

RECENT STUDIES ON ORGANIC MATTER IN NIGERIAN SOILS

BY

John A. Fagbenro
Forestry Research Institute of Nigeria,
P. M. B. 5054, Ibadan, Nigeria

and

Akinola A. Agboola
Department of Agronomy, University of Ibadan,
Nigeria.

SUMMARY

Humic substances of organic matter were extracted with 0.1M neutral sodium pyrosphosphate ($\text{Na}_4\text{P}_2\text{O}_7$), 0.1M Sodium hydroxide (NaOH) and acidified dimethyl sulphoxide (DMSO) from five soil types representing four ecological zones in Southern Nigeria. All the examined characteristics of the extracted humic substances were found to vary with the extractants and soil types. In addition, the following observations were made:

- (i) Extractability of organic matter was affected by the type of clay mineral in the soils.
- (ii) $\text{Na}_4\text{P}_2\text{O}_7$ might not be suitable for the extraction of pure humic substances especially from the acid tropical soils.
- (iii) Organic matter in the experimental soils might be higher than what is usually estimated as organic carbon in the extracted humic acids was lower than the assumed 58 per cent.

However, more research work is required before any conclusions could be made in respect of the above-listed observations.

INTRODUCTION

Organic matter, or more accurately, the humic substances of soil organic matter, has been widely shown to play an important role in determining the supply and mobility of most of plant nutrients. Its beneficial effects on the physical and biological properties of soils have also been well documented.

In the tropics where the soils are usually kaolinitic and inert, organic matter is synonymous with their fertility (Agboola and Fagbenro, 1985). This is because organic matter increases cation exchange capacity and base absorption of soil, improves soil buffering capacity and reduces toxicity of other elements. Thus, in order to estimate the quality of a soil, in properties related to structure and plant growth, it would be imperative to determine the organic status of that soil (Yormah, 1980). And because of the importance of organic matter to soil fertility and classification, in addition to knowing the amount of total (undecomposed, partially decomposed and humified) organic matter in a soil, it is necessary to know the composition of the various forms of organic matter present in that soil. Completely humified organic matter (humic substances) is the most stable and most important form of soil organic matter in so far as soil properties and plant growth are concerned hence this paper is mainly based on this form of organic matter.

Organic matter and its humic substances in temperate soils have been researched extensively since the end of the last century (Fagbenro, et al, 1984). Many methods of extracting them from the soil and of characterizing them have been explored (e.g. Bremner, 1950; Kononova, 1961; Swift, 1968; Hayes and Swift, 1978). Even here, there is still much to know about organic matter formation, characteristics and significance for soil productivity. Hayes (1984) and Swift (1984), have respectively, reviewed the procedures used for the isolation and fractionation of soil humic substances and they have shown that there are no accepted methods which can be relied upon to provide homogeneous fractions of the unaltered substances. Up to the present date, absolute values cannot be put on the amount of organic

matter present in any soil sample. For example, after the determination of the total carbon content of a particular soil sample, it is still difficult to know what conversion factor to apply to the carbon value in order to estimate the organic matter content. This is because the C:H:O:N ratios in the different organic components can vary significantly.

In Nigeria, research on the composition and properties of organic matter in our soils is virtually not in existence. Yet, it is believed that the intractable erosion problems and the general soil infertility that are the bane of tropical agriculture are largely due to inadequacy and poor understanding of nature of organic matter in these soils. There is therefore the justification for the continued research into soil organic matter systems either here in the tropics or in the temperate regions of the world.

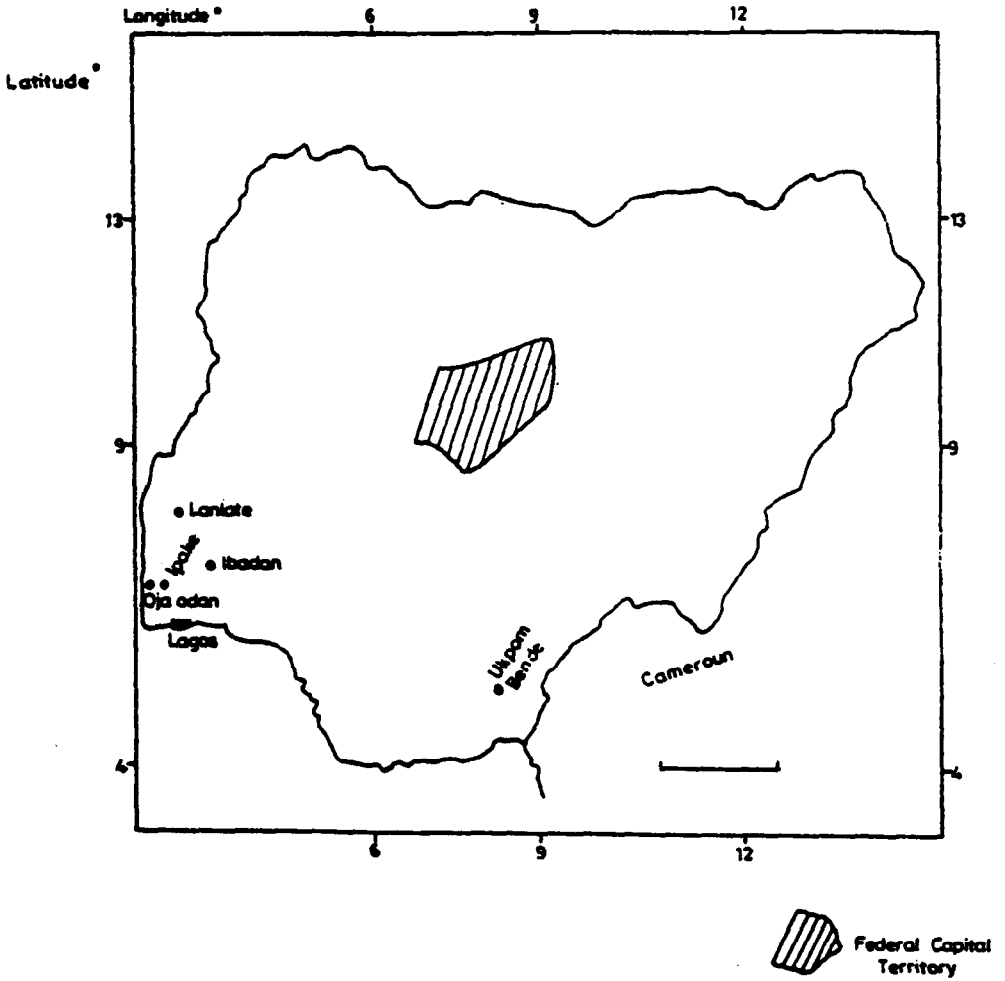
EXPERIMENTATION

Field Sampling: After a preliminary survey of many soils with varying organic matter contents, five areas representing four ecological zones in Southern Nigeria were selected for study. These areas are Ukpom Bende (UB), Ibadan (IB), Lanlate (LA), Ipake (IP) and Oja-Odan (OO) (Figure 1). Soil samples were taken from the top 10cm. Some relevant information on the experimental soils is presented in Table 1. In Ukpom Bende, Ibadan and Ipake, samples were collected from uncleared, secondary rain forests which were probably 50 - 100 years old; at Oja-Odan, soils under a 20-year old teak plantation were sampled while the Savannah soil (Lanlate) was from a farmland which had lain fallow for 5 to 10 years.

Analytical methods

Soil reaction was determined with Unicam PW 9418 pH meter using 2/1 (water/soil) suspension; total organic matter content was by Wakley-Black method (Allison and Moodie, 1965); particle analysis by sedimentation; clay mineralogical determination was effected by using a Phillips PW 1720 X-ray generator at wavelength of 1.54178Å. Ash contents of the soil and humic substances were determined by igniting the oven-dry (105°C) samples in a muffle furnace at 500°C for 18 hours. Total carbon,

Fig. 1. Map of Nigeria showing location of study sites.



hydrogen and nitrogen in the humic substances were analysed using Perkin Elmer 240 automatic elemental analyser while absorbance readings of humic extracts were made at both 465nm (E_4) and 665nm (E_6) using a Shimadzu Recording UV-240 Spectrophotometer.

Extraction procedures

Three solvent systems, 0.1M Sodium hydroxide (NaOH) which is commonly recommended, neutral solution of 0.1M sodium pyrophosphate ($Na_4P_2O_7$) and a dipolar aprotic solvent, acidified dimethyl sulphoxide (Ac. DMSO) were selected to extract humic substances from the soils. Hayes and Swift (1978) have discussed the modes of action of these different systems.

50g of each untreated, air-dried soils were extracted. Soil samples were extracted once with ac. DMSO whereas extraction with NaOH was carried out on the soil residue left after the $Na_4P_2O_7$ extraction. Soil-extractant mixtures were centrifuges at 10,000 r p m for 30 minutes.

Humic acids (HA) and fulvic acids (FA) in the NaOH and $Na_4P_2O_7$ extracts were separated after acidification to pH 1 with HCl. DMSO solution extracts were passed through XAD-8 resin beds to separate the solvent from the humic substances (HS). The DMSO was washed out with 0.1M HCl followed by distilled H_2O . The adsorbed HS were recovered as described by Law and Hayes (1984). The HS were then separated into HA and FA fractions as above. The HA (precipitate) was washed with distilled water, centrifuged, dialyzed against distilled water until free of Cl^- . The dialyzed HA was then freeze-dried. FA was likewise treated.

Fractionation of extracts

15mg of extract was dissolved in 25 cm^3 buffer (0.025M $Na_2B_4O_7$ + 0.1M NaCl) and the same buffer was used as the column eluant. The dissolved extract was subjected to gel-filtration on column (60 x 3 cm) packed with Sephacryl (S100). Column eluates (automatically collected in 10- cm^3 aliquots at the rate of 14.2 minutes) were monitored for colour (absorbance at both 465 and 665nm).

Table 1: Some relevant properties of the experimental Soils

Properties	Ukpom Bende (UB)	Ibadan (IB)	Lanlate (LA)	Ipake (IP)	Oja-Odan (OO)
pH (H ₂ O)	4.9	6.2	6.5	5.6	6.2
Organic matter (%)	8.2	1.4	2.0	5.6	0.8
Sand (%)	0.6	63.4	57.1	54.7	76.0
Silt (%)	22.6	23.5	26.1	16.4	16.3
Clay (%)	76.8	13.1	16.8	28.9	7.7
Texture (USDA)	Clay	Sandy loam	Sandy loam	Sandy clay loam	Loamy sand
Classification	Vertisol	Alfisol	Oxisol	Oxisol	Oxisol
Main clay mineral type	Montmorillonite/ Kaolinite	Kaolinite	Kaolinite	Kaolinite	Kaolinite
Mean ann. rainfall (mm)	2143	1155	931	1211 ^a	1211 ^a

^a Rainfall data used were from a nearby town to the two sites where there is a meteorological station.

RESULTS AND DISCUSSION

Preliminary Organic Matter Extraction

Results of series of experiments on the effects of salt concentration of the extractant, acidification of Dimethyl sulphoxide, mode of soil drying and acid-pretreatment prior to extraction of organic matter from the soils have been reported in an earlier paper (Pagbenro *et al*, 1984).

Characterization of Extracted Organic Matter

Colour quotient (E_4/E_6 ratio), elemental composition of both humic acid (HA) and fulvic acid (FA), HA: FA ratio,

amount of organic matter extracted and pattern of distribution of their molecular weights are among the parameters usually used to characterise organic matter in soils. It is believed that many of the properties of soil organic matter vary according to the above characteristics.

In this study, organic matter in the experimental soils was characterised using above mentioned parameters. Results are presented in Tables 2 to 5 and Figures I to IX.

Colour quotients

Data for this parameter are presented in Table 2. In general, quotients for organic matter from Ibadan, Lanlate, Ipake and Oja-Odan were similar. That of Ukpom Bende was evidently different from the rest. Similar trend was observed among the three extractants indicating that organic matter in this soil might be fundamentally different from the rest with respect to molecular weight and degree of humification.

Table 2: Data for colour quotients, E_4/E_6 ratio, of humic substances extracted from 5 untreated soil types with three solvent mixtures.
(Mean values of 3 replicates)

Soil Type	Solvent Mixture	Absorbance		Colour Quotient (E_4/E_6)
		465 nm (E_4)	665 nm (E_6)	
UB	0.1M $\text{Na}_2\text{P}_2\text{O}_7$	0.791	0.101	7.81
IB		0.720	0.168	4.29
LA		0.764	0.176	4.33
IP		0.810	0.193	4.20
OO		0.784	0.184	4.27
UB	0.1M NaOH	0.805	0.121	6.65
IB		0.392	0.091	4.31
LA		0.440	0.100	4.39
IP		0.431	0.099	4.34
OO		0.339	0.076	4.44
UB	Ac. DMSO	1.752	0.258	6.80
IB		1.112	0.249	4.47
LA		1.183	0.264	4.48
IP		1.190	0.267	4.46
OO		1.081	0.250	4.33

Fig. 11. Variation in yield of extracted humic and fulvic acids among the three solvent mixtures.

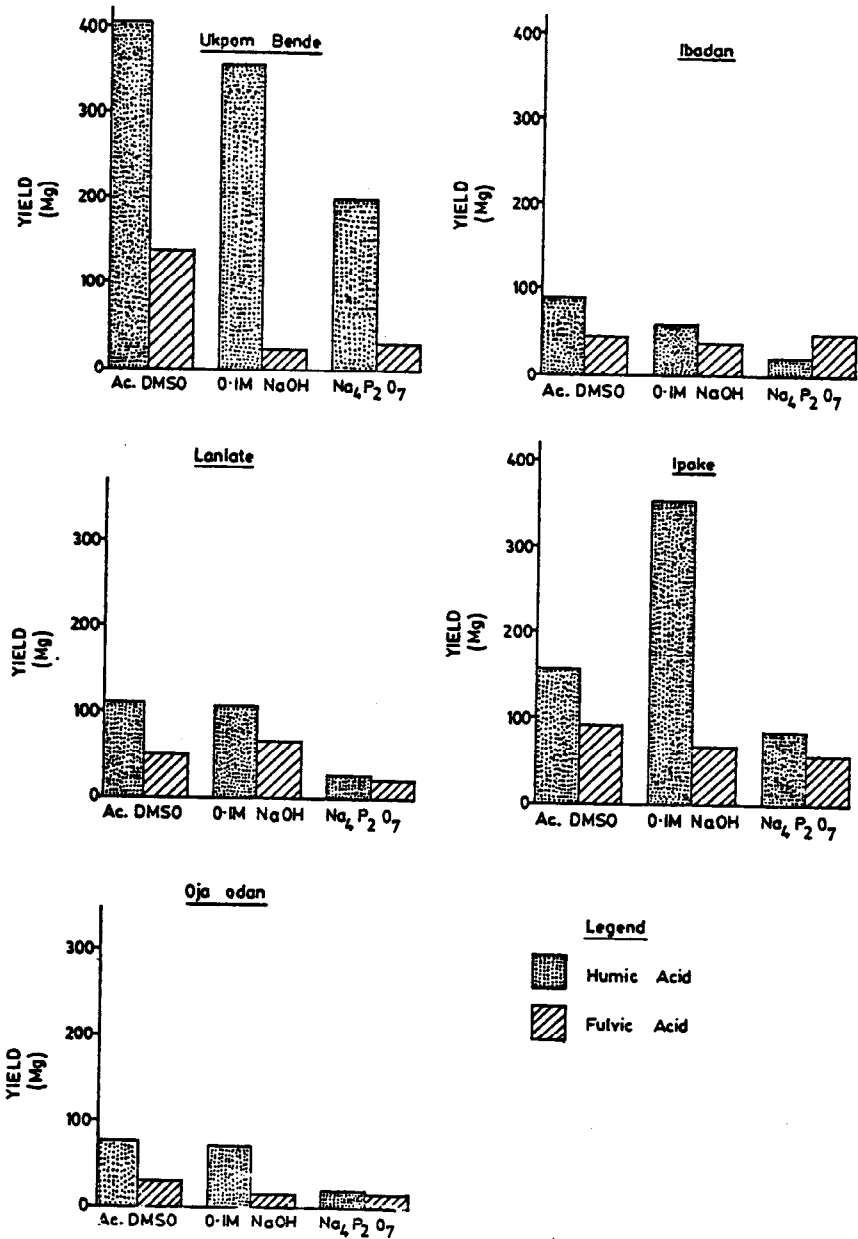
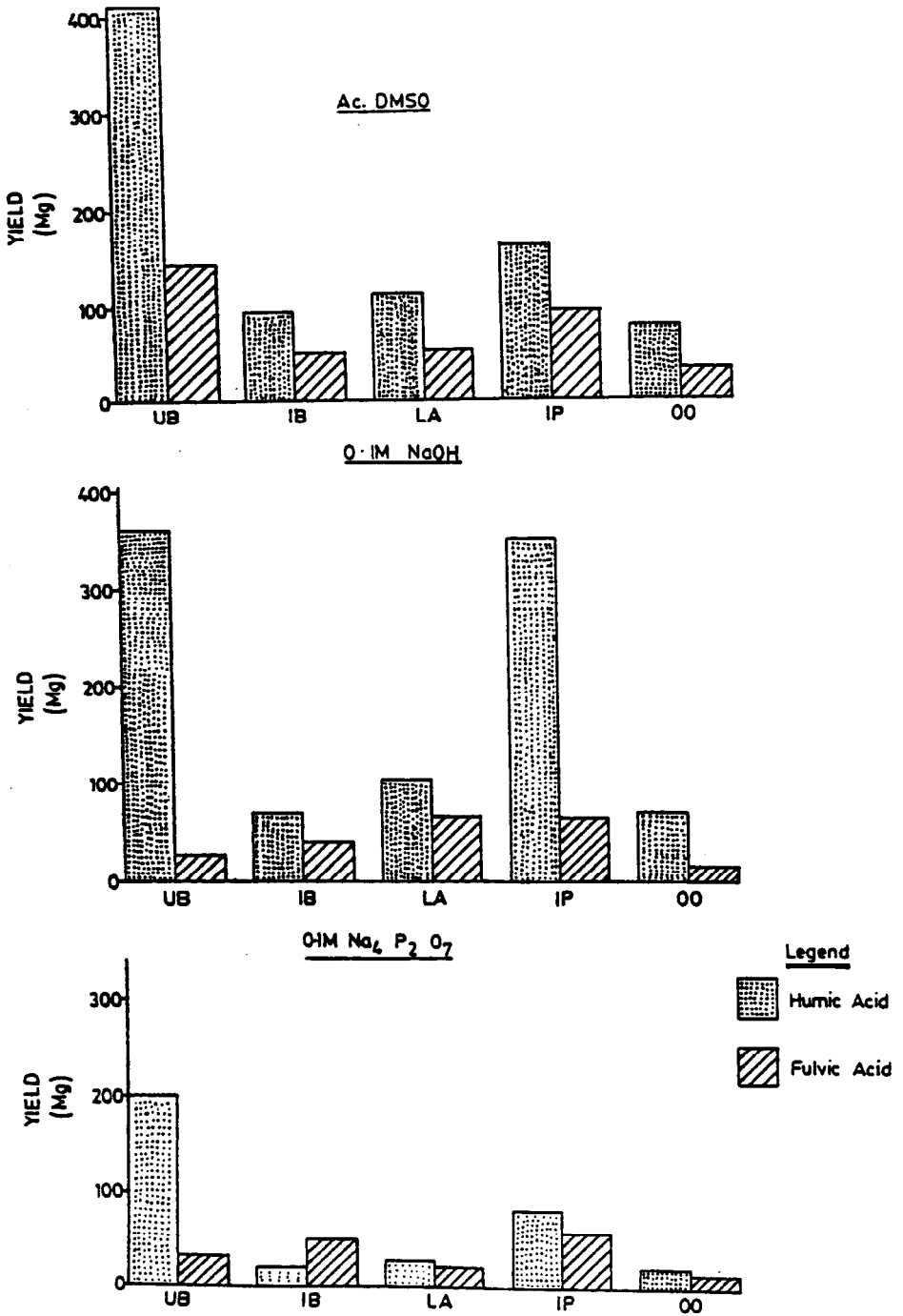


Fig. III. Variation in yields of humic and fulvic acids among the five soil types.



Elemental analysis

Elemental analysis (Table 3) evidently shows how the type of extractant can influence composition of these humic polymers. Generally, the data indicate that the carbon contents of the humic acid materials extracted by the acidified DMSO were greater than those for sodium hydroxide and pyrophosphate. Under acidified DMSO, the data suggest a carbon content maximum for the humates from both Ukpom Bende and Lanlate soils indicating presence of high molecular weight humic acids. The data also show significant differences between the humic and fulvic materials from two of the soils which is confirming the fact that fulvic acid is always more oxidized than humic acid. Table 3 also shows that the carbon contents of humic acid extracted with acidified DMSO from the five soil types varied from 28.2 to 37.5 per cent, averaging 34.6 as against 58 per cent commonly assumed. Based on these figures, the multiplying factor is 2.889 in contrast to 1.724 usually applied to the carbon value in order to estimate the organic matter content. Granted that the humic acids contained some quantity of ash and that the work being reported here is preliminary, it is possible that organic matter in our soils is higher than what is usually estimated. More work is certainly required in this sensitive area of organic matter research.

Table 3 further shows that the ash contents of humic materials varied especially with extractant. Extracts by $\text{Na}_4\text{P}_2\text{O}_7$ had the highest ash content. According to Hayes et al (1975), this indicates that an extract-extractant complex was formed at low pH values. This means that $\text{Na}_4\text{P}_2\text{O}_7$ may not be very suitable for acid tropical soils.

Quantity of organic matter extracted

In Table 3 are also presented percentage of organic matter extracted from different soil types by different solvent mixtures but amounts of humic substances quantitatively extracted are shown in Table 4. Variations in the extracted total organic matter and humic acid were statistically significant whereas those of fulvic acid were not (Table 5). These variations (Figures II to IV) may be partly due to (1) differences in the quantity and type of clay minerals in the soil (Fagbenro et al, 1984),

Fig. IV. Combined yields of extracted humified organic matter μ by the three solvent mixtures for each soil type.

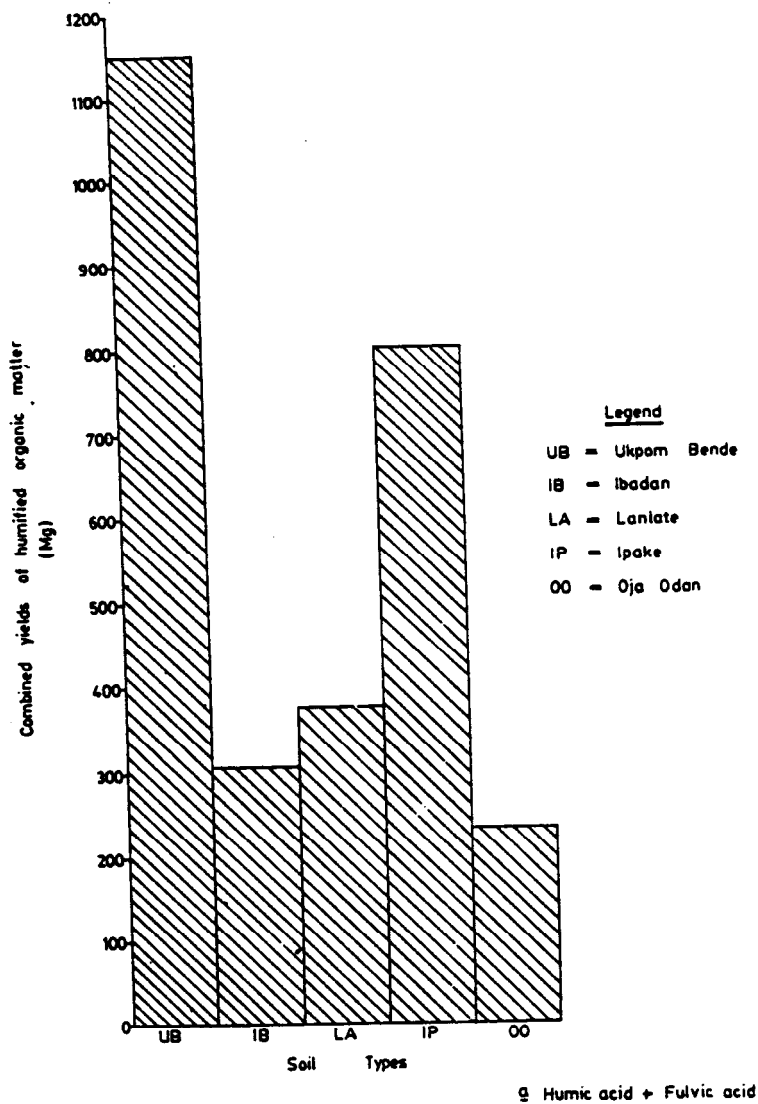


Table 3: Yields and compositions of humic acid (HA) and two Fulvic acid (FA) fractions extracted from the 5 soil types using 3 solvent mixtures.

Soil Type	Solvent mixture	Yield <u>a</u> (% of total soil OM)	Frac-tion	Elemental compo-sition (%)			Ash
				C	H	N	
UB	0.1M $\text{Na}_4\text{P}_2\text{O}_7$	5.6	HA	29.7	3.4	2.1	47.4
IB	"	9.9	HA			N.D.	40.4
LA	"	4.6	HA	31.3	2.3	2.7	47.0
IP	"	4.9	HA	26.2	3.2	3.1	38.2
OO	"	8.7	HA	26.6	2.1	2.2	41.6
UB	0.1M NaOH	11.5	HA	28.0	2.3	1.5	46.4
IB	"	17.4	HA	30.4	3.9	4.3	36.3
LA	"	20.9	HA	37.6	4.1	3.0	19.2
IP	"	16.7	HA			N.D.	33.5
OO	"	27.5	HA	29.4	3.7	1.8	24.6
UB	Ac. DMSO	13.2	HA	37.5	1.7	3.1	18.5
"	"	N.D.	FA	27.8	1.2	3.7	21.1
IB	"	19.7	HA	28.2	3.0	1.3	31.4
LA	"	15.8	HA	37.3	2.4	2.4	31.9
"	"	N.D.	FA	21.7	2.2	1.1	31.5
IP	"	18.7	HA	33.6	4.0	3.3	27.2
OO	"	26.7	HA	36.5	3.0	3.0	25.7

a HA + FA on ash - and moisture - free basis

(ii) Kinds and abundance of multivalent cations (Hayes and Swift, 1978), (iii) degree of humification of total organic matter in the soils as well as (iv) differences in the modes of action of the different systems.

Fig. V. Gel chromatography of humic acids extracted with three solvent mixtures.

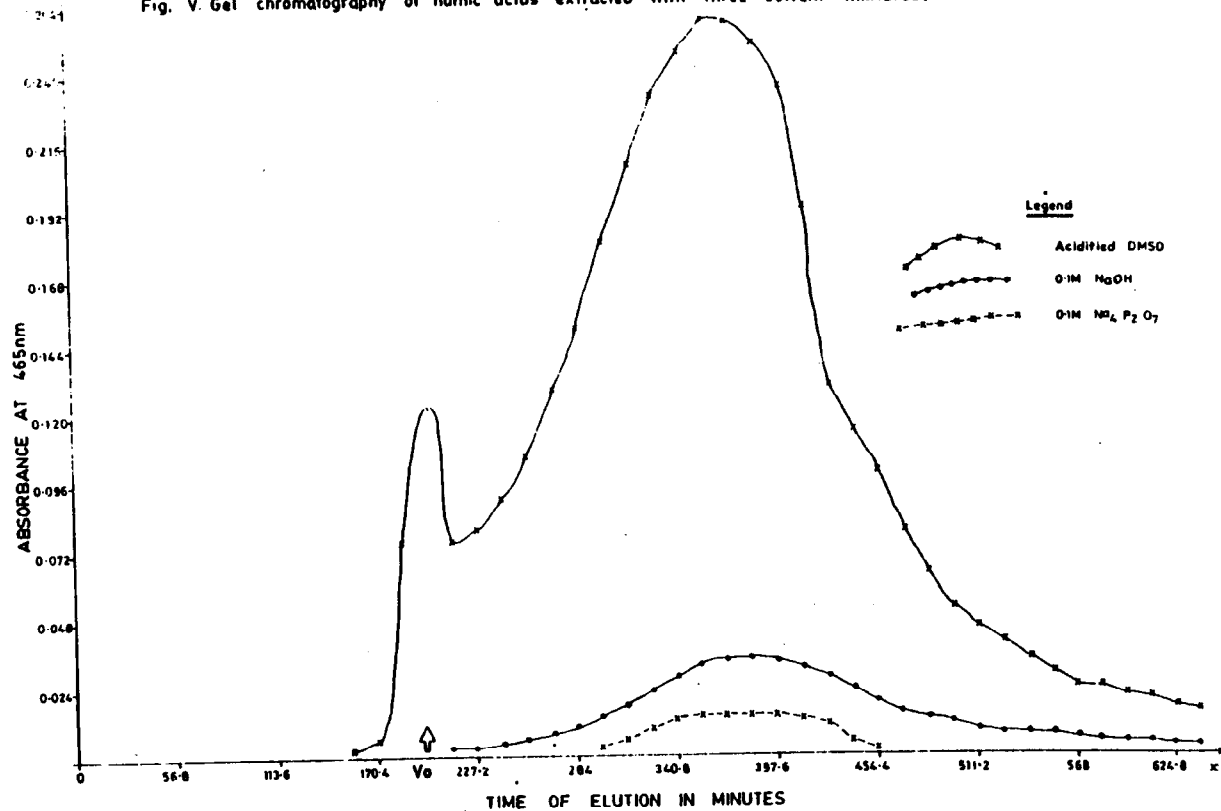


Table 4: Quantity^a of extracted humic acid (HA) and fulvic acid (FA) and their ratios with respect to soil types and solvent mixtures

Soil Type	Solvent system	Fraction (mg)		Ratio HA:FA
		HA	FA	
UB	0.1M Na ₄ P ₂ O ₇	198.2	30.9	6.5
IB	"	21.6	47.9	0.5
LA	"	25.3	20.6	1.3
IP	"	83.3	54.2	1.6
OO	"	18.9	15.7	1.2
UB	0.1M NaOH	357.7	22.7	15.8
IB	"	60.5	37.9	1.6
LA	"	106.7	66.6	1.6
IP	"	353.1	65.2	5.5
OO	"	73.3	15.5	4.7
UB	Ac. DMSO	404.8	137.2	2.9
IB	"	92.3	45.4	2.1
LA	"	109.4	48.2	2.3
IP	"	155.2	88.5	1.8
OO	"	76.4	30.2	2.5

a On moisture - and ash - free basis

Ratio of the content of HA to that of FA

As presented in Table 4, there were differences, even though statistically insignificant (Table 5), in HA:FA ratios among the extractants and soil types. Differences among the extractants indicate that extraction mechanism among the extractants were not the same (Swift, 1968). On the other hand, differences among soil types show the extent these soils are oxidized or internally drained. By this result, Ukpom Bende, with the highest ratio, was the least drained (and this is evident on the field) while Ibadan the most well drained.

Pattern of molecular weight distribution of organic matter

Soil humified organic matter is a diverse mixture of organic substances consisting mainly of high molecular weight polymeric compounds.

Fig. VI. Gel chromatography of humic acids extracted from Lanlate soil with the three solvent mixtures.

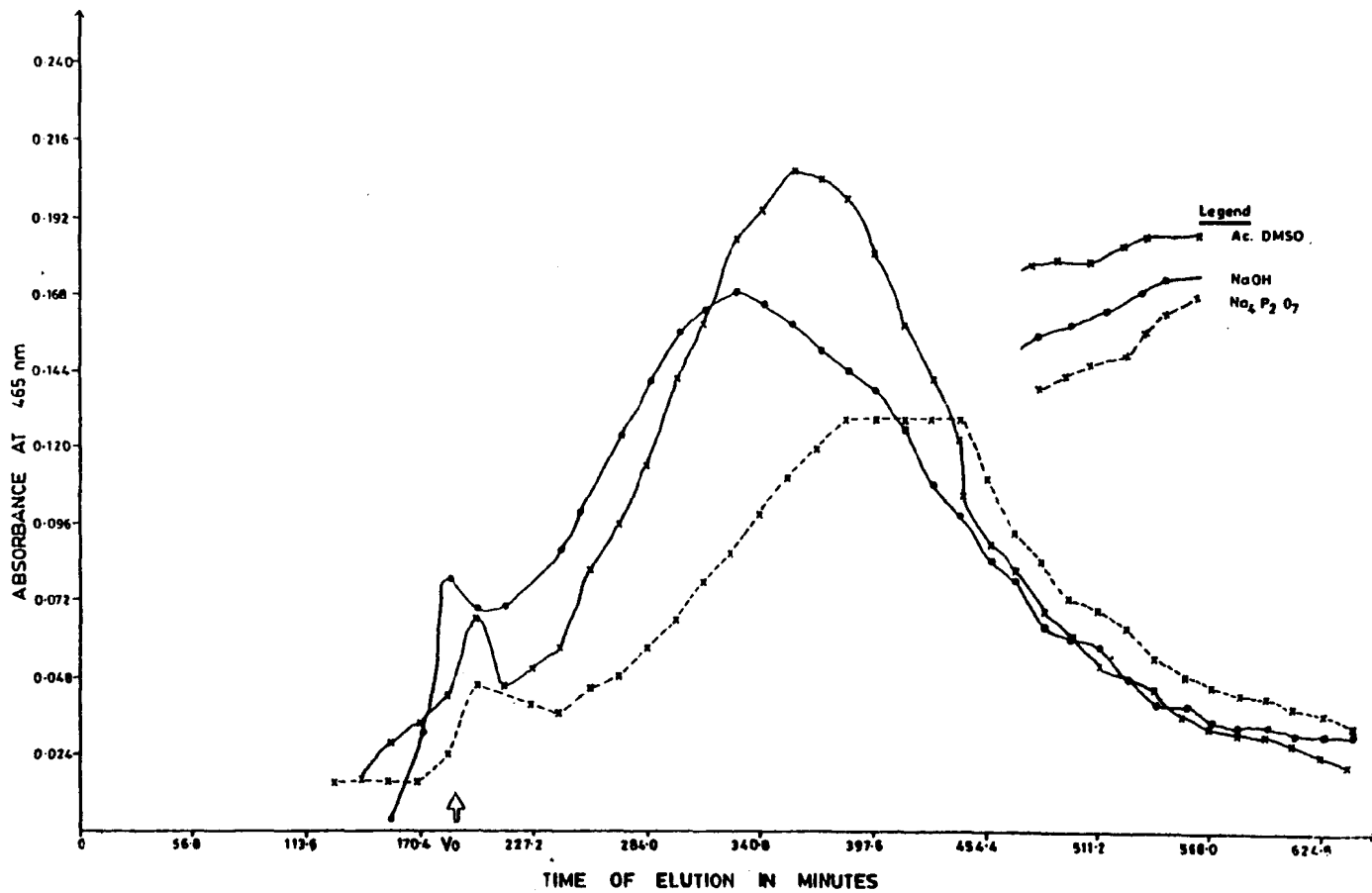
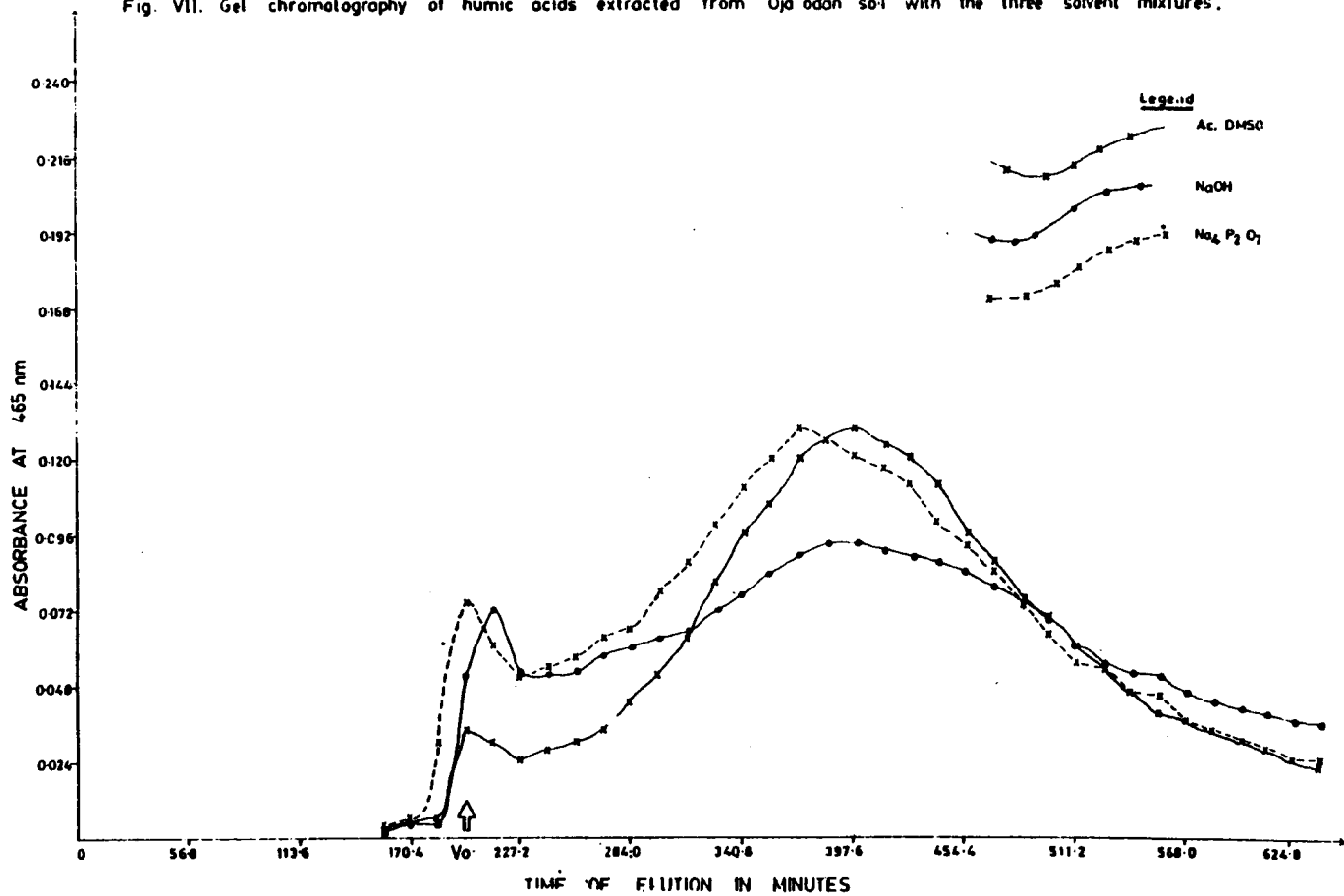


Fig. VII. Gel chromatography of humic acids extracted from Oja odan soil with the three solvent mixtures.



Figures V, VI and VII show elution patterns of humic acids extracted by ac. DMSO NaOH and $\text{Na}_4\text{P}_2\text{O}_7$ from Ukpom Bende, Lanlate and Oja-Odan soils respectively. Figures VIII, IX and X present patterns for the humic acids extracted from the soil types and from a poultry manure sample ($\text{Na}_4\text{P}_2\text{O}_7$ only) with the three solvents. Materials eluted in the void volume (V_0) in all the figures were considered to have high molecular-weight values. It can be seen (Figure v) that

Table 5: Analyses of variance based on moisture and ash-adjusted yields of HA and FA extracted from the 5 soils with the 3 solvent mixtures.

Source of variation	SSD	MSD	F
Soil type (HA)	158924.75	39731.19	10.45**
Extractant type (HA)	41304.75	20652.38	5.43*
Soil type (FA)	4428.01	1107.00	1.38
Extractant type (FA)	3622.71	1811.36	2.25
Soil type (HA:FA ratio)	97.18	24.30	3.01
Extractant type (HA:FA ratio)	41.63	20.82	2.58
Soil type (% OM extracted)	255.23	63.81	5.12*
Extractant type (% OM extracted)	412.23	206.12	16.54**

Residual (Error) and Total excluded under source of variation; degrees of freedom (df)

= 4 (soil type)
= 2 (Extractant)

SSD = sum of square deviation

MSD = mean square deviation

** = significant at 1% level

* = significant at 5% level

only humic acid extracted by ac. DMSO has fraction with molecular weight more than 100,000. The result shows the relative difficulty of extracting HS from the very clayey, montmorillonitic Ukpom Bende soil with NaOH and $\text{Na}_4\text{P}_2\text{O}_7$. The gel chromatography patterns indicate that the humic acids extracted from this soil by these two solvents had intermediate and low molecular-weight values. This can be explained by the fact that NaOH and $\text{Na}_4\text{P}_2\text{O}_7$ could usually be expected to extract the more highly oxidized materials which are generally recognised to be the lower molecular-weight components in humic acids. However, this pattern was less evident for Lanlate and

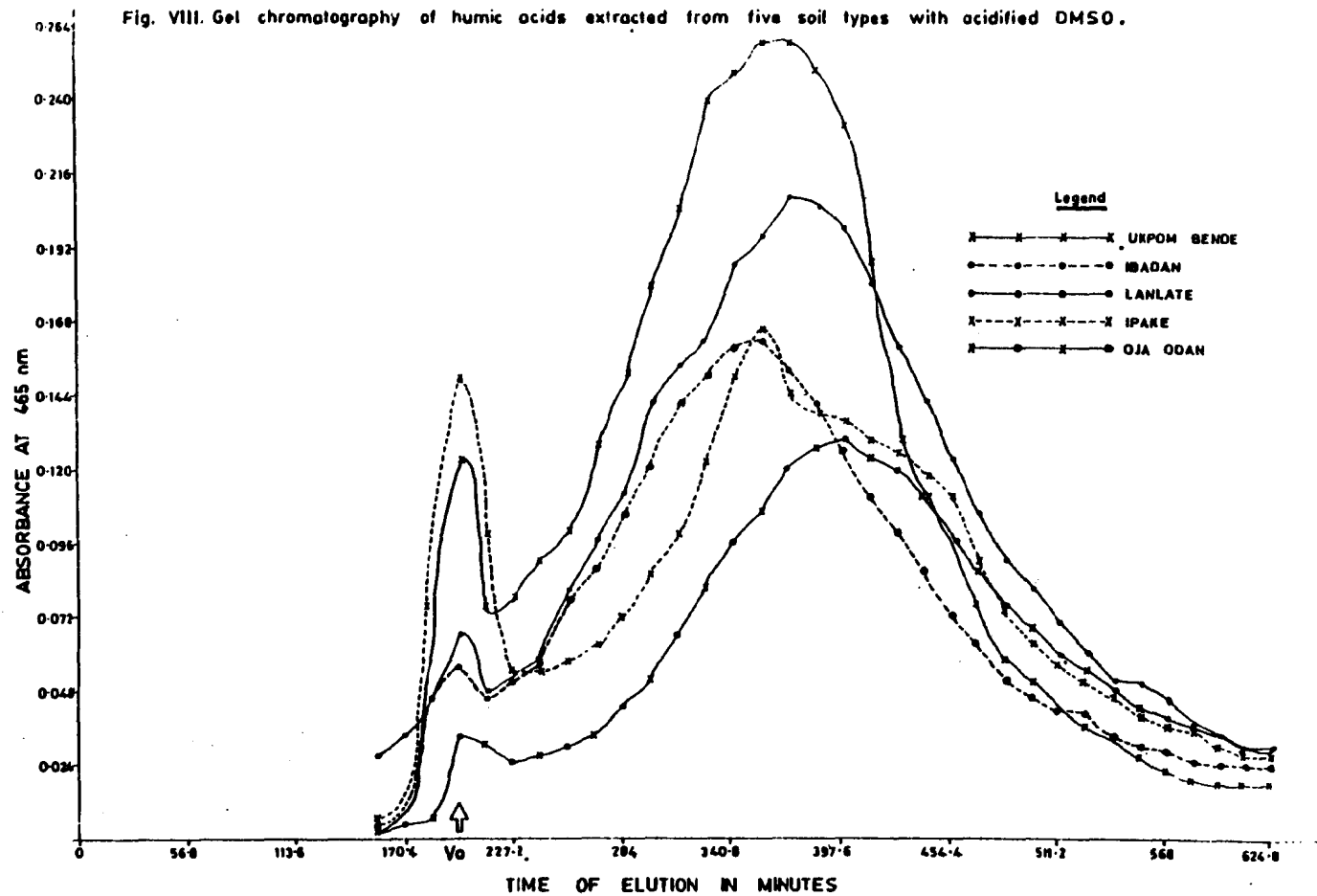


Fig. IX. Gel chromatography of humic acids extracted from four soil types with sodium hydroxide.

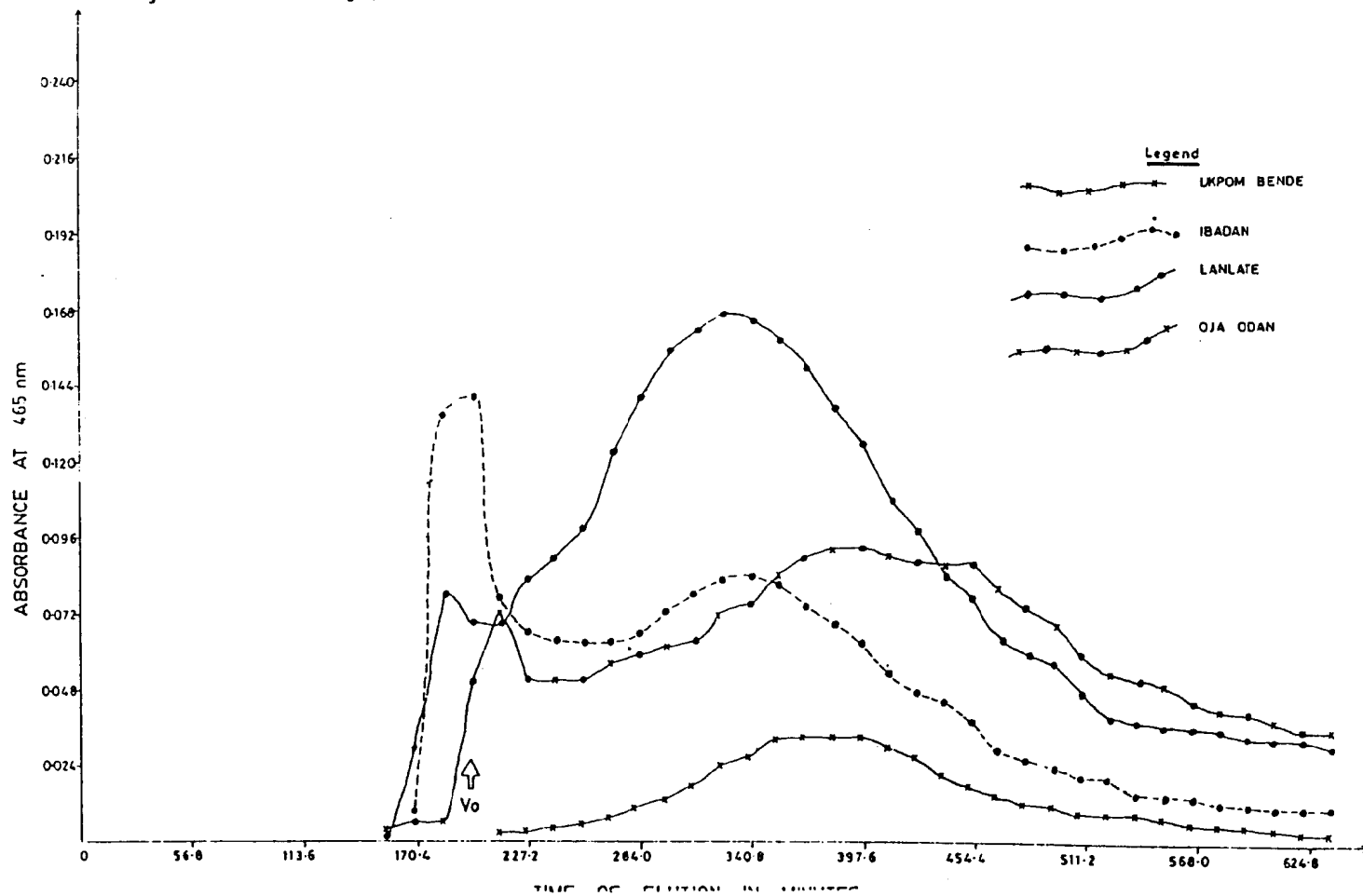
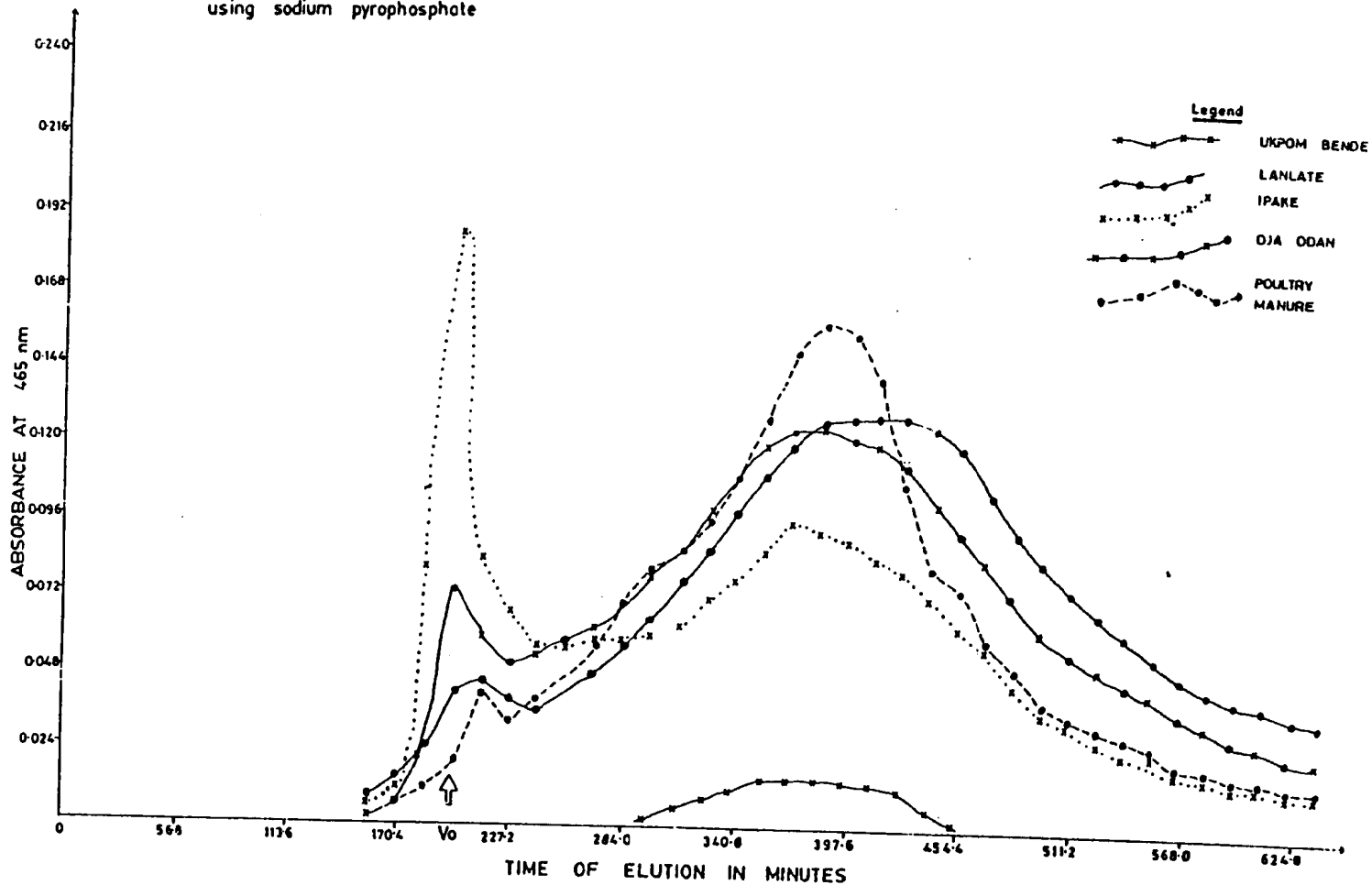


Fig. X. Gel chromatography of humic acids extracted from four soil types and from a poultry manure sample, using sodium pyrophosphate

525



Oja-Odan soils which are sandier and kaolinitic. The three solvent mixtures extracted HA with high molecular weight from these last two soils (Figures VI and VII).

It is evident that both ac. DMSO (Figure VIII) and $\text{Na}_4\text{P}_2\text{O}_7$ (Figure X) extracted greatest amount of high molecular-weight humic acid respectively from Ipake soil than from other soils examined whereas NaOH (Figure ix) extracted more high molecular-weight humic acid from Ibadan soil. This result would seem to indicate that the type of extractant and soil can affect pattern of distribution of molecular-weight of organic matter polymers.

LITERATURE CITED

- Agboola, Akinola A. and John A. Fagbenro. 1985. Soil organic matter and its management in the humid tropics with particular reference to Nigeria. Invited paper presented at the ISSS Commissions IV and VI Conference, July 21-27. Ibadan, Nigeria. 70 pp.
- Allison, L. E. and C. D. Moodie. 1965. Carbonates In Methods of Soil Analysis. Part 2: 1379-1396, C. A. Black (Ed.) Am. Soc. Agron., Inc., Madison.
- Bremner, J. M. 1950. Some observations on the Oxidation of soil organic matter in the presence of alkali. J. Soil Sci. 1: 198-204.
- Fagbenro, John, M. H. B. Hayes, I. A. Law and A. A. Agboola. 1984. Extraction of soil organic matter and humic substances from two Nigerian soils using three solvent mixtures. Paper presented at the 2nd meeting of International Humic substances Society, Birmingham, England, 22 - 28 July.
- Hayes, M. H. B., R. S. Swift, R. E. Wardle and J. K. Brown. 1975. Humic Materials from an organic Soil: A comparison of extractants and of properties of extracts. Geoderma 13: 231-245.
- Hayes, M. H. B. and R. S. Swift. 1978. The Chemistry of soil organic colloids In: The Chemistry of Soil Constituents. Eds. Greenland, D. J. and M. H. B. Hayes. John Wiley and Sons, New York.
- Hayes, M. H. B. 1984. Extraction of humic substances from soil. In G. R. Aiken, P. McCarthy, D. McKnight and R. L. Wershaw, Humic substances. I. Wiley, New York. In press.
- Kononova, M. M. 1961. Soil Organic Matter. Its nature, its role in soil formation and in soil fertility. Pergamon Press, Oxford.

- Law, I. A. and M. H. B. Hayes. 1984. Extraction of Humic substances from soil using acidified Dimethyl Sulphoxide. Paper presented at the 2nd Meeting of International Humic substances Society, Birmingham, England, 22-28 July.
- Swift, R. S. 1968. Physico-chemical studies on soil organic matter. Ph.D. Thesis, University of Birmingham, England.
- Swift, R. S. 1984. Fractionation of soil humic substances. In G. R. Aiken, P. McCarthy, D. McKnight and R. L. Wershaw, Humic substances I. Wiley, New York. In Press.
- Yormah, T. B. R. 1980. The composition and Properties of selected samples from a Tropical Soil Profile. Ph.D. Thesis, University of Birmingham, England.