

Pyrolysis gas chromatography of humic substances from different origin

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Introduction

In recent years the application of different new techniques has allowed considerable progress in the study of the structure of the humic substances, however, much remains to be learned about their origins, synthesis, chemical structure, and reactions (*Schnitzer and Khan, 1972*).

The methods most frequently used to characterize the humic substances are: elementary composition, functional group analyses, IR and UV spectrophotometry, as well as degradative techniques both oxidative and reductive. All these techniques have made it possible to establish some characteristics of the humic substances from different origins, but these are not very specific since even though there are differences between them, these are not very significative.

The degradative method, more successful till now, is the alkaline permanganate oxidation of the methylated materials (*Schnitzer and Desjardins, 1970, Khan and Schnitzer 1971, Ogner 1973*). This method yielded two types of major products: benzenecarboxylic acids and phenolic acids, but in the distinct humic substances studied, these compounds, with some exceptions, are always the same, even though they appear in different amounts.

The objective of this work has been to describe the pyrolysis behaviour of humic acids (HA) and fulvic acids (FA) from different origin and extracting reagents. This technique has been scarcely used with humic substances (*Nagar 1963, Wershaw and Bohner 1969, Kimber and Searle 1970, Murzakov 1970, Gómez Aranda et al. 1972*), and it is attaining a great development, especially the denominated flash pyrolysis used to obtain fingerprints of a large number of polymers and related substances. The main impediment to it is the secondary or side reactions during the experiments, but with the employment of modern apparatus, the principal factors affecting these secondary reactions are minimized, and consequently its extent.

In the present paper only the low boiling point compounds have been studied.

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Material and methods

The origin of samples and extracting reagents employed are listed in table 1.

Table 1: Origin and classification of samples

Ursprung und Einteilung der Proben

HA	FA	Horizon	Extracting reagents	Source	Geographical origin
	1	B _h	NaOH	Podzol	Lugo, Spain
	2	B _h	HCl	Podzol	Lugo, Spain
	3	B _h	Na ₄ P ₂ O ₇ : NaOH	Podzol	Lugo, Spain
4		B _h	NaOH	Podzol	Lugo, Spain
5		B _h	Na ₄ P ₂ O ₇ : NaOH	Podzol	Lugo, Spain
6		A ₁	NaOH	Fersialitic	Sevilla, Spain
7		A ₁	Na ₄ P ₂ O ₇ : NaOH	Fersialitic	Sevilla, Spain
8		Ap ₁	NaOH	Vertisol	Sevilla, Spain
9		Ap ₁	Na ₄ P ₂ O ₇ : NaOH	Vertisol	Sevilla, Spain
10			NaOH	Lignite	La Coruna, Spain
11			Na ₄ P ₂ O ₇ : NaOH	Lignite	La Coruna, Spain

Methods of extraction and purification of soil HA and FA were analogous to those previously described (Vila et al. 1974, Martín et al. 1974).

The lignite HA's were extracted as follows: 50 g of lignite finely ground were extracted in a *Soxhlet* apparatus during 48 hr. with a mixture ethanol: benzene (1:1). The dry residue (46.2 g) was divided into two parts and extracted, under N₂ atmosphere with 0.1 N NaOH solution and Na₄P₂O₇: NaOH (1:1) 0.1 M respectively. As the NaOH solution did not extract anything, the lignite was washed with water and treated with HCl 1 N at room temperature during 24 hr, washed till Cl⁻ free and then again treated with 0.1 N NaOH.

In both, the extraction were continued till there was no colour in the extract. These were acidified and the coagulate centrifuged, washed with water, dialyzed and dried on a rotaevaporator and then in a desiccator over P₂O₅ at room temperature. The yields were 9.4 g for the NaOH extract (40.6 %) and 8.8 g for the mixture extract (38.4 %).

Acid hydrolysis: 1 g of every HA (the FA were not hydrolyzed) was treated with 100 ml of 1 N HCl during 24 hr, according to Riffaldi and Schnitzer (1973). The residues were washed, dialyzed till free of Cl⁻ and dried at 60 °C.

Analytical methods: Carbon and Hydrogen were determined by dry combustion, Nitrogen by the automated *Dumas* method and Oxygen was calculated by difference. The oxygen-containing functional groups were measured by the methods described by Schnitzer and Khan (1972).

Air oxidation: 1 g of every samples was oxidized at 170 °C during 600 hr according to Wright and Schnitzer (1961).

Pyrolysis: The pyrolysis were made in a Pyroprobe 100 Solids Pyrolyzer of the Chemical Data System, attached to a Hewlett Packard 5750 G gas chromatograph with two flame ionization detectors. 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 pyrolyzer.

The conditions were:

Pyrolysis temperature	700 °C
Pyrolysis chamber temp.	200 °C
Temperature raise	20 °C/msec.
Pyrolysis time	10 sec.

The chromatographic conditions were:

Injector temperature	250 °C
s.s. column	10 ft × 1/8 in.
Packing	Chromosorb 102
Oven temperature	50-200 °C + 15 min. isoth.
Rate	10 °C/min
Detector temperature	300 °C
Gas	N ₂
Flow rate	45 ml/min
Recorder speed	1/4 in./min

Results

Analytical characteristics of the humic substances are shown in table 2. The values are similar to those found in the literature, with the exception of the E₄/E₆ ratios for samples 2 and 3 (*Martín 1975a*).

Table 2: Analytical characteristics of humic substances

Analytische Charakteristik der Huminstoffe

elementary composition					major oxygen containing functional groups (meq/g)							
Sample	C	H	N	O	ash%	total acidity	carboxyls	phenolic OH	alcohol OH	carbonyls	E ₄ /E ₆	% pyrolyzed
1 FA-N	50.2	4.6	1.8	43.4	5.6	12.1	7.9	4.2	2.8	2.8	7.6	55.4
2 FA-C	48.1	4.3	0.9	46.7	5.4	12.6	8.6	4.0	3.3	3.8	12.0	60.6
3 FA-P	50.8	3.8	1.0	44.4	3.7	12.1	9.3	2.8	3.3	2.9	11.8	51.7
4 HA-PN	59.4	4.2	3.3	33.1	3.0	10.5	4.2	6.4	0.0	4.1	4.4	55.0
5 HA-PP	54.9	4.1	3.2	37.8	7.1	12.2	5.5	6.8	0.0	4.1	4.4	56.9
6 HA-RN	56.8	5.3	4.6	33.3	1.0	6.8	3.9	2.8	3.8	4.9	4.6	56.2
7 HA-RP	58.8	4.4	3.5	33.3	0.9	8.8	4.4	4.4	1.2	3.6	3.9	56.7
8 HA-NN	57.7	5.6	5.8	30.9	2.0	5.7	3.1	2.5	4.1	2.8	5.0	55.6
9 HA-NP	58.4	4.9	4.5	32.2	2.5	8.0	3.7	4.3	1.7	2.1	4.3	56.3
10 HA-LN	58.4	4.3	0.9	36.4	0.5	9.3	3.4	5.9	0.4	2.6	5.0	53.4
11 HA-LP	57.5	4.1	1.1	37.3	1.0	9.3	3.5	5.8	0.0	4.1	5.1	54.6

A pyrogram, representative of those produced by all humic substances, is shown in figure 1. All samples studied produce the same low b.p. compounds, differing only in the peak height of some of them.

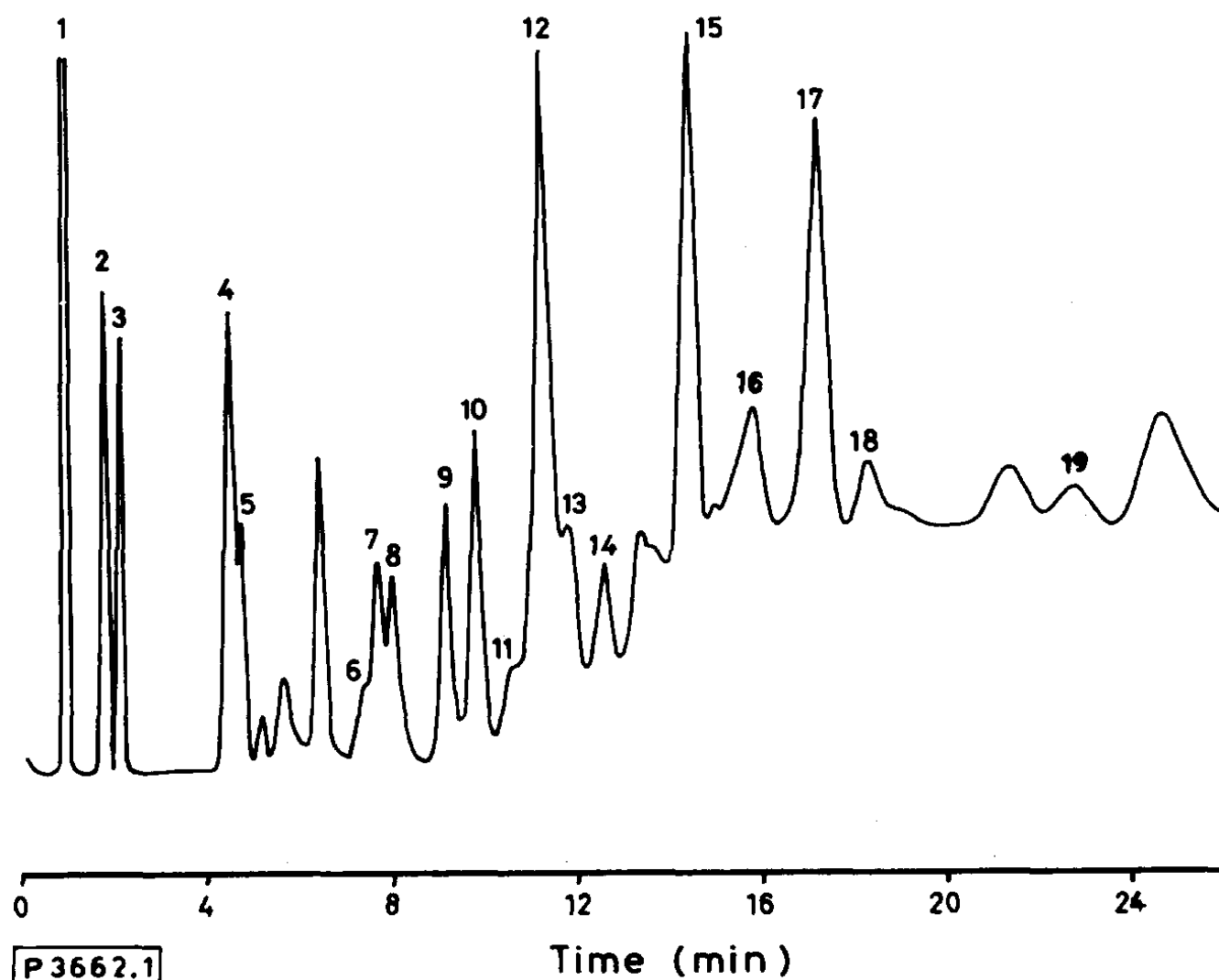


Figure 1: Pyrogram of low b. p. compounds of an HA

Pyrogramm von niedrig siedenden Verbindungen einer Huminsäure.

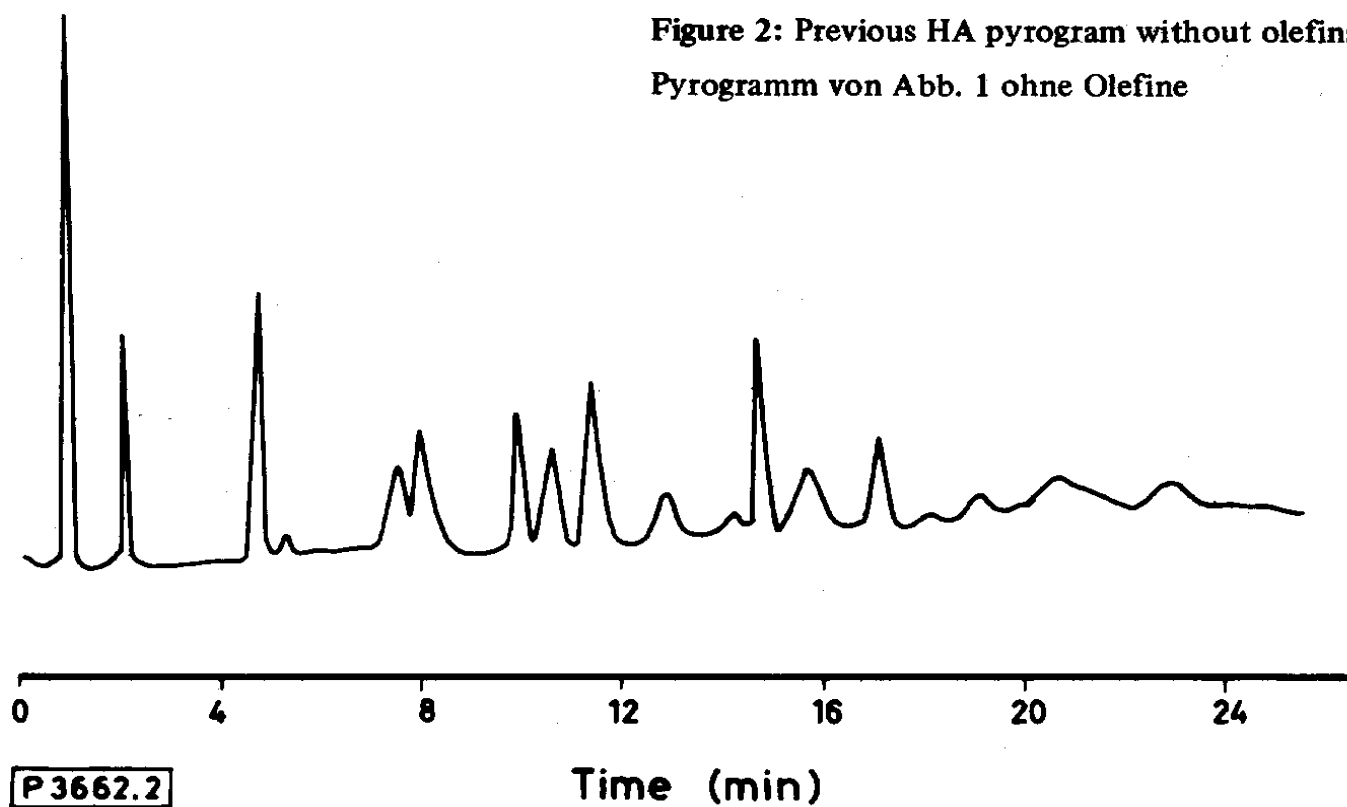
By subtractive processes the pyrolysis products were separated in three groups: alkanes, olefins and aromatics. With the employment of a precolumn of $\text{HgSO}_4:\text{H}_2\text{SO}_4$ (20 % HgSO_4 in 20 % H_2SO_4 , *Innes et al.* 1963), the pyrogram shown in figure 2 was obtained, where only the alkanes and aromatics are present. With a precolumn of $\text{Ag}_2\text{SO}_4:\text{H}_2\text{SO}_4$ (4 % Ag_2SO_4 in 95 % H_2SO_4 , *Innes et al.* 1963), the pyrogram shown in figure 3 was obtained, where olefins and aromatic have been subtracted. Also these pyrograms are representative of those obtained for all humic substances.

By means of retention time of known compounds and co-chromatography, the compounds listed in table 3 were identified.

As have been pointed out by *Kimber and Searle* (1970), that the compounds produced in the pyrolysis of humic substances arise from the molecule periphery,

Figure 2: Previous HA pyrogram without olefins

Pyrogramm von Abb. 1 ohne Olefine

**Figure 3: Pyrogram of fig. 1 without olefin and aromatic compounds**

Pyrogramm von Abb. 1 ohne Olefine und ohne Aromaten

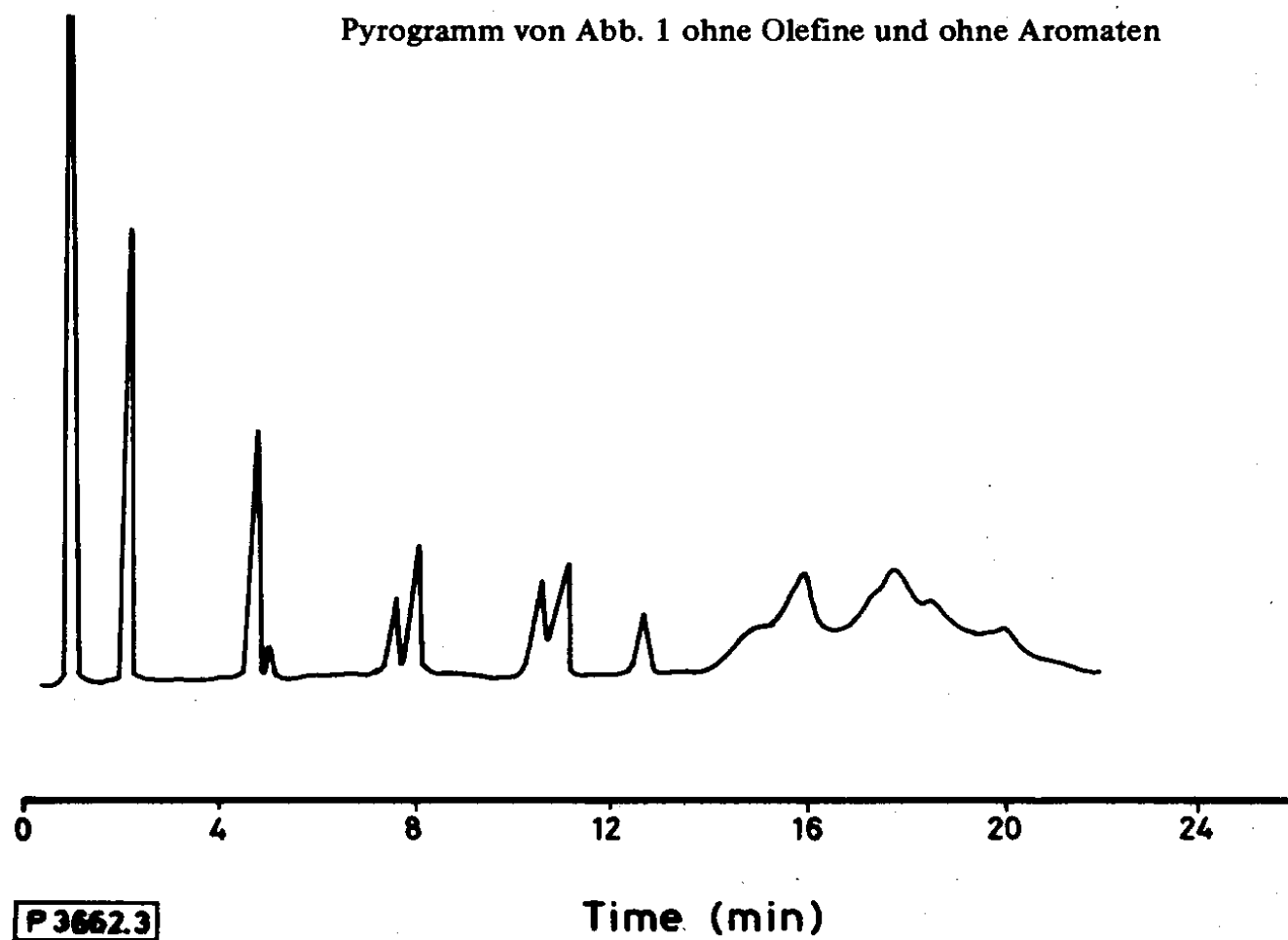
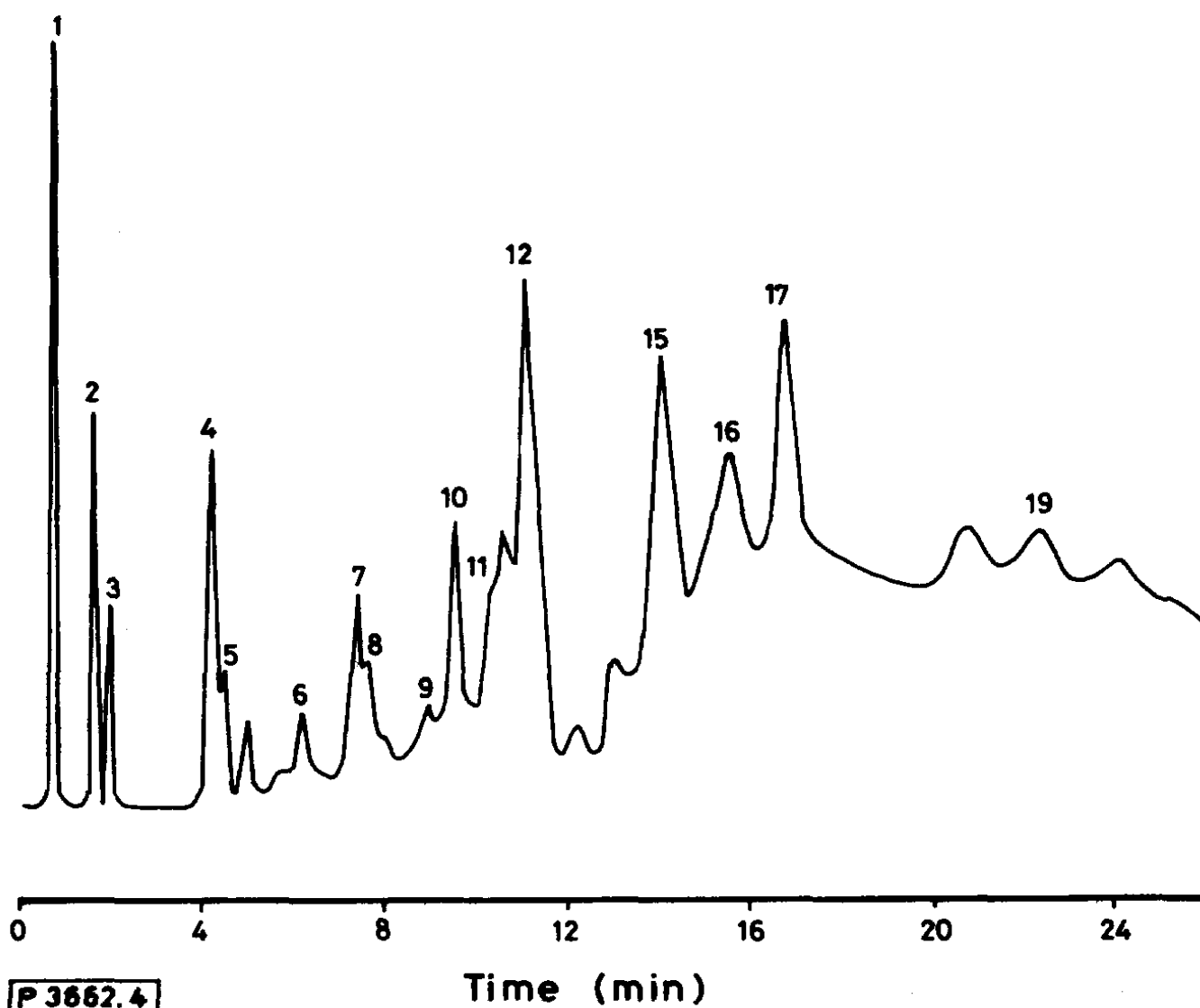


Table 3: Low b. p. compounds identified in the pyrolysis of humic substances

In den Pyrolyseprodukten von Huminstoffen identifizierte, niedrig siedende Verbindungen

Alkanes	Olefins	Aromatics	Inorganics	Others
1 methane	2 ethylene	15 benzene	carbon monoxide	10 acetone
3 ethane	4 propylene	17 toluene	carbon dioxide	12 acetic acid
5 propane	7 butene-2-cis	19 phenol	water	13 furan
6 butane	8 butene-2-trans			18 furfuryl alcohol
11 pentane	9 pentene 1			
14 hexane				
16 heptane				

**Figure 4:** Pyrogram of low b. p. compounds of an acid hydrolyzed HA

Pyrogramm niedrig siedender Verbindungen von einer sauer hydrolysierten Huminsäure

and a great proportion of these supposing substances can be eliminated by acid hydrolysis without affecting the rest of the molecule (Riffaldi and Schnitzer 1973), the humic substances were hydrolyzed and the residues pyrolyzed. A representative pyrogram is shown in figure 4.

The pyrograms are also qualitatively identical to those obtained before hydrolysis, but there have been some changes in the peak heights of several compounds. In general there is a decrease in methane (1), ethylene (2), ethane (3), propylene (4) and propane (5), remaining almost equal the rest of the compounds.

Benzene (15) and toluene (17) are found in all pyrograms and decrease upon hydrolysis. Furane (13) a compound that may arise from the polysaccharide impurities of the humic substances (Wershaw and Bohner 1969), disappears almost completely upon hydrolysis and the same occurs with furfuryl alcohol (18). These two compounds are not produced in the pyrolysis of lignite HA's. Phenol (19) increases in all pyrograms upon hydrolysis.

Figure 5 shows the pyrogram obtained after air oxidation at 170 °C during 600 hr. All the peaks have almost disappeared including those corresponding to aromatic compounds.

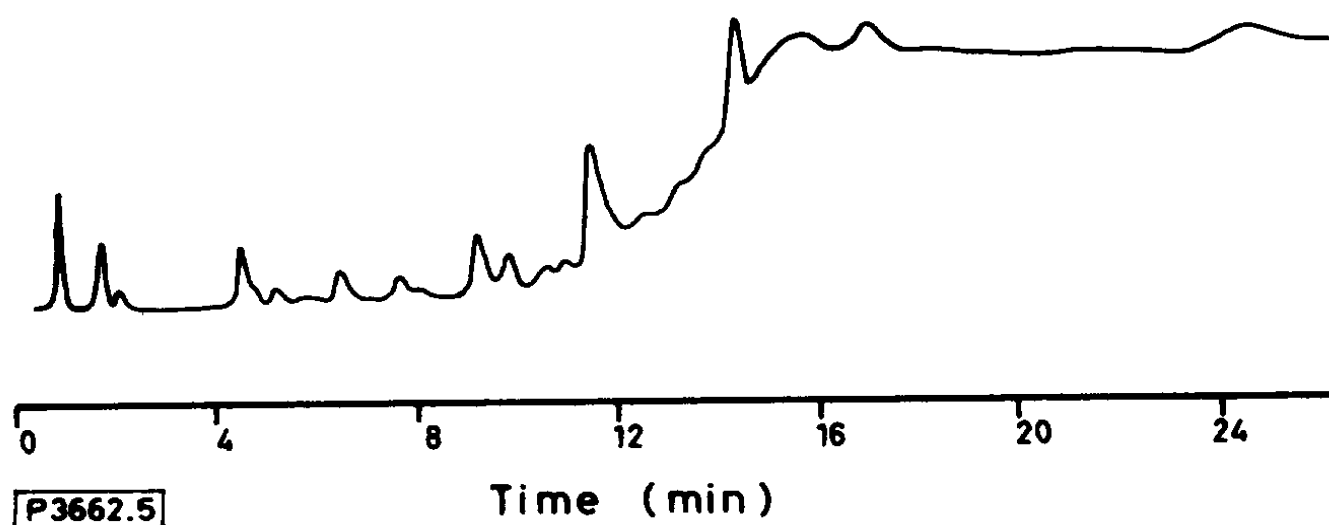


Figure 5: Pyrogram of an air oxidized HA

Pyrogramm einer luftoxidierten Huminsäure

The HA's extracted with $\text{Na}_4\text{P}_2\text{O}_7 : \text{NaOH}$ present always less peak height than those extracted with NaOH . The formation of low b.p. compounds on pyrolysis decreases in the order:

HA's from vertisol > HA's from fersialitic soil > HA's from pdozol > FA's from podzol > HA's from lignite.

Conclusions

The alkanes and olefins obtained by pyrolysis of humic substances are to a great extent low b.p. compounds, and these can arise principally from aliphatic and/or

alicyclic chains more or less long, present in the molecule, either directly or by breakdown and also from radical reactions.

Though there are no direct methods for determining aliphatic chains in the HA molecule, the majority of authors affirm that these are constituted by an aromatic core. In opinion of *Haworth* (1971), to this core are attached polysaccharides, proteins, simple phenols and metals. The two first release alkanes and olefins on pyrolysis and both may be eliminated or reduced by purification processes and by acid hydrolysis and although the pyrograms of hydrolyzed HA's have less peaks height, the decrease does not reflect the removal of such substances. *Kimber* and *Searle* (1970) found a positive relation between the hydrolyzable nitrogen and the production of benzene and toluene. As a general rule the HA's extracted with NaOH have a high N-content and they produce higher peaks. However in the FA case, the FA-C with an N-content of half that of FA-N has a benzene peak four times higher, being this result not in agreement with the above supposition.

Ogner and *Schnitzer* (1971), and *Khan* and *Schnitzer* (1971), have suggested a structure for FA made up of phenolic and benzene-carboxylic acids which can adsorb organic compounds such as alkanes in a proportion of 0.16 %, of which only 3 % were extractable by organic solvents, remaining the rest firmly bonded. If a similar quantity may be presumed in the HA, these are the origin of a part of the low b.p. compounds produced by pyrolysis.

On the other hand the production of pyrolysis products is catalyzed by ash content or some of its components since the reduction of those by a HCl:HF treatment (*Khan* 1971) reduce considerably the pyrolysis components (*Martin*, unpublished data).

As in the case of oxidative and reductive methods, the humic substances produce by pyrolysis (at least with respect to the low b.p. products) the same compounds but in different amounts, with the exception of some components derived from the polysaccharide impurities.

Martin (1975b) has proved that a NaOH solution extract the so called brown humic acids while $\text{Na}_4\text{P}_2\text{O}_7$:NaOH extract a mixture of brown and gray humic acids. By pyrolysis the former release more volatile products than the latter, so the expected order of pyrolytic products formed

HA's extracted with NaOH > HA's extracted with $\text{Na}_4\text{P}_2\text{O}_7$:NaOH is accomplished.

In HA whose analytical data are similar, like in the lignite HA's, by flash pyrolysis is possible to detect little differences perhaps induced during the extraction and purification procedures.

The pyrolysis gas chromatography of low b. p. compounds produce fingerprints, but as has been pointed out by *Schnitzer* and *Khan* (1972), "it is not possible to

properly relate the pyrolysis products to the structures present in the original humic materials, until more basic research of simple model compounds is done".

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Summary

Humic substances produce by pyrolysis among low boiling point compounds alkanes and olefins. The unique difference found in the humic and fulvic acids is not the presence or absence of some compounds but their amount. The production of such compounds is catalyzed in part by the ash content, and they arise through radical reactions principally from the aliphatic and/or alicyclic chains attached to the core. When the humic substances are oxidized by heating in air the alkanes and olefins are not produced in the pyrolysis.

By pyrolysis gas chromatography it is possible to detect little differences among humic substances not found by the usual analytical techniques.

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Pyrolytische Gaschromatografie von Huminstoffen unterschiedlichen Ursprungs.

von *F. Martín*

Die Pyrolyse von Huminstoffen liefert unter anderen niedrig siedenden Substanzen Alkane und Olefine, deren Anteil bei Fulvo- und Huminsäuren unterschiedlich ist. Diese Verbindungen entstehen durch Radikalreaktionen aus aliphatischen oder alicyclischen Ketten; ihre Bildung wird zum Teil durch den Aschegehalt der Huminstoffe katalytisch beeinflusst. Nach dem Erhitzen von Huminstoffen an der Luft werden weder Alkane noch Olefine pyrolytisch gebildet. [3662]