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Differential thermal analysis of soil from Panchanganga River Basin, Kolhapur

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ABSTRACT

Thermal behavior being one of the physical property of any material, it gives fair estimation of constituents, nature and usage of material. The traditionally adopted procedure for thermo gravimetry and calorimetry are tedious, time consuming and involve elaborate human intervention. In the thermal analyzing system, use of electronic sensors for the physical measurement increases the sensitivity, accuracy and ease of operation. Characterization of soil in the temperature range of 30 to 800 °C at 50 mv full scale in Differential Thermal Analysis indicated presence of Kaolinite, and Smectite group of clay minerals associated with Micas.

Key words : *Differential Thermal Analysis, Kaolinite and Smectite, CEC, Endothermic and Exothermic , Peak temperature curves.*

Study area

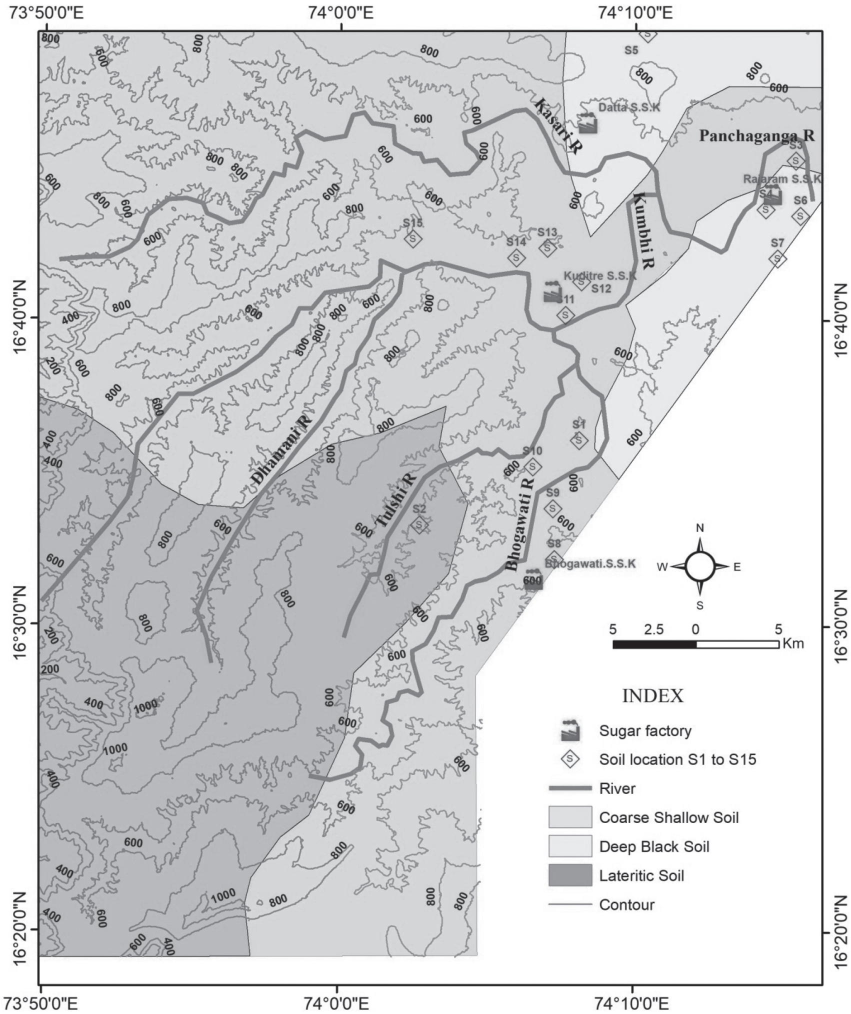
The Panchanganga river basin lies in the area bounded by latitude 16^0 18′ 00''N to 16^0 50′00'' N and longitude 73^0 50′ 00'' E to 74^0 16′ 6.42'' E. The river basin has been carved out in basalt flows of the Deccan Volcanic Province. These rocks now form the valley side, hills and ridges within the basin. At higher altitudes they have been converted into laterites that contain pockets of bauxites. The soils derived from these rocks form a thin veneer on the valley floor. Because of the intensive weathering of parent rock and their transportation downstream, well developed alluvial deposits are formed on the banks of rivers. The thickness of the alluvial soil varies from 5 to 10m in the valley portions of the Panchanganga river basin. As shown in Fig.1. within the river basin, three types of soils can be demarcated. Black cotton soil is well developed in the north and north-western part of the basin and all along the bank of the river Bhogawati. Reddish brown lateritic soil is well developed on the plateau in the western and central part of the basin. In the southern part of the Kolhapur city a thin layer of coarse soil is developed on weathered basalts.

Soil sampling

Fifteen representative soil samples were collected from cropland, from a depth of 10-15 cm. About 1.5 kg.of sample was collected in a polythene bag and dried in the laboratory before grinding and sieving. The samples were collected only once during the course of work. The location of these soil samples are shown in Fig.1.

Methodology

The soil samples were crushed and the clay fraction was separated by International Pipette Method as per the procedure given by Carver (1971).



The sample was sieved through 300 mesh and fine fraction was collected on pan and transferred to 1000ml graduated cylinder. About 15 mL of 10% solution of sodium hexametaphosphate (dispersing agent) was added, and sample was stirred for five to ten minutes in order to ensure an even distribution of sediment throughout the cylinder. After 24 hours, the dispersal of the particles were checked, and distilled water was added up to 1000 mL mark, and the sample was stirred again and kept for overnight 250 ml of this solution was collected from the cylinder from a depth of 10 cm by dipping the pipette into the solution. The solution so collected was centrifuged and the residue was dried under room temperature. This clay fraction was then used for DTA analysis. To support the DTA analysis reports, Cation Exchange Capacity (CEC) of soil sample was determined.

Thermal Analysis

Thermal analysis was carried out on a Rigeku-889 El model thermoflux. Initially the sample was dried at 60 °C in near vacuum (1 mm pressure) for an hour to remove adhering moisture. About 7 mg of powder was then heated at constant heating rate of 10 °C/min through a temperature range of 30 to 800 °C at 50 mv full scale. DSC at 100% full scale was obtained. Peak temperatures were estimated from values of electromotive force of thermocouple using standard table provided by the manufacturers. The temperatures at which endothermic and exothermic reactions took place were recorded for further interpretations.

Review of Literature

The proposition that soil thermograms represent characteristic properties and can be used to characterize soil organic matter quality has existed for decades. However, only recently has the number of tested soils and fractions been large enough to test this proposition and the potential link between thermal and biological soil organic matter stability (Alain F.Plante *et al.,* 2009). The mineralogy of clay constituents in the soil overlying Deccan basalts has been studied with the help of Differential Thermal Analysis and Infra-red Spectroscopy by Uma Nagpal and Powar (1987) and Patil *et al.,* (1990 & 1991). A similar study was done by Roonwale and Srivastava (1991) along the west coast transect in the Indian ocean and by Haile *et al.,* (1991) on the sediments of West Bengal. The application of DTA in identification of minerals was made by (Mackenzie, 1957). Wallach (1913) and Fenner (1913) were the pioneer workers in applying thermal analysis to clays. The work of Smykatz Kloss (1974) finds wide application of thermal analysis in the mineralogical studies. The fertility of soil depends upon the CEC, texture and structure of soil, which in turn depends upon the composition and type of soil. The degree of weathering is also an important factor controlling the soil type. The contact of rocks and water produces clays, either at or near the surface of the earth (Velde, 1995). The clays from the weathered rocks fall into three main classes in the order of decreasing chemical complexity : the smectite, the illite and the Kaolinite clay minerals. Deer *et al.,* (1978) classified the clay minerals into five main groups, based on the basal spacing viz. kandite group (7A*), illite group (10A*), smectite group (15A*), vermiculite group (14.5A*) and palygorskite group. Grim (1968) suggested a classification based on the distinction of shape of the clay minerals and expandable or non-expandable characters of the 2:1 and 1:1 and 1:1 layer silicates into amorphous, allophone group and crystalline group.

Results and Discussion

DTA results are plotted in the form of continuous curve in which the thermal reactions are plotted against furnace temperatures with endothermic reactions conventionally shown as downward deflection and exothermic reactions as upward deflection from horizontal base line. The DTA of clay minerals show characteristic endothermic reactions due to dehydration and to loss of crystal structure, and exothermic reactions due to the formation of new phase/s.

In the present study, the soil samples were subjected to differential scanning in the temperature range of 30 to 800 °C. DTA curves some representative samples is given in Figure 1 & 2 and Peak temperature of reaction recorded for all clay samples from Differential Scanning Curves is given in Table 1.

The inclined portion of the DTA curve has been attributed in the literature to the presence of organic matter in the clay minerals(Thanikachalam & Viswanathan, 1973). From the Figs. 1.1 it is clear that most of the soil samples show an endothermic peak between 80 - 100 °C. This can be attributed to

Table 1. Peak temperature of reaction recorded for clay samples from Differential Scanning Curves

Sample No.	Endothermic (°C)		Exothermic (°C)		CEC (meq/100gm)
	1	2	1	2	
S1	99	486	323	408	21.00
S2	99	497	329	402	20.00
S3	85	564	334	413	35.00
S4	85	486	339	430	24.00
S5	113	498	334	421	28.00
S6	106	497	328	425	24.00
S7	106	497	334	430	35.00
S8	99	564	328	413	28.00
S9	99	486	329	418	28.00
S10	99	575	334	449	25.00
S11	99	497	323	430	22.00
S12	106	486	329	430	28.00
S13	99	497	323	413	30.00
S14	99	486	323	419	32.00
S15	99	497	329	402	23.00

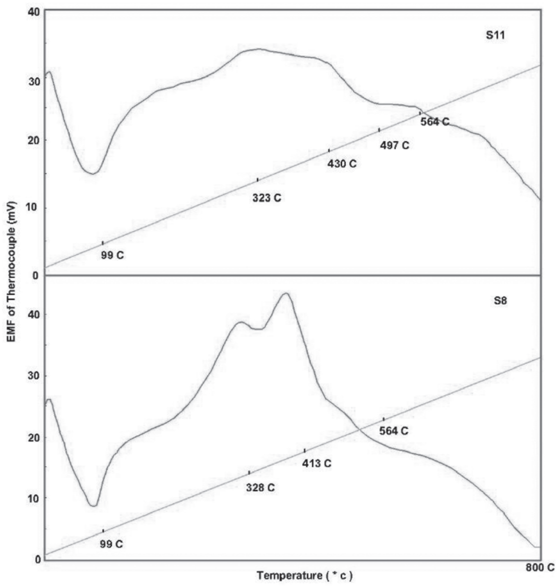


Fig. 1. DTA curve for soil samples

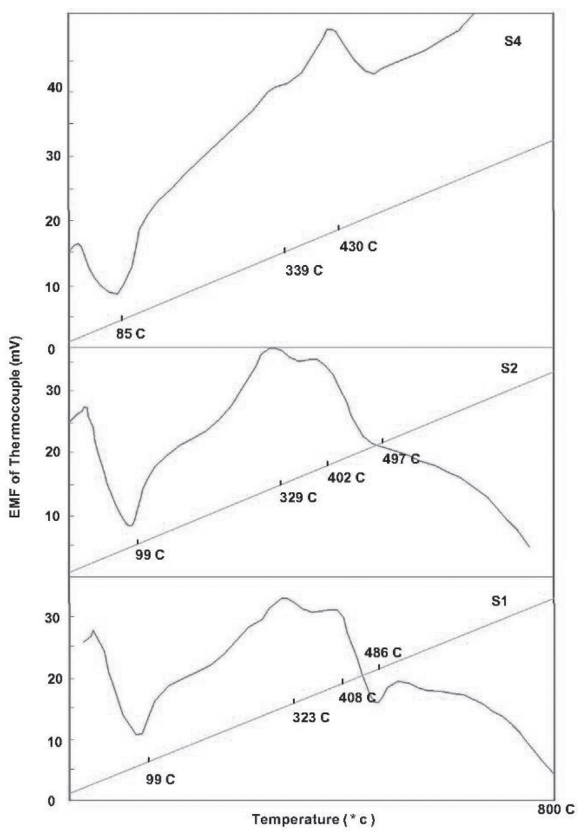


Fig. 2. DTA curve for soil samples

the loss of moisture at lower temperature. The second endothermic peak was observed between 486 to 500°C in all the soil samples reflecting the presence of smectite group of clay minerals; except (Sample Nos S_3, S_8, S_{10}) in which it was between 564 - 575°C which is a characteristic of Kaolinite group of minerals. The endothermic peak at 560 °C can be attributed to dehydration and deformation of structure of Kaolinite (Smykatz-Kloss, 1974). The endothermic peak in the temperature range of 486 - 498 °C reflects the dehydration and decomposition of the structure. A strong endothermic peak at 100 - 110 °C and 500 °C and weaker peak at 300 °C may also indicate the presence of polygorskite group of clay minerals. The soil sample S_5 showed and endothermic peak at 113 °C which may indicate the presence of halloysite. This peak might have occurred due to the evaporation of water which has occupied the inter layer space (Smykatz – Kloss, 1974).

Almost all the samples showed an exothermic peak between 300 - 330 °C which may be due to the oxidation of some ferrous iron in high iron beidellite variety called nontronite (Meckenzie, 1970). This peak can be ascribed to the presence of limonite (Smykatz Kloss, 1974). The endothermic peak between 95 - 107 °C and exothermic peak between 415 - 444 °C may indicate the presence of micas (sericite, biotite or illite).

The presence of kaolinite, smectite or polygorskite group of clay minerals cannot be confirmed by the presence of endothermic peaks in the lower temperature range. The Kaolinite minerals show characteristic exothermic peak between 950 to 970 °C, and reflect the crystallization of Kaolinite or Spinel phase, whereas Smectatite group of clay minerals show a sharp exothermic peak between 840 to 920 °C and reflect the recrystallisation of a new structure – a kind of mullite (Smykatz Kloss, 1974). According to Henry (1951), the ratio of tetrahedral to octahedral sheets in Kaolinite is 1:1 and in Montmorllonite it is 2:1 and also the relative particle size of Kaolinite is larger than Montmorllonite, which as a result have lower CEC values for Kaolinite and higher for Montmorllonite. In the present study, the CEC of the black cotton soil around Kolhapur showed value as high as 35 meq/100 g of soil, as against 23 meq/100 g of soil for medium black or lateritic soil. This indicates that the black cotton soils are dominated by Montmorllonite and medium black or lateritic soils by Kaolinity minerals.

Conclusion

The DTA revealed that the clay is an admixture of minerals in different proportions. The Differential Scanning Curves in temperature range of 30 to 800C shows that the clay minerals are largely of Kaolinity and Smectite (Montmorllonite) group of clay minerals. The black cotton soils are dominated by Montmorllonite and medium black or lateritic soils by Kaolinite minerals. The endothermic peak between 95 - 107 °C and exothermic peak between 415 - 444 °C indicate the presence of micas (sericite, biotite or illite). There is scope to study the Infrared / XRF pattern to confirm the presence of these mineral groups to confirm the DTA results of mineral characterization.

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