. | 0·60 | 0·80 | 0·65 | 0·58 |
| 9 | Navadah .. | 0·63 | 0·69 | 0·61 | 0·52 |
| 10 | Balasore .. | 0·57 | 0·62 | 0·54 | 0·62 |
| 11 | Tripura, Sahabad .. | 1·21 | 1·32 | 1·21 | 1·35 |
| 12 | Kanke, Ranchi .. | 0·74 | 0·92 | 0·85 | 0·88 |
| 13 | Jagadishpur, Buxar .. | 0·62 | 0·74 | 0·62 | 0·57 |
| 14 | Cuttack .. | 0·57 | 0·77 | 0·66 | 0·80 |
| 15 | Patna .. | 0·60 | 0·73 | 0·64 | 0·60 |
| 16 | Patporia, Motihari .. | 1·30 | 1·38 | 1·19 | 1·30 |
| 17 | Kishunpore, Motihari .. | 0·84 | 0·96 | 0·78 | 0·88 |
| 18 | Bahawara, Harinagar .. | 0·62 | 0·78 | 0·56 | 0·60 |

soil to dryness on a water-bath with excess of sulphurous acid. The soil is then powdered and mixed with a mixture of lead chromate and potassium chromate (lead chromate 1 part and potassium chromate 10 parts) in the proportion 2 : 1 and introduced into the combustion tube through the porcelain boat. The combustion is then proceeded as usual, only the ignition is done at a lower temperature. No sulphurous acid treatment was needed for other five carbonate-free soils.

The data recorded in Table II has been subjected to statistical analysis (Table III) where the differences in between the different methods have been tested with student's '*t*'. The results in the third column show that differences between A and B are highly significant whereas those between A and C and A and D are of the same order though 'D' shows closer agreement with the standard method A. This would be evident from the magnitude of the intra-class correlation coefficient as recorded in column 5 of the Table III referred to above. Further it has already been pointed out in para 1 above that C suffers from not too exact an end-point.

TABLE III

*Statistical evaluation of different methods employed for the estimation of organic carbon in soils*

| (1) | (2) | (3) | (4) | (5) |
|---|---|---|---|---|
| | Mean | S.E. | Prob. (*t*) | Intra-class correln. coefficients |
| A–B .. | −0·1229 | 0·0151 | Less than 0·001 | .. |
| A–C .. | 0·0407 | 0·0280 | 0·175 | 0·8720 (Bet. A & C) |
| A–D .. | −0·0107 | 0·0203 | 0·608 | 0·9356 (Bet. A & D) |

Where A stands for the standard method.
B „ Walkley & Black's method.
C „ Puri's method.
D „ Pot. ferricyanide method.

## 3. SUMMARY

1. Potassium permanganate in acid medium is found to decompose on heating and the rate of decomposition increases with the period of boiling.

2. A method for estimation of organic carbon in soil by oxidation with alkaline potassium ferricyanide solution is outlined.

3. The results obtained by the potassium ferricyanide method are shown to agree more closely in calcareous soils than other methods with those obtained by the standard dry combustion method. Besides the method is more exact in view of its very sharp end-point.

## 4. Acknowledgements

The work was carried out as part of the Sugarcane Research Scheme in Bihar partly financed by the Imperial Council of Agricultural Research to whom grateful thanks are due. The assistance rendered in the analytical work by M. Farooque is appreciated.

## References

Khanna, K. L., and Sen, S. C. .. *Jour. Ind. Agric. Sci.*, 1938, **8**, 441–46.

———— .. *Proc. Ind. Acad. Sci.*, 1942, **15**, 456–60.

Nostitsz, A. O. .. *Boden V. Pflanzenernahr*, 1936, **1**, 95–101.

Puri, A. N. .. *Soil Sci.*, 1937, **44**, 323–27.

Walkley, A., and Black, I. A. .. *Ibid.*, 1934, **37**, 29–38.