BLACK COTTON SOIL

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INTRODUCTION

THE paper deals with investigations into the properties of organic matter in black cotton soils and attempts to explain the factors responsible for the dark colour of the soil. The dark colour was previously attributed to the presence of titaniferrous magnetite,[1] magnetite,[2] a high C: N ratio,[3] exchangeable calcium,[4] the clay substance itself or organic matter.[6] Organic carbon as the cause of the black colour was discredited[7-8] as it was found that the colour was unaffected by treatment with H_2O_2 or NaOH. The conclusions reached were at variance with one another, and many of the results reported were not confirmed by subsequent investigations. No systematic analysis was carried out before and after treatment and the colour changes were observed mainly by visual observations and hence subjectively.

In the present paper an objective and systematic approach is made. Colour changes are estimated by a tintometer and expressed in terms of Munsell notation.[12] The organic carbon content was estimated before and after the treatments and the DTA technique was employed to study the thermal characteristics of the reactions involved. It is hoped that the results reported here afford an acceptable solution to the problem and throw some light, not only on the agricultural use of the soil and soil genesis, but also prove helpful in brick-making and similar industries where such soils are used.

EXPERIMENTAL

A typical sample of black cotton soil obtained from a brick field from Indore, Madhya Pradesh, was taken for the investigations. The mechanical analysis of the soil was carried out using sodium hexametaphosphate as the dispersing agent. The soil was also chemically analysed. The base exchange capacity was found out. These results are given in Table I. Organic carbon content was estimated by the Walkley and Black method.[9]

TABLE I

Composition of black soil from Indore

(*a*) *Mechanical composition* (*soil*)

Clay (·002 mm.)	Silt (·02 mm.)	Sand
53·3	19·8	26·9

(*b*) *Chemical composition* (*clay fraction*)

			Per cent.
SiO_2	..	..	48·65
Al_2O_3	..	..	12·83
Fe_2O_3	..	..	9·35
K_2O	..	..	Traces
TiO_2	..	..	Traces
CaO	..	..	7·87
MgO	..	..	2·26
Insolubles	..	..	1·49
Loss on ignition	..	..	17·33
SiO_2/Al_2O_3	..	..	6·42
$SiO_2/Al_2O_3 + Fe_2O_3$		..	4·39

Different treatments, such as heating in air or vacuum and treatments with different oxidising agents and soil extractants were tried. The colour changes, observed in each of these cases, using a tintometer and expressed in terms of the Lovibond scale and Munsell notation, are given in Tables II and III. The value of the neutral tint tabulated is a measure of the dullness of the colour.

Differential thermal analysis was carried out semi-automatically on the treated and untreated soil samples. The temperature of the furnace was raised uniformly at a rate of 10° C./min. using a Leeds and Northrup Programme Controller triggered by a chromel-alumel thermocouple, placed outside the specimen block. The specimen block was of Grimshaw and Roberts pattern[10] and was made of ceramic material. The differential thermocouple, made of chromel-alumel was connected to a sensitive Galvanometer. The Galvanometer readings were taken manually. The thermograms obtained are given in Fig. 1.

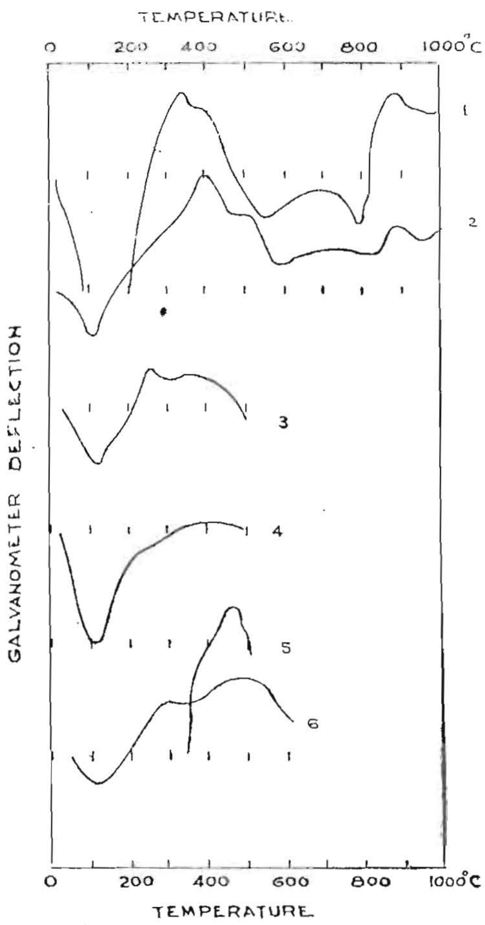

FIG. 1. Thermograms of black cotton soils subjected to various treatments.

(1) Clay fraction. (2) Vacuum-heated at 400° C. (3) Sodium hexametaphosphate treated. (4) Hydrogen peroxide (hot). (5) Hydrogen peroxide (cold). (6) Sodium hydroxide.

DISCUSSION OF RESULTS

The sample of Indore soil contains about 54% clay fraction. The base exchange capacity is 53·6 m.e./100 gm. when referred to the total soil and about 100 m.e./100 gm. when referred to the clay fraction alone. The SiO_2/Al_2O_3 and SiO_2/R_2O_3 ratios are 6·42 and 4·39 respectively and K^+ is present only in traces. These results, as well as the DTA diagrams, indicate the presence of montmorillonite in the sample.

The organic carbon content of the soil as determined is 0·45%. This is reduced to 0·16% and 0·02% when the soil is heated in air to 300° C. and 400° C. respectively with a progressive decrease, within this temperature range. The colour of the sample gradually changes as indicated by the reduction in the neutral tint to 2·7 at 300° C. and finally to 1·6 at 400° C. The increase in red observed is to be ascribed to the sintering of Fe_2O_3. The corresponding DTA curve of the untreated soils with a strong exothermic peak at 325° C., followed by another at 410° C., should represent a stepwise oxidation of the organic content of the soil. The rest of the reactions indicated at higher temperatures represent the loss of lattice water and the break-down of the lattice. The initial endothermic peak between 100 and 200° C. indicates loss of physically held water only.

Heating the soil to 400° C. in vacuum on the other hand increased the dark colour, the neutral tint increasing from an initial value 3·0 to 4·6 for the treated soil. The carbon content was naturally not reduced and remained at 0·39% at 400° C. The small reduction of 0·06% carbon is probably due to some burning of the organic matter to elemental carbon which cannot be detected in the Walkley and Black method. The vacuum-heated soil when heated in air loses the dark colour, above 600° C., at about which temperature the elemental carbon is oxidised. The higher endothermic peaks in the DTA curve of the vacuum-heated sample is reduced to a small extent.

Treatment with hydrogen peroxide.—Treatment with hydrogen peroxide at room temperature failed to remove the dark colour of the sample, the neutral tint reduced from 3·0–2·7 only and the organic matter from 0·45–0·39% only. This observation is in conformity with those of other workers.[6-8]

However, when the soil was treated with hydrogen peroxide at 80° C. for 6 days, the carbon content was reduced almost to 0% and the neutral tint fell from 3·0–1·2 indicating the removal of the dark colour. Worall[11] reported that lignin humus fraction of clay got oxidised by H_2O_2 treatment only at 80° C. The DTA diagram of the soil so treated fails to show the exothermic peaks whereas the diagram for the soil after cold treatment continues to show them.

Dichromate treatment.—Treatment with acidified potassium dichromate destroyed the dark colour of the sample, reducing the neutral tint from 3–1·8. When the dichromate-treated sample was heated in vacuum it failed to show any deepening of the colour. This indicates the absence of organic matter in the sample and also shows that the deepening of the dark colour in the soil on heating under vacuum is due to the reduction of the part of organic matter to elemental carbon.

Extraction with sodium hydroxide.—Using Worall's method,[12] 150 gm. of black soil was repeatedly extracted with 500 c.c. of 10% NaOH at boiling point. The colour was only partially transferred to the alkaline ex which on addition of HCl precipitated a small amount of humic acid. treated sample, on analysis, gave 0·3% carbon only. The neutral colour of the residue changed from 3·0–2·3 only. Evidently NaOH could re the colour only to a minor extent. Such would not be the case if the or matter in the original soil contained free humic acid. This is fu supported by the fact that extraction with a hot solution of ammonia di also reduce the colour. Negative results were recorded when lignin sought to be detected by the standard phloroglucinol and sodium h chlorite and sodium sulphite tests. Only a small reduction of the thermic peaks is observed for the NaOH-treated sample.

Extraction with sodium hexametaphosphate.—This method was f successful at Rothamsted[13] for extracting soil humus matter. The pr sample when extracted with N/25 hexametaphosphate did not prove eff in the removal of dark colour. On the other hand, when the soil extracted with 10% boiling solution of the hexametaphosphate, the ne value was brought down to 1·2 and the carbon content reduced to 0 The DTA diagram of the soil so treated shows the highly reduced peak to the residual organic matter only which is not responsible for the colour.

The DTA curve of the untreated sample shows that oxidation of or matter occurs in two stages as shown by the two peaks, one at 325° C. an other at 410° C. Soveri[14] observed double exothermic peaks in c Fennoscandian clays. He has shown that the peak at 330° C. is caus water-soluble or precipitated humic complexes. In some cases he ob another less pronounced peak at about 380–470° C. Thermograms of sample treated with cold hydrogen peroxide exhibits a single exoth peak corresponding to a temperature of 410° C. The treatment doe reduce the dark colour of the soil. Hot hydrogen peroxide practically nates both the peaks and also removes the dark colour. This indicate the fraction of organic matter responsible for the dark colour is oxidi 410° C. Phosphate treatment reduces the intensity of the dark colo well as the area of the two peaks appreciably. Removal of humic acid soil by phosphate treatment shows that a part of the organic matter fo complex with the clay mineral. Sodium hydroxide treatment also re the area of both the peaks, but the reduction in area is much less tha obtained by the phosphate treatment. This corroborates the fact phosphate ions are more efficacious in removing the anions which are att on the positive sites available on the edges of the clay crystal. All th dence points to the fact that part of the organic matter in black soil a complex with the clay mineral and part is in the uncombined state. The existence of clay complex has now been well established. The fraction which combines with clay mineral is naturally more resistant to the action of the destructive agencies and therefore requires prolonged H_2O_2 treatment at a temperature of 80° C. for its destruction. It also oxidises at a higher temperature compared to other fraction.

Thus, the presence of 0·45% organic carbon in the sample, the fact that a sensible reduction of that percentage by either methods adopted is always accompanied by the destruction of dark colour and the fact that whenever there is no reduction of carbon content, the dark colour continues to persist, shows that the colour of the black soil is primarily due to its organic content, which may, in part at least, be in combination with the clay mineral.

Summary

Black cotton soil from Indore (Madhya Pradesh) which is predominantly composed of montmorillonite contained 0·45% organic matter. A sensible reduction of the organic content by any method was invariably followed by a corresponding reduction in its dark colour. Treatment with 10% sodium hexametaphosphate at boiling point or with H_2O_2 at 80° C. or the dichromate were effective in removing the colour. NaOH does not remove the organic matter nor the dark colour of the soil except only slightly. Heating in air at 400° C. oxidises the organic matter and hence removes the colour. Heating in vacuum however is obviously ineffective. DTA studies show that the oxidation of the organic matter, which is responsible for the dark colour, occurs in stages at 325° and 410°C.

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