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Characterisation of Organic Matter in Four Soils of Peninsular Malaysia. III. Characteristics of Metal Fulvate and Metal Humate Complexes Prepared in the Laboratory

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Metal humates and metal fulvates were prepared in the laboratory by reacting humic acid and fulvic acid extracted from Rengam soil (Typic Paleudult) with the metal ions Cu^{2+}, Zn^{2+}, Mn^{2+}, and Fe^{3+} at pH 5. The complexes formed were characterised by chemical, infra-red, X-ray, differential thermal and thermogravimetric analyses.

Results showed that both COOH and phenolic OH groups were involved in the complexation of the metal ions to humic and fulvic acids. From differential thermal and thermogravimetric analyses, it was observed that the main decomposition peak of humic acid was shifted to higher temperatures while for fulvic acid, the main decomposition peak was shifted to lower temperatures on interaction of the acids with the metal ions Cu^{2+}, Zn^{2+}, Mn^{2+}, and Fe^{3+}. The main decomposition peaks of the metal humates and fulvates were observed to lie in the same vicinity i.e. *in the range of 300°C to 349°C.*

In soils and waters, humic acid (HA) and fulvic acid (FA) interact with metal ions to form soluble and insoluble organo-metallic complexes. The water-soluble complexes are thus available to roots. As yet, no information is available on the nature and characteristics of the organo-metallic complexes present in the soils of Peninsular Malaysia. This paper describes the preparation of such complexes in the laboratory and discusses the major analytical characteristics of the complexes formed.

MATERIALS AND METHODS

Humic and Fulvic Acids

Humic and fulvic acids were extracted and purified from Rengam soil as described by Norhayati Moris and Verloo[1]. The metallic humates and fulvates were prepared by interacting a known amount of the purified humic or fulvic acid with the cations Cu^{2+}, Zn^{2+}, Mn^{2+} and Fe^{3+}.

Preparation of Metallic Humates

To 100 mg of the purified HA, 3 ml of 0.1 *N* NaOH and 20 ml of distilled water were added. The mixture was stirred for a few minutes until a clear solution was obtained, then 4 ml of 1 mmole stock metal solution was pipetted into the mixture and the pH of the reaction mixture was adjusted to 5 with dilute hydrochloric acid. The mixture was stirred for 1 h at room temperature. In the case of iron humate (Fe-HA), the pH was adjusted to

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2.5 to avoid excessive formation of iron hyroxide.

Preparation of Metallic Fulvates

To 75 mg of the purified FA, 25 ml of distilled water was added and the mixture stirred until all of the FA had dissolved, 2 ml of the 1 mmole stock metal solution was pipetted into it and the pH of the reaction mixture was adjusted to 5 with 0.01 *N* NaOH. The mixture was stirred for 1 h at room temperature. In the case of iron fulvate, the pH was adjusted to 2.5 to avoid excessive hydroxide formation.

Purification of Metallic Humates and Fulvates

The reaction mixture was transferred to cellulose tubing and dialysed against distilled water, with daily change of the water, until no Cl^- was present in the outer solution (as tested with silver nitrate solution). The solution was first preconcentrated by warming in an oven at 40°C for two to three days and then freeze-dried.

Analysis of the Complexes

Elemental composition of the complexes. The percentage C and H of the humate and fulvate components of the complexes formed were determined by using the elemental analyser[2].

The percentage metal ions present in the complexes was determined after digesting the complexes with 5:1 HNO_3: HCl mixture, dissolving the residues in 1 *N* HCl, and analysing the metal ions in solution by inductively coupled plasma optical emission spectrophotometry.

Infra-red spectroscopic measurements. Infra-red spectra of the complexes were recorded on a Beckman spectrophotometer using the KBr technique.

Differential thermogravimetric and thermal analysis. For differential thermogravimetric analysis, 10 mg of the complex was taken and heated at a constant rate of heating of 15°C per minute under nitrogen atmosphere. The analysis was performed with a Du Pont 900 Thermal Analyser.

For differential thermal analysis, 10 mg of the complex was diluted with alumina and analysed with the Du Pont S9 model. The apparatus was run at a constant rate of heating of 20°C per minute under nitrogen atmosphere.

X-ray analysis. X-ray diffraction of the complex was obtained using the Phillips X-ray diffractometer (PW 1050/25) and Co K_α radiation.

RESULTS AND DISCUSSION

Elemental Composition of the Complexes

Due to the very small yield of complexes, chemical analysis had to be restricted to the more important characteristics. *Table 1* lists the chemical composition of the complexes and their moisture content. The moisture content of the complexes was estimated from the thermogravimetric studies whereby percentage loss of weight at 105°C was taken as percentage loss due to dehydration of water molecules.

Percentage humic or fulvic acid present in the complexes was estimated by multiplying percentage C in the complexes by the conventional factor 1.72. From *Table 1*, it is observed that the percentages of all the constituents in the complexes when added up gave values which range from 91.35% to 95.97%. The 5% to 8% of the weights which are unaccounted for can be attributed to the presence of water molecules which are tightly bound to the organic macromolecules and are not removed at 105°C.

Figures 1 and *2* show the IR spectra of HA and metal humates respectively while *Figures 3*

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TABLE 1. CHEMICAL COMPOSITION AND MOISTURE CONTENT OF METAL HUMATES AND FULVATES

Complex	C (%)	H (%)	Organic matter (%)	Metal (%)	Moisture (%)	Total (%)	Total % corrected for as conte
Cu-HA	46.15	5.18	79.38	2.25	13.00	94.63	95.97
Zn-HA	45.81	5.23	78.79	3.10	12.00	93.89	95.22
Mn-HA	46.25	5.32	79.55	1.69	13.00	94.24	95.58
Fe-HA	45.71	5.08	78.62	2.02	12.50	93.14	94.16
Cu-FA	33.92	6.38	58.34	3.12	12.50	73.78	95.75
Zn-FA	35.21	6.41	60.56	1.40	12.00	73.99	91.35
Mn-HA	35.64	6.36	61.30	1.26	15.00	77.56	95.75
Fe-FA	33.87	6.82	58.25	1.83	14.50	74.58	92.07

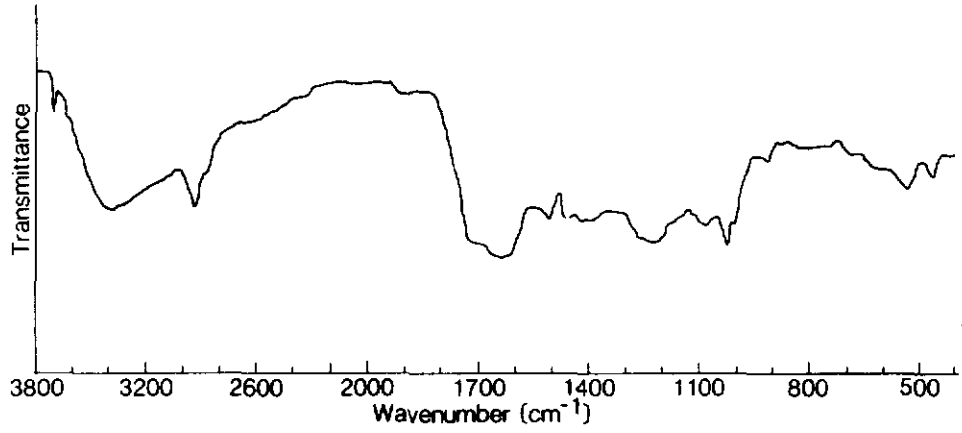

Figure 1. Infra-red spectrum of humic acid.

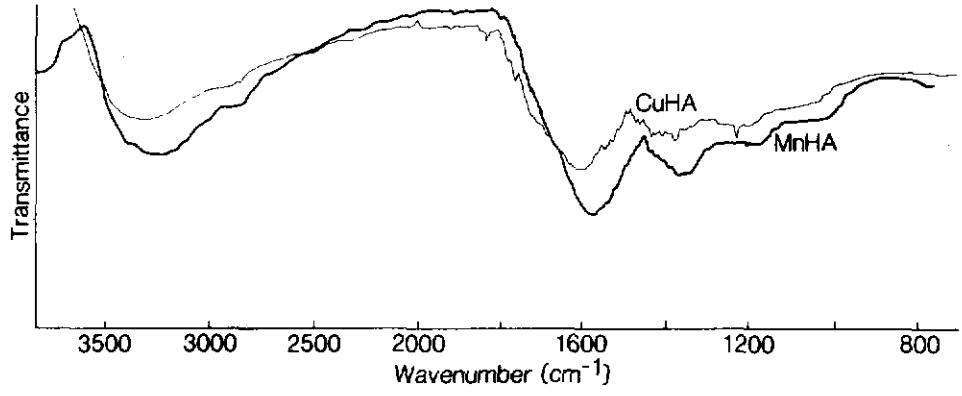

Figure 2. Infra-red spectra of metal humates.

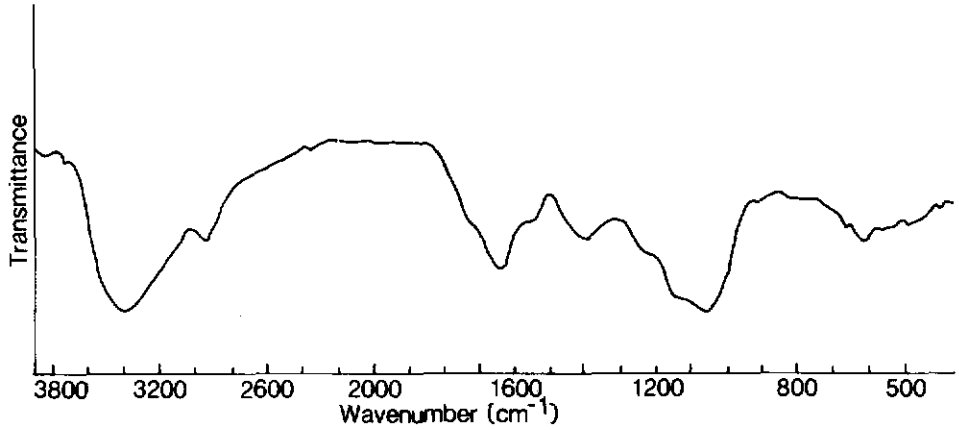

Figure 3. Infra-red spectrum of fulvic acid.

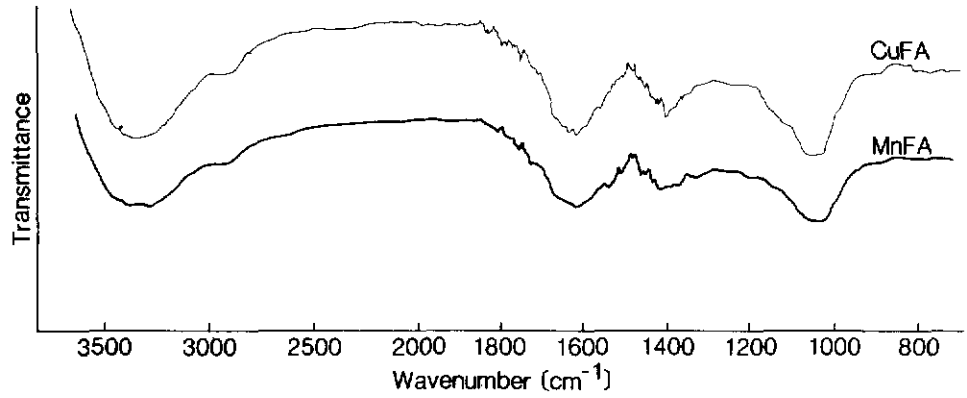

Figure 4. Infra-red spectra of metal fulvates.

and *4* show the IR spectra of FA and metal fulvates respectively. The main differences between the spectra of the metal humates and that of HA lie in the region 1800 cm^{-1} to 1600 cm^{-1} and 1400 cm^{-1} to 1200 cm^{-1}, while those of the metal fulvates and that of FA lie in the region 1800 cm^{-} to 1600 cm^{-1} only.

The shoulders at 1725 cm^{-1} were absent from the spectra of the metal humates and fulvates. These shoulders which are assigned to the C = O of COOH groups were present in the spectra of both HA and FA. With the absence of these shoulders and a corresponding widening of the 1610–1640 cm^{-1} band in the spectra of the metal complexes, it can be deduced that the free COOH groups in the acid molecules have been converted to the carboxylate, COO^{-}, to which the metal ions are bonded by means of electrovalent linkages[3,4].

From *Figure 2,* it can be observed that the spectra of the metal humates show bands at 1400 cm^{-1}. These bands were absent in the spectrum of HA. In the case of the metal fulvates, the bands at 1400 cm^{-1} were slightly more prominent (with the exception of the spectrum of Mn-FA) than the spectrum of

FA. These observations further substantiate the fact that the COOH groups in the acids have been converted to the carboxylate form, COO^-, to which the metal ions are bound.

For the spectra of the metal humates, the band at 1225 cm^{-1}, which was present in the spectrum of HA, was absent. This band can be assigned to the C-O stretching of phenolic OH groups[5]. The shoulder between 1200 cm^{-1} and 1100 cm^{-1}, assigned to C-O stretching of phenols and/or alcohols was less pronounced in the spectra of the metal fulvates. Thus, it can be deduced that phenolic OH groups were also involved in the metal-organic matter interactions.

Thermogravimetric and Differential Thermal Analysis

Thermogravimetric and differential thermal (DTA) analyses were used in this study as a discriminatory tool, to compare the thermal behaviour of HA and FA with that of the metal complexes. *Figures 5* and *6* illustrate the thermal behaviour of the complexes as they were progressively heated. These curves have also been used to estimate the moisture contents of the complexes, whereby percentage loss of weight at 105°C is taken as loss due to dehydration of water molecules.

For all the complexes, except FeFA and FeHA, 10% or less of the substance remained after ignition at 900°C *(Figures 5* and *6)*.

Figures 7 and *8* show the thermographs of the metal humates and metal fulvates respectively. The thermographs of the metal humates show differences in their reaction peaks as compared wtih that of HA, especially in the region of 215°C to 530°C. In addition, the thermographs of the individual metal humates also exhibit differences in character from each other.

For copper humate, the exotherm at 341°C is very broad and is followed by a sharp base line shift in the endothermal direction at 680°C, while for zinc humate, a small endotherm at 301°C is observed prior to the exotherm at 341°C. A very weak base line shift in the endothermal reaction can be seen at 740°C. In the case of manganese humate, the exotherm at 329°C is followed closely by an endotherm at 402°C, while the exotherm at 321°C for iron humate is followed by an endotherm at 357°C.

The thermograph of the untreated FA is characterised by two endotherms at 193°C and 305°C and a broad exotherm at 450°C *(Figure 8)*. The thermographs of the metal fulvates exhibit differences from that of FA in the 160°C–457°C range. The endotherm at 305°C of FA is absent in the thermographs of all the metal fulvates. The exotherm at 450°C of FA is observed at lower temperatures in the metal fulvates, *i.e.* at 317°C in copper fulvate; at 300°C in zinc fulvate; at 349°C in manganese fulvate and at 321°C in iron fulvate. Zinc fulvate is observed to exhibit a slight endotherm at 351°C.

Thus, it can be concluded from the above observations that individual elements influence differently the thermal stabilities of complexes formed by the interactions of the metals with organic matter fractions, as depicted by the DTA curves. These differences in stability are most likely related to the differences in the type of bonds that the metals form with the organic matter fractions. Similar observations have recently been reported by Schnitzer and Ghosh[6]. *Table 2* summaries the different types of thermal behaviour of the complexes.

The major peaks in the vicinity of 300°C for HA and the metal humates indicate the temperature at which the main decomposition of the molecules take place. It is observed that the presence of the metals shifted the decomposition peak to higher temperatures. For FA, the main decomposition peak is at 450°C. However, in the metal fulvates, this

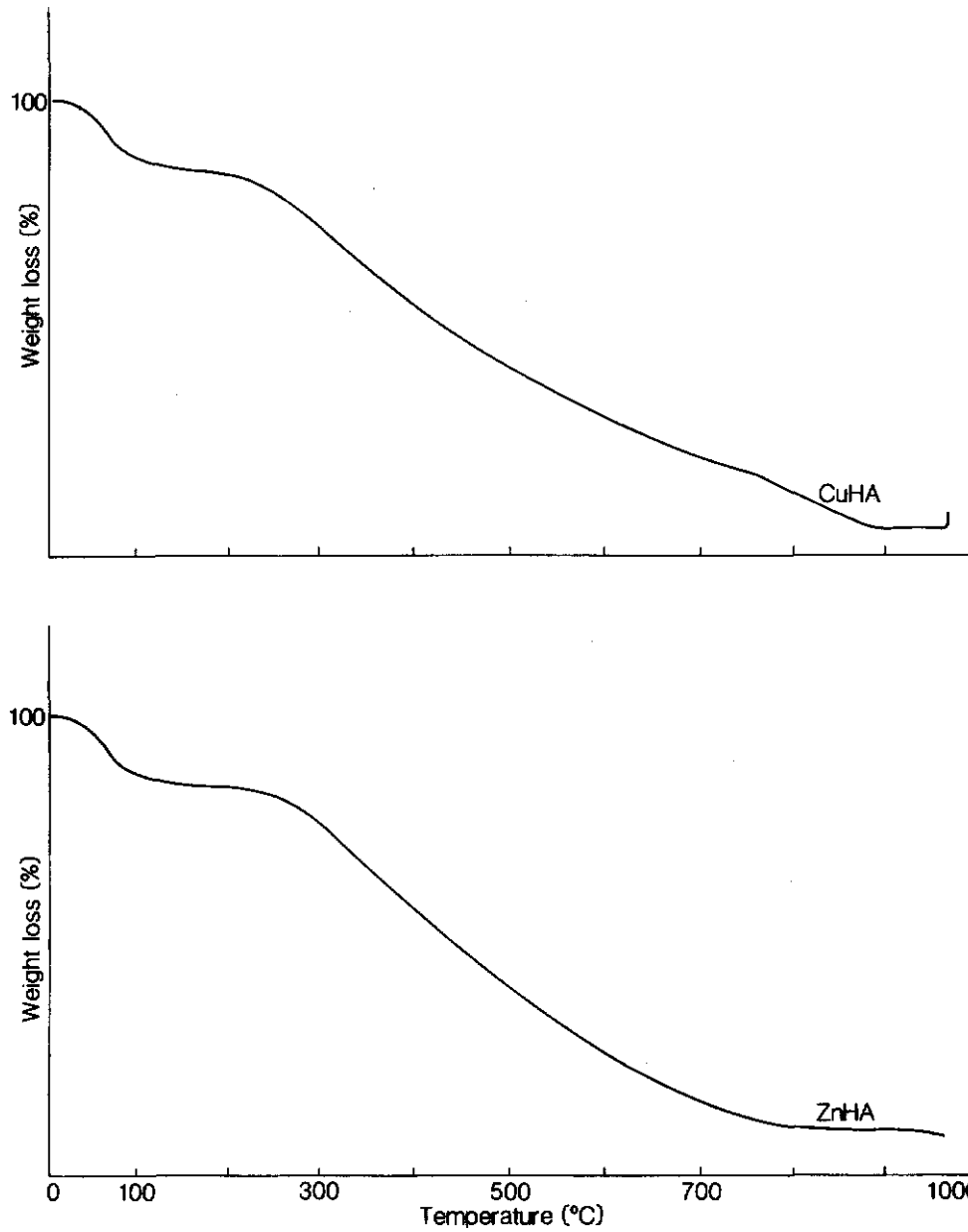

Figure 5. Thermogravimetric curves of metal humates.

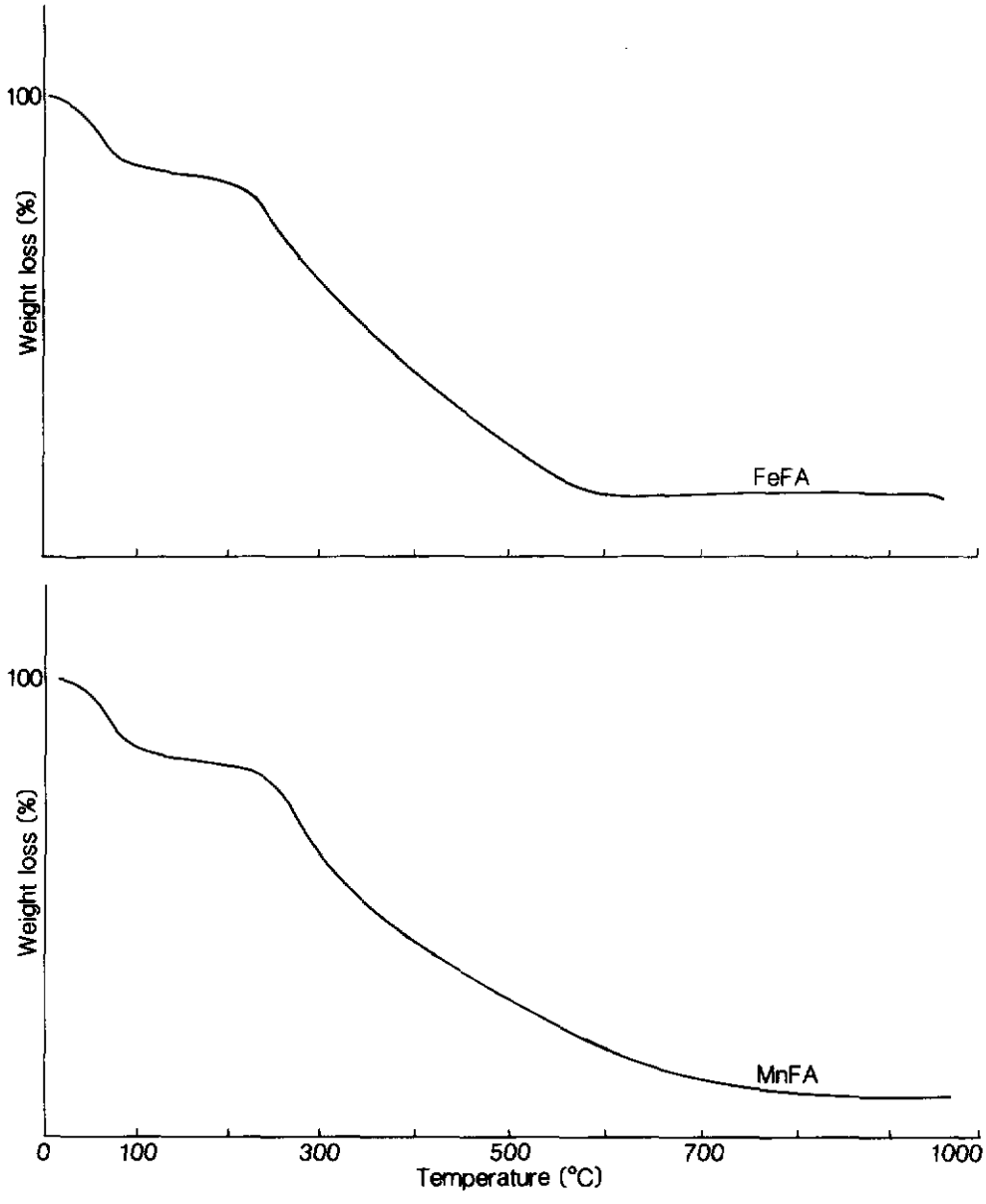

Figure 6. Thermogravimetric curves of metal fulvates.

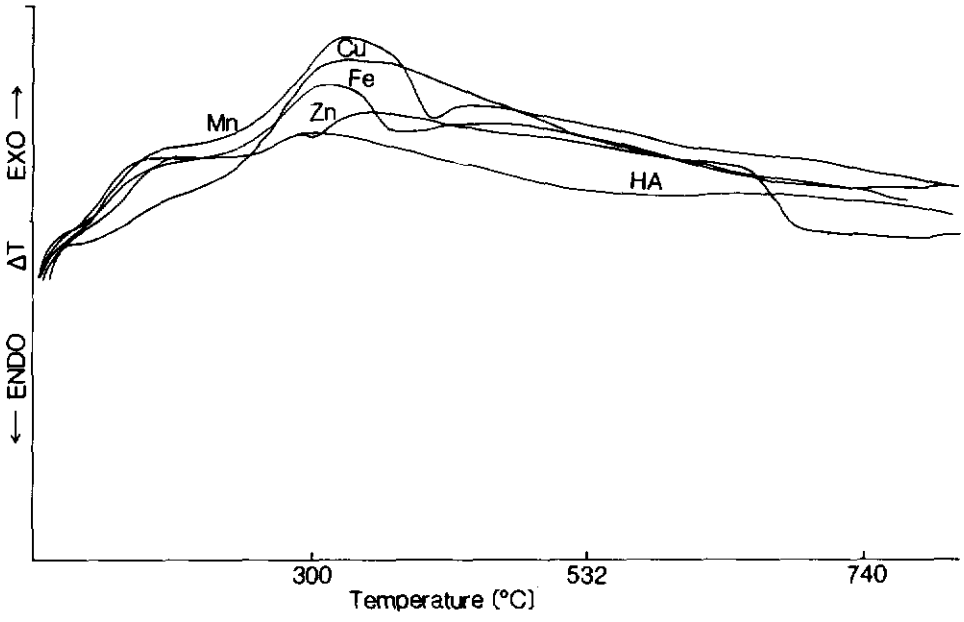

Figure 7. Thermographs of metal humates.

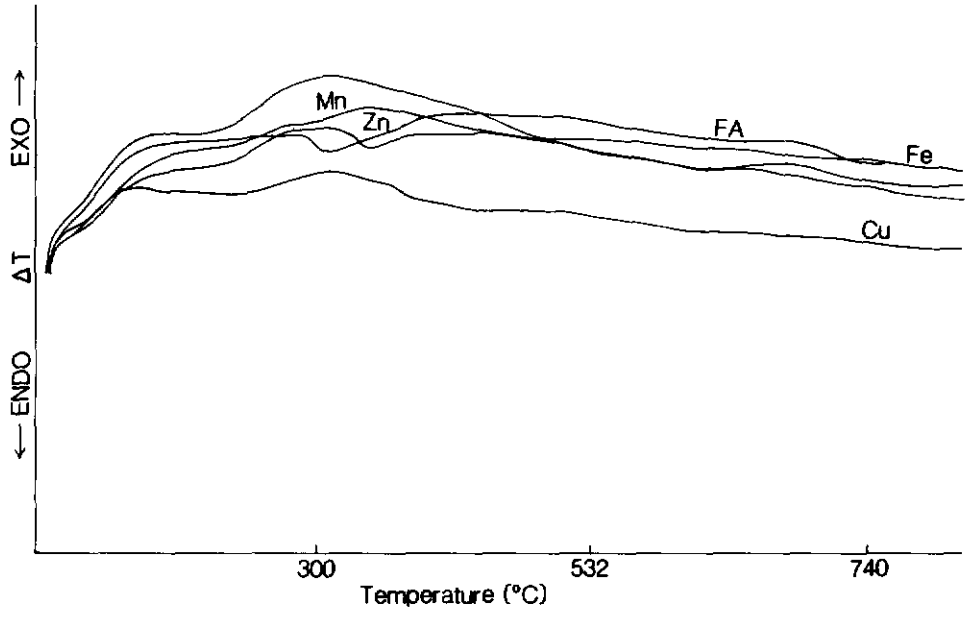

Figure 8. Thermographs of metal fulvates.

TABLE 2. DIFFERENTIAL THERMAL ANALYSIS DATA OF METAL HUMATES AND FULVATES

Complex	T°C (−)	T°C (+)
HA		53sh**; 159sh**; 301b**
CuHA	680s*** (bs)	53sh**; 159sh**; 341b***
ZnHA	301sm**; 740*(bs)	53sh**; 141sh**; 341b**
MnHA	402sm*	53sh**; 145sh**; 329b***
FeHA	357m**	53sh**; 145sh**; 321b***; 400b*
FA	305s**	35sh*; 120sh*; 450b**
CuFA		35sh*; 120sh*; 317b**
ZnFA	351m**	35sh*; 145sh*; 300b**
MnFA		35sh*; 145sh*; 349b**
FeFa		35sh*; 145sh*; 321b***

Peak sizes

b = broad; m = medium; s = sharp; sm = small; sh = shoulder
(bs) = base line shift in the endothermal direction
T(−) = *endotherm*; T(+) = *exotherm*

Peak intensities

* = weak
** = medium
*** = strong

peak is shifted to lower temperatures (300°C–349°C). It is interesting to note that the main decomposition peaks of both the metal humates and fulvates lie between 300°C and 349°C although the peaks of the starting materials, that is, HA and FA, are different from each other (301°C for HA and 450°C for FA). Even more surprising is the similarity of the main decomposition peaks of the iron humate and iron fulvate.

These observations imply that the metal ions could have reacted with both the COOH and phenolic OH functional groups of HA and FA in such a way as to yield complexes of roughly similar structure, which could also represent the optimum spatial arrangement of the metal in the molecules of HA and FA. The metal fulvates could also be more strained than the metal humates as indicated by the lowering of the main decomposition peaks. Similar deductions were also reached by Schnitzer and Ghosh[6] from the results of their recent study on water-soluble fulvic acid-copper and fulvic acid-iron complexes.

X-ray Analysis

As for HA and FA, x-ray diffractograms of the metal humates and fulvates showed diffused diffraction peaks and failed to provide any evidence of crystallinity in the complexes.

CONCLUSION

From the IR spectra of the metal humates and fulvates, it was observed that both COOH and phenolic OH groups were involved in the complexation of the metal ions to the HA and FA molecules. Chemical analyses showed that Zn was bound to HA more than Cu or Mn or Fe. In the case of FA, Cu was bound the

most followed by Fe. Zinc and Mn were bound in about the same amounts.

The thermal stability of the complex prepared is influenced by the type of bonds formed between the metal ions and the acid. The lowering of the main decomposition peak of FA on interaction with the metal ions suggest that complexation resulted in the FA molecules to be more strained.

The main decomposition peaks of the metal humates and fulvates were observed to lie in the same range, *i.e.*, between 300°C and 349°C. This implies that complexation of the metal ions to HA and FA could have resulted in complexes of roughly similar structures, which could also represent the optimum spatial arrangement of the metal ions within the molecules of HA and FA.

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REFERENCES

1. NORHAYATI MORIS AND VERLOO, M. (1984) Characterisation of Organic Matter in Four Soils of Peninsular Malaysia. I. Extraction, Fractionation and Purification of Humic Substances. *J. Rubb. Res. Inst. Malaysia,* **32(1)**, 30.

2. NORHAYATI MORIS (1982) Organic Matter and Micronutrients in Some Soils of Peninsular Malaysia: Interactions and Influence on Plant Growth. Ph. D. Thesis, State University of Ghent, Belgium.

3. SCHNITZER, M. AND HOFFMAN, I. (1967) Thermogravimetric Analysis of the Salts and Metal Complexes of a Soil Fulvic acid. *Geochim. cosmochim. Acta,* **31**, 7.

4. GRIFFITH, S.M. AND SCHNITZER, M. (1975) The Isolation and Characterisation of Stable Metal-Organic Complexes from Tropical Volcanic Soils. *Soil Sci.,* **120(2)**, 126.

5. SCHNITZER, M. AND KHAN, S.U. (1972) Humic Susbtances in the Environment. New York: Marcel Dekker, Inc.

6. SCHNITZER, M. AND GHOSH, K. (1982) Characteristics of Water-Soluble Fulvic Acid-Copper and Fulvic Acid-Iron Complexes. *Soil Sci.,* **134(6)**, 354.