RETENTION OF ORGANIC COMPOUNDS IN A HUMIC ACID FROM LIGNITE

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SUMMARY
    A lignite humic acid was found to retain a variety of hydrophobic compounds which could be removed by repeated extraction with hexane and chloroform and analyzed by capillary GC and GC-MS. While in the hexane extracts only series of n- and branched alkanes were found, the subsequent extraction with chloroform releases different types of compounds such as saturated, unsaturated, cyclic and branched fatty acids, long chain dicarboxylic acids, long chain w-hydroxyacids and n-alkanols, as well as dehydrophytol and the isoprenoid C(18) ketone as individual components. Results on the possible sources and retention mechanisms of these compounds are discussed.

INTRODUCTION

    Solvent extraction has been widely applied to remove easily accessible organic material occluded within the coal macromolecular framework, and the molecular composition of coal extracts has been used in studies of coal depositional history, mode of formation and molecular structure (ref. 1). Unfortunately, extract yields are seriously limited by the solvent accesibility to parts of the coal structure (ref.2), and the operating retention mechanisms are not yet well known. It is, however, accepted that the extractability of coals decreases while the maturation level increases, which suggests that the retention effect would be due to a physical trapping in the closed porosity rather than adsorption effects on functional groups (ref. 3).

    The comparatively higher functionality in low-rank coals is mainly due to their high content on humic acids (HA). While much research has been done on interactions between the sedimentary

humic fractions with inorganic moities (refs. 4,5), little is known about their potential ability to retain hydrophobic organic compounds, not directly extractable from the coal by mild solvent treatments, as occur with humic substances (HS) from other environments. Thus, as pointed out by Schnitzer (ref.6), HS may fix, stabilize and preserve by different mechanisms, over long periods of time, relatively large amounts of hydrophobic organic compounds, including toxic pollutants and petroleum source materials, contributing to their transport, dispersion and sedimentation in the environment.

Within a detailed study on the organic geochemical characteristics of the different organic fractions present in a Spanish lignite, the aim of this work was to investigate the qualitative composition of the low molecular weight components associated to the HA fraction in order to discusse their possible sources and operating retention mechanisms. Our approach included the removal of bitumens before the alkaly extraction of HS. This pretreatment might be regarded in our case as a useful, indispensable analytical step, which does not have any known structural bearing to the humic fraction (refs. 7,8).

MATERIAL AND METHODS

The lignite sample was taken from a depth of 2m from the Arenas del Rey (AR) deposit, belonging to the Miocene Granada basin (South Spain). Chemical and petrographic data on this lignite, as well as the nature of its bituminous fraction were published elsewhere (ref. 9).

The extraction and purification of the HA was accomplished by standard methods (ref. 10) from a lignite sample previously Soxhlet extracted with toluene. The separation procedures are

summarized in the scheme of fig.1. Extracts were methylated with diazomethane in ether and silylated with BSTFA prior to the analysis by GC and GC-MS.

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                    ┌────────┐
                    │Lignite │ 270 mesh-screen
                    └────────┘
                        │ toluene
                        │ Soxhlet (48h)
          ┌─────────┐   │   ┌───────────┐
          │ Bitumen │───┴───│ Residue I │
          └─────────┘       └───────────┘
                                │ NaOH 0.1N
        ┌──────────────────┐    │   ┌────────────┐
        │ Humic Substances │────┴───│ Residue II │
        └──────────────────┘        └────────────┘
                │ H⁺
    ┌──────────────┐   │   ┌─────────────┐
    │ Fulvic Acids │───┴───│ Humic Acids │
    └──────────────┘       └─────────────┘
                                │ hexane
                                │ chloroform
                                │ ultrasonic
                          ┌──────────┐
                          │ Extracts │──► Analysis by GC and GC/MS
                          └──────────┘
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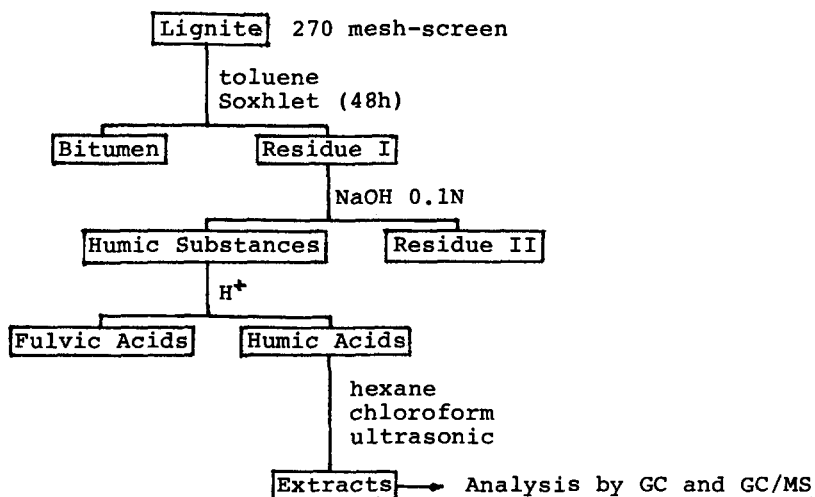
Fig.1.- Flow diagram for the isolation of organic compounds
        associated to the HA fraction.

A Hewlett Packard 5730 A model gas chromatograph equipped with flame ionization detector (FID) and a Hewlett Packard 5988 A gas chomatograph-mass spectrometer-computer system were used for the separation and identification of individual components. The separation of compounds was achieved using a 25 m (0.32 mm i.d.) SE-52 fused silica capillary column, with the oven temperature programmed from 100 to 300 $^{\circ}$C at a rate of 6 $^{\circ}$C/min with 15 min final hold. Helium at a flow rate of 1.5 ml/min was used as carrier gas. The identity of the individual compounds was determined using capillary gas chromatography (on the basis of retention times and coinjection with standards), mass fragmentography (by key single ion monitoring for the different homologous series), low resolution mass spectrometry and

comparison with published and tabulated data. Molecular ions in most of the series were determined by CI (with methane as reagent gas) mass spectrometry in GC mode.

All solvents were of high purity g.l.c. grade and were checked for purity by gas chromatography.

RESULTS AND DISCUSSION

The sequential extraction of the lignite HA with n-hexane and chloroform releases different series of compounds. While in the hexane extracts only series of normal and branched alkanes were found, the chloroform ones contains different types of compounds such as saturated, unsaturated, cyclic and branched fatty acids, long chain -,w-dicarboxylic acids, long chain w-hydroxyacids and n-alkanols, as well as dihydrophytol and the isoprenoid C(18) ketone as individual components. To the best of our knowledge, alkanols, hydroxyacids, aliphatic diacids and ketones were not previously found in extracts of HS from soils or sediments.

The distributions of the series of n-alkanes, n-fatty acids and n-alkanols are shown in Fig.2. The n-alkane series in the range C(13) to C(31) shows an uncommon distribution with a maximum at C(14). The homologs with chain lenghts <C(20) that may be of microbial origin , are more predominant than those of chain lenghts >C(20), characteristics from higher plants. The branched alkanes consist mainly of the isoprenoids pristane (Pr) and phytane (Ph) in a relation Pr/Ph of 1.8 typical of brown coals (ref. 11).

The n-fatty acid series range from C(12) to C(32) with a maximum at C(16). The n-fatty acids <C(20), typical of living organisms, are more predominants than the homologs >C(20), which have an algal and/or higher plant origin. Also, branched chain
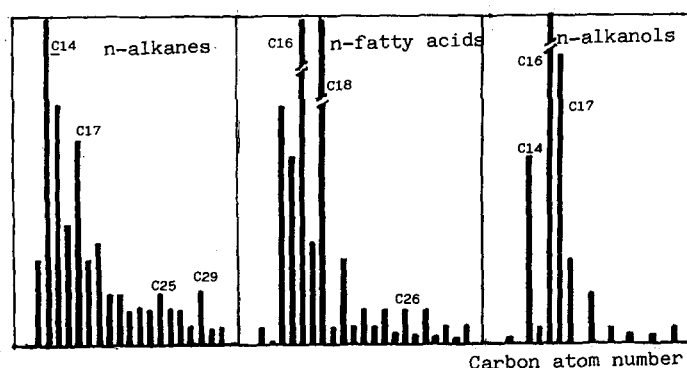
Fig.2.- Distributions of the homologous series of n-alkanes,
n-fatty acids and n-alkanols isolated from the
lignite HA fraction.

fatty acids (C(14) C(19)) along to the C(17) and C(19)
cyclopropanoidacids, both good indicators for a bacterial lipid
origin (ref. 12), were also present.

The isolation of the unsaturated fatty acids C(16:1), C(18:1)
and C(18:2) might be considered as a strong indication of the
recent contribution of plant materials and/or bacteria. However,
Chaffee et al. (ref. 13) reported the presence of the same
unsaturated acids in brown coals taken from bore cores at depths
near to 100 m. below the surface. They did not give any
explanation on the highly unusual presence of these compounds
because of their inherent instability under geological conditions.

n-Alkanols range from C(12) to C(28) with a strong even to
odd predominance and the n-C(16) homolog as major component. The
C(16) to C(18) alkanols may reflect components of bacterial or
algal wax esters while higher homologs are common constituents of
higher plants (ref. 14). Some branched alkanols of 15 and 17
carbon atoms were also detected.

The chloroform extracts also contain minor amounts of the
isoprenoids 6,10,14-trimethylpentadecan-2-one and dihydrophytol,

both typical degradative products of phytol (ref. 15).

The partial chromatogram of the Fig.3 shows the series of long chain alkanoic ∝,w-dicarboxylic acids and w-hydroxyacids identified in the chloroform extract.
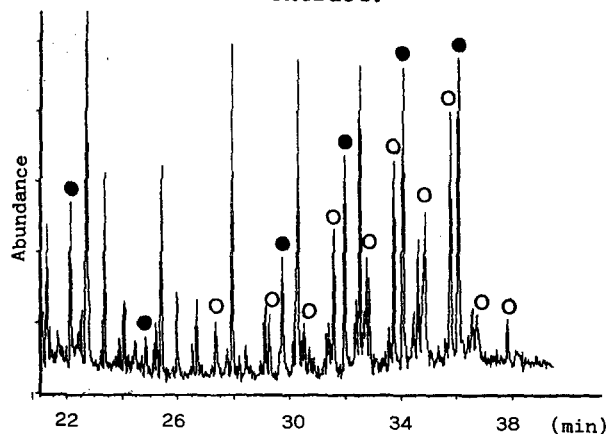

Fig.3.- Partial chromatogram of the HA chloroform extract after methylation and silylation, showing the series of long chain α,w-dicarboxylic acids (O) and w-hydroxyacids (●).

α,w-Dicarboxylic acids range from C(22) to C(30) whereas the w-hydroxyacid series consists only of the even carbon atom homologs ranging from C(16) to C(28). Although both series exhibit the same maximum at C(28) and similar distributions, the diagenetical relationship between them proposed by Douglas et al. (ref. 16) is not apparent in our case. As α,w-dicarboxylic acids are also generated by bacterial oxidation of hydrocarbons and/or monocarboxylic acids (ref. 17), their appearance in the HA fraction of this lignite might not reflect the indigenous organic matter but rather microbial oxidation of an appropiate substrate (ref. 18).

The nature and distributions of the major isolated compounds clearly indicate that they are probably not reflecting indigenous organic matter, but originated from recent contribution of plant materials and microbial biomass. This was to some extent expected

due to the low depth of the site where the sample was taken. Therefore, a possible release of lipid plant materials during the alkaline extraction step of Residue I (see Fig. 1) might be considered as the main source of the series of components found in the HA extracts. The acid-base treatment used for the extraction of the humic substances, lead probably to a new batch of organic compounds, wich were originally not extracted because they were chemically linked to the macromolecular matrix.

With respect to the possible retention mechanisms, general hypothesis can be considered. According to the classical view of Schnitzer (ref. 6) the isolated compounds may correspond to compounds 'entrapped' into the humic structure or adsorbed on the humic molecules. In the same way, the results are also consistent with the generalized model of HA proposed by Wershaw (ref. 19). In this model, hydrophobic compounds will partition into the hydrophobic interiors of the humic micelles or 'membrane-like' structures.

On the other hand, several authors (refs. 3,20) pointed out that in a lignite, low molecular weight molecules could be trapped as complex structures probably through hydrogen bonding and ester linkage during early diagenesis, and may be partly protected from extraction during laboratory separation procedures of geopolymers.

In any case, from the above results it may be concluded that HS from low rank coal, like HS from other environments, have the ability to retain or fix a certain proportion of hydrophobic materials, wherever they arise, which can be extracted by mild solvents.

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