

Humic acids from lignite. 1. Analytical characteristics and thermal degradation

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Humic acids (HA) extracted from a lignite with two alkaline reagents have been studied. In contrast to humic acids extracted from soil HA, the lignite acids show no differences in their physical and chemical analyses with the exception of the total carbonyl content. After acid hydrolysis the analytical characteristics do not change, but their behaviour on Sephadex indicates a molecular condensation. The parent material has similar characteristics to those reported in the literature and also shows no analytical differences after acid hydrolysis, but a number of i.r. absorption bands, due to kaolinite, the only clay mineral present, disappear after this treatment. By pyrolysis/gas chromatography both the lignite and the humic acids produce several low-b.p. compounds, the same in the three cases but in different amounts. By methylation it has been proved that a great part of such compounds are produced by radical reactions. Some, which do not increase on methylation, may indicate the presence of some longer chains in lignites.

Many of the studies to elucidate the structure of humic substances have been carried out on humic acids (HA) extracted from coal, and most of the methods applied for their characterization have also been previously applied to some types of coal.

One of the principal problems in humus chemistry is related to the extraction of humic substances. Many extractants have been applied and the data obtained differ markedly from each other. It is not yet clear whether the extractants affect the structure, basically those of $\text{pH} > 7$, or if every extractant takes up a determined fraction of the humic substances. The latter is possible because of the polydispersity of these substances, especially those extracted from soils. The formation of humus is a dynamic process, beginning with the degradation of high-molecular-weight compounds to HA, fulvic acids (FA) and finally to carbon dioxide and water; hence in a soil all the possible humification stages coexist and therefore the different extractants and purity criteria used may produce the different results reported in the literature.

Lignite is a material from which it is possible to extract a large quantity of HA, and most of the available data on coal HA are from this source¹. The subject of this and subsequent papers is the physicochemical characterization of HA extracted from a Spanish lignite (Puentes de Garcia Rodriguez, La Coruña) with two alkaline reagents. NaOH and $\text{Na}_4\text{P}_2\text{O}_7$:NaOH solutions, which have shown (ref. 2; and Martín, F., unpublished) that HA extracted from the same soil type present striking differences.

EXPERIMENTAL

The humic acids were extracted according to the following procedure: 50 g of finely ground lignite were extracted in a Soxhlet apparatus for 48 h with a mixture of ethanol and benzene (1:1). The dry residue (46.2 g) was divided into two equal parts.

One part was extracted under a nitrogen atmosphere and

shaking with 200 ml of a 0.1 N NaOH solution at room temperature. This solution extracted nothing, so the lignite was washed with water until the pH was 7, and then treated with 200 ml of 1 N HCl for 24 h at room temperature. This was centrifuged and washed with water until there was no Cl^- reaction. A further treatment with NaOH produced a mild degree of extraction that was repeated until the extracts were colourless. The extracts were centrifuged at 15 000 g, precipitated with 2 N HCl, centrifuged, washed, dialysed until free from Cl^- , dried at 60°C, and stored in a desiccator. The yield of HA was 9.4 g.

The other 23.1 g portion was extracted with 200 ml of a 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$:NaOH (1:1) solution in the same conditions as stated above. The acid treatment was not necessary in this case. The yield was 8.8 g.

C and H were determined by the dry combustion method, and N by the automated Dumas method. Functional groups were determined as previously reported².

The methylation procedure was as follows: 0.5 g of each sample was refluxed for 16 h with 10 ml dimethylsulphate and 18 g of anhydrous K_2CO_3 in 30 ml acetone. The acetone was removed under vacuum and the reaction mixture was acidified to pH 2 with 1 N HCl. The coagulated sample was centrifuged, washed with distilled water till free from Cl^- and dried. The above procedure was repeated three times.

The lignite and HA were hydrolysed as follows: 0.5 g of sample was refluxed for 16 h with 100 ml 6 N HCl under nitrogen atmosphere. The residues were separated by centrifuging, dialysed till free from Cl^- and dried.

I.R. spectra were run on KBr pellets (1 mg sample + 200 mg KBr) on a Perkin-Elmer 621 spectrophotometer.

U.V. and visible spectra were determined after dissolving 5 mg of each HA in 10 ml 0.05 N NaHCO_3 solution, and recorded on a Hitachi Perkin-Elmer 124 spectrophotometer.

Pyrolysis was achieved in a CDS pyrolyser (100 Solids Pyrolyser) attached to a 5750 G Hewlett Packard gas chromatograph with dual flame-ionisation detector.

The samples (1 mg) were inserted in a thin-walled quartz tube of 25 mm length and 2.5 mm i.d. and placed in the platinum coil of the pyrolysis probe.

Table 1 Elementary composition of untreated and hydrolysed lignite and HA

	% daf basis														Atomic H/C		Atomic O/C	
	C		H		N		S		O		Ash (db)		b	a	b	a		
	b	a	b	a	b	a	b	a	b	a	b	a						
L-PGR	64.4	64.6	4.7	4.9	1.2	0.0	3.6	n.d.	26.1	30.4	21.5	9.3	0.88	0.91	0.30	0.35		
HA-L-N	63.9	61.8	4.7	3.6	1.0	1.6	n.d.	n.d.	30.4	32.9	3.8	2.1	0.88	0.71	0.36	0.40		
HA-L-P	62.9	62.6	4.5	3.5	1.2	1.6	n.d.	n.d.	31.4	32.2	4.5	2.3	0.86	0.67	0.37	0.38		

b: Untreated

a: After hydrolysis with 6 N HCl

Table 2 Oxygen in functional groups of untreated and hydrolysed lignite and HA (% of coal, daf)

	Total acidity		Carboxyl		Phenolic OH		Alcoholic OH		Total CO	
	b	a	b	a	b	a	b	a	b	a
L-PGR	5.9	8.0	1.6	2.2	4.2	5.9	1.0	0.0	(16.0)	2.0
HA-L-N	9.3	9.5	3.4	3.2	5.9	6.3	0.4	0.0	2.6	2.2
HA-L-P	9.3	9.5	3.5	3.3	5.8	6.2	0.0	0.0	4.1	2.2

The operating conditions for pyrolyser and gas chromatograph were:

Pyrolyser	
Pyrolysis temperature	700°C
Pyrolysis-chamber temp.	200°C
Heating rate	20°C/ms
Pyrolysis time	10 s
Gas chromatograph	
Injector temperature	250°C
Detector temperature	300°C
Column	3.05 m X 3.2 mm (1/8 in) o.d. stainless steel
Packing	Chromosorb 102
Gas	N ₂
Flow rate	40 ml/min
Column temperature	50–150°C programmed at 10°C/min
Recorder speed	0.25 in/min

RESULTS AND DISCUSSION

The yields of HA extracted with NaOH and the mixture were 37.6% and 35.5% of the parent material respectively. These are high proportions compared with those reported in the literature³.

The elementary composition of the parent material and HA are shown in Table 1 (L-PGR represents lignite, HA-L-N the HA extracted with NaOH, and HA-L-P those extracted with the mixture).

There are not many differences between the parent material and the HA. Although the extraction procedure was not the same and therefore not strictly comparable, the same is true of HA extracted with aqueous KOH at 200°C from coal⁴. The carbon contents of the HA lie within the literature values for lignite HA⁵ but are higher than those for soil HA⁶. The atomic H/C and O/C ratios also lie between the ratios given for coal HA⁵.

Functional groups of the lignite and HA are shown in Table 2.

There are some differences in the functional groups of the parent lignite and HA, though not between the HA themselves except in the case of the carbonyl groups. The determination of this group by the method of Fritz *et al.*⁷ in the lignite sample is not very accurate, even though the results are reproducible. The high value obtained may be due to the decomposition of the reagent catalysed by the ash present. The values for total acidity increase from the lignite to the HA, and the same occurs with carboxyl and phenolic hydroxyl groups. The low or null content of alcoholic hydroxyls, also noted by Brooks and Sternhell⁸ for Victorian brown coal, is significant.

In Table 3 is shown the distribution of oxygen in the functional groups.

There are marked differences in the distribution; the values for lignite are similar to those reported by Brooks and Sternhell⁸, but the HA have different distributions from those found in the literature for HA from coal and soil⁶. In the latter, oxygen in carboxyl represents approximately 50% of total oxygen. The oxygen accounted for in the HA is however of similar magnitude to that accounted for in soil HA.

Figure 1 shows the i.r. spectra of lignite and HA. The band at 3380 cm⁻¹ (H bonded OH) is sharper in lignite than in HA. In lignite the bands at 2900 cm⁻¹ and 2850 cm⁻¹ (aliphatic C-H stretching vibration) appear more intense and clear. The band at 1720 cm⁻¹ (C=O of COOH) is similar in both HA and higher than in lignite, in agreement with chemical data. The intensity of the band at 1600 cm⁻¹ (C=C of aromatic ring) is quite similar in the three spectra. The band at 1425 cm⁻¹ (COO⁻) is more pronounced in lignite than in HA. In the latter there is a band at 1200 cm⁻¹ (phenolic OH) not present in lignite. From this wavelength till 650 cm⁻¹ there are no more absorption bands in the spectra of the HA but in lignite the following bands, characteristics of kaolinite, are present: 1120 cm⁻¹ (Si-O stretching), 1036 cm⁻¹ (Si-O stretching), 1014 cm⁻¹ (Si-O of Si-O-Al), 934 cm⁻¹ (OH bending) and 916 cm⁻¹ (OH bending).

The u.v. and visible spectra of HA are featureless showing neither maxima nor minima, as usual in humic substances.

Table 3 Distribution of oxygen in functional groups of untreated and hydrolysed lignite and HA (% of total oxygen)

	O as COOH		O as phenolic OH		O as alcoholic OH		O as total CO		O accounted for	
	b	a	b	a	b	a	b	a	b	a
	L-PGR	19.6	23.1	25.7	31.0	6.1	0.0	—	10.5	—
HA-L-N	35.5	31.1	31.0	30.6	2.1	0.0	13.7	10.7	82.4	72.4
HA-L-P	35.5	32.8	29.5	30.8	0.0	0.0	21.1	10.9	86.1	74.5

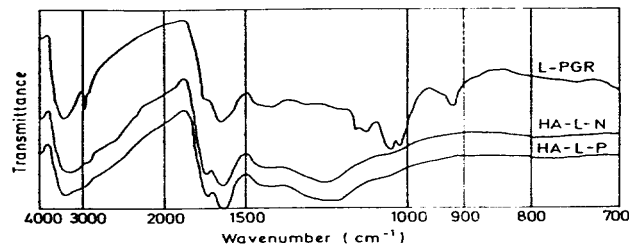


Figure 1 I.R. spectra of lignite and HA

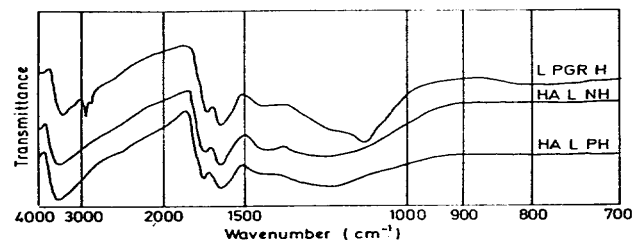


Figure 2 I.R. spectra of hydrolysed lignite and HA

The E_4/E_6 ratio, used as condensation index, has values of 5.1 in both HA, being in the range of brown humic acids.

The elution patterns of the HA on Sephadex G-100 (Figure 3) were also similar. These showed a separation into two fractions, one ($>100\ 000$) detected as a small peak and the other, the bulk of the material, with a molecular size in the range of 100 000 or lower.

Acid hydrolysis of the HA has been proposed as a useful procedure for the preparation of more homogeneous and relatively ash-free material⁹ and it has also been applied in the studies of coal with the same purpose.

Figure 2 shows the i.r. spectra of the parent lignite and HA after acid hydrolysis (designated as L-PGR-H, HA-L-NH and HA-L-PH respectively). There are no differences between the HA before and after hydrolysis^{9,10}, but in lignite there was an increase of the absorption at 1725 cm^{-1} accompanied by a decrease of the band at 1400 cm^{-1} and at the same time a disappearing of the absorptions at 1120 cm^{-1} , 1036 cm^{-1} , 1014 cm^{-1} , 934 cm^{-1} and 916 cm^{-1} from kaolinite. With the acid treatment there was a decrease in ash from 21.5% to 9.3% (Table 1).

In Table 1 (columns a) are shown the elementary compositions of the three samples after hydrolysis. There is a decrease in C and H and an increase in N in both HA. The latter does not occur in soil HA in which there is a decrease, often very marked, in N.

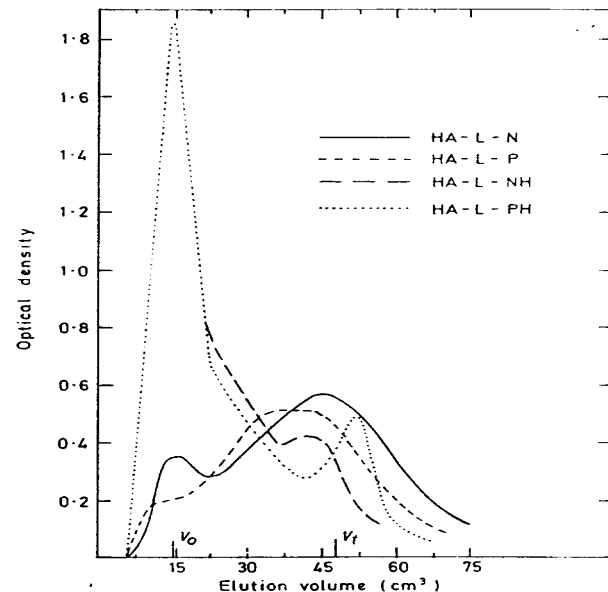


Figure 3 Elution curves of HA and hydrolysed HA from Sephadex G-100

In Table 2 (columns a) are shown the functional groups of lignite and HA after acid hydrolysis. This treatment tended to increase total acidity, especially in lignite, even though not much in the HA. In the acid-treated lignite CO was determined and the value found is in agreement with those reported in the literature⁷. Total CO decreases in HA upon hydrolysis, contrary to what occurs in soil HA^{9,10}. As there has been a decrease in the C content and a consequent increase in O while the functional groups did not change, the oxygen assigned to these also decreased (Table 3).

According to the E_4/E_6 ratios after hydrolysis (4.4 for both HA) there has been a condensation in the structure. This is shown in the behaviour on Sephadex (Figure 3). After hydrolysis the elution patterns are markedly different since the first peak (molecular size $>100\ 000$) now constitutes the bulk of the material.

Figures 4, 5 and 6 show the low b.p. compound pyrograms obtained from the lignite and HA. As with soil HA¹¹, there are not qualitative but quantitative differences. By retention time, co-chromatography and subtractive processes the compounds listed in Figure 4 were identified.

With the exception of the propylene peak (4), the HA produce a greater amount of alkanes and olefins than

Alkanes	Olefins	Aromatics	Others
1 Methane	2 Ethylene	13 Benzene	9 Acetone
3 Ethane	4 Propylene	15 Toluene	10 Acetic acid
5 Propane	7 Butene-2-trans	16 Phenol	
6 Butane	8 Butene-2-cis		
11 Pentane			
12 Hexane			
14 Heptane			

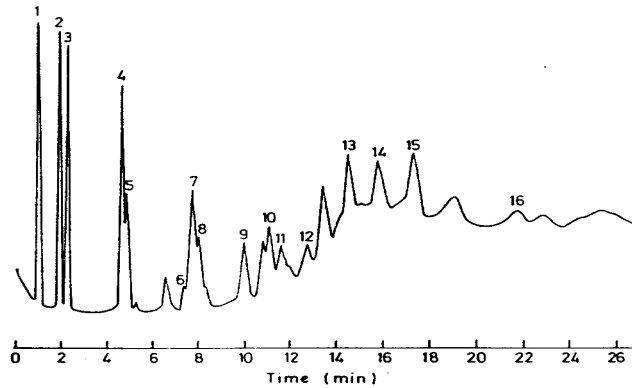


Figure 4 Low b.p. compounds pyrogram of lignite

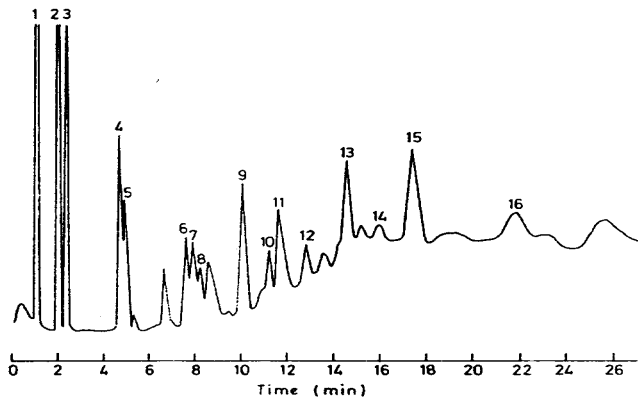


Figure 5 Low b.p. compounds pyrogram of HA-L-N

lignite, and the HA extracted with NaOH produced more than that extracted with $\text{Na}_4\text{P}_2\text{O}_7\text{:NaOH}^{11}$. On hydrolysis there is reduction of the peak heights, but qualitatively the pyrograms remain identical.

After exhaustive methylation the pyrograms present some changes. In Figure 7 is shown the pyrogram of one of the methylated HA (HA-L-N). In the three samples there have been increases in methane (1), ethylene (2), ethane (3), acetone (9) as well as a peak not identified (18). A new peak (17) appears assigned to methanol and consequent on the methoxyl groups introduced by methylation. In the HA the above cited increases were higher and extended also to propylene (4), propane (5), butane (6), butenes (7 and 8) and pentane (11).

SUMMARY AND CONCLUSIONS

The effects of the two extractants on the analytical characteristics of the isolated HA are not significant, unlike the effects encountered in soil HA². In soils the humification process is continuous, and at all times the different stages of this process are present: every extractant isolates a portion of the humic substances according to its ability for one determined fraction. So, in a vertisol, the employment of the same two reagents as in the present work has extracted different fractions, the NaOH solution extracting the so-called brown humic acids while the mixture extracts these together with grey humic acids¹².

In lignite the humification process has ceased and the HA would be in a defined stage, so that in this case the different extractants isolate the same fraction, the total present in

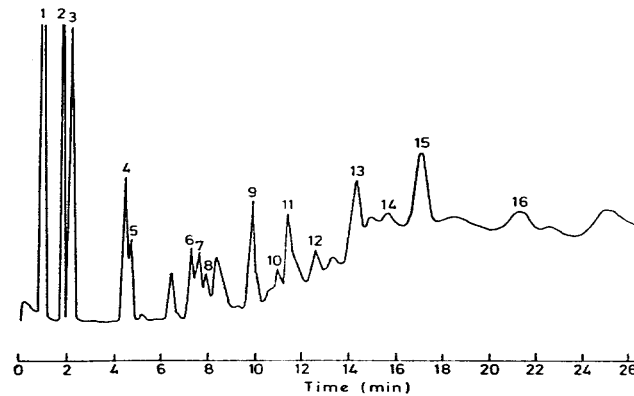


Figure 6 Low b.p. compounds pyrogram of HA-L-P

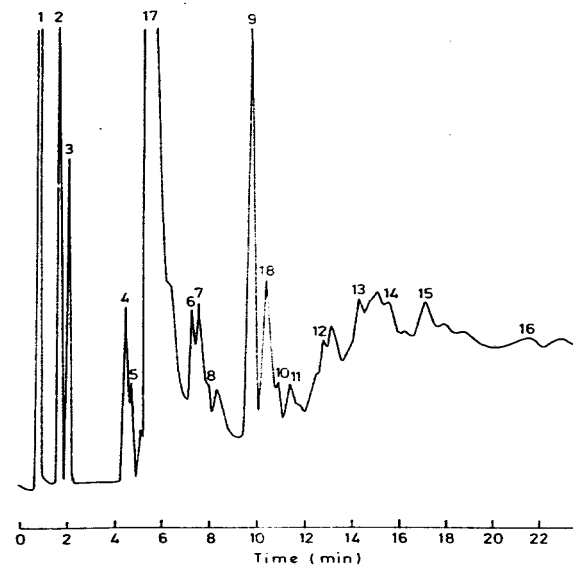


Figure 7 Low b.p. compounds pyrogram of methylated HA-L-N

lignite. The yields of HA extracted and the analytical characteristics studied are similar, showing only small differences that may be due to the analytical methods or to changes induced by extractants during the extraction procedure. The most marked difference between the HA and lignite lies in the total carbonyl content. The method used gives a very high value and its accuracy should be tested by further experiments.

The lignite ash is mainly constituted by kaolinite, as has been demonstrated by X-ray diffraction, and this is responsible for the i.r. absorption bands at 1120, 1094, 1036, 1014, 934, 916, 800, 750 and 700 cm^{-1} that disappear on acid hydrolysis. This treatment, recommended for soil-HA purification⁹, does not seem to affect the elementary composition and oxygen-functional-group distribution in lignite HA but it makes them more similar. However, it produces a condensation of the molecule as is shown in the elution through Sephadex.

The low b.p. compound pyrograms of lignite and HA show quantitative differences. The three samples produce the same compounds as soil HA¹¹ but to a lesser extent. By pyrolysis/gas chromatography it is possible to detect small differences not found by the usual techniques applied in the studies of humic substances. Pyrolysis produces complex pyrograms which differ primarily in peak height, not in the presence or absence of some components. The different peak heights are evidence of some structural differences in the lignite HA.

It has been shown that a great part of the products obtained by pyrolysis increases on methylation, indicating by this fact that at least a proportion, not defined, of alkanes and olefins arises from side reactions. Martín¹¹

has verified that after an oxidation the pyrogram peaks, and therefore the aliphatic chains responsible for such compounds, disappear. Mazumdar *et al*¹³ claimed that the only aliphatic chains definitely known in coal are methyl groups. As some of the compounds found by pyrolysis do not increase on methylation, it is possible that they arise from longer chains present in lignite and also in its HA.

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