

CHEMICAL NATURE OF SPECIES ASSOCIATED WITH MOBILE PROTONS IN
COALS; A STUDY BY FIELD IONIZATION MASS SPECTROMETRY

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INTRODUCTION

Proton n.m.r. investigations of coals swollen in deuterated pyridine showed that the free induction decay /FID/ consists of Gaussian and Lorentzian components related to two populations of protons which have widely different degrees of rotational mobility (1-5). The Gaussian component of FID has been unanimously ascribed to the macromolecular part of the coal matter that is supposed to have very limited rotational mobility. These publications as well as the ensuing debates (6-8) however, reflected the controversy regarding the nature of the Lorentzian /mobile/ protons in coals.

One view is that all Lorentzian protons can be attributed to molecules that are free to rotate in cages of the macromolecular network. Since the free molecules may be differentiated in their sizes and may have restricted freedom of rotation, their spin-spin relaxation times may be also differentiated and account for numerous populations of various mobilities within the group of Lorentzian protons.

The other view is that a significant part of the Lorentzian protons, especially those of lower mobility, may be also associated with fragments of the macromolecular network that can rotate due to a single C-C or C-O bond linking such fragment to the network.

The controversy cannot be easily clarified; there is no experimental technique available that could isolate all the free molecules and would leave intact the macromolecular network.

A more realistic approach is a separation of a mixture of free molecules and structural units linked to the network by single bonds, after these bonds have been cleaved by heat treatment of the coal. An insight into the composition of such mixture can provide information on the nature of species that are likely to be associated with the mobile protons. It seems that pyrolysis-field ionization mass spectrometry can be used in order to attain this goal.

Recently, an improved experimental setup for time-resolved in-source pyrolysis /py./ field ionization /f.i./ mass spectrometry /m.s./ has been described (9) and examples of its application to studying various biomaterials have been shown. There is a number of characteristic features of the py.-f.i.m.s. that are relevant to coal studies. Due to an increase of temperature of a sample in the direct introduction system of the mass spectrometer at heating rates around 1 °C per second and recording magnetic scans in 10 °C intervals, the volatilized species are not effected by a

higher temperature than is needed for their volatilization and detection. High vacuum and short residence time of the volatiles in the ion source of the spectrometer also reduce significantly secondary reactions between the species. The volatiles undergo soft ionization in the high electric field to produce molecular ions, with essentially no fragmentation ions. Hence, the mode of heating and ionization coupled with frequent scanning, can provide information about the composition of the material. When the py.-f.i.m.s. is applied to a coal, a mixture of free molecules as well as some parts of the macromolecular network is volatilized (10). Heating a coal to around 500 oC in the mass spectrometer should result in thermal decomposition of various single bonds that link structural units in the network (11). Although it is difficult to ascertain whether all free molecules and the structural units in question are volatilized in the mass spectrometer, this volatilized material certainly represents a high proportion of them.

The present paper shows such py.-f.i.m.s. data for a low rank bituminous coal. More specifically, the molecular weight distribution of volatilized material as well as elemental composition of its major components, are determined.

EXPERIMENTAL

The coal studied, 78 % C and 15.8 % O daf, is derived from Carboniferous deposits from the Ziemowit mine in Poland. Its petrographic composition / % vol.dmmf/ is: vitrinite, 60; exinite, 12; and inertinite, 40.

Proton n.m.r measurements of Zeeman relaxation for the same coal showed (12) that the fraction of mobile protons is 32 % of all protons. Assuming that the content of hydrogen in the mobile and immobile phases of the coal is approximately the same, the relaxation measurements indicate that the coal mobile phase content is app. 32 wt % of organic material.

Previously the py.-f.i.m.s. of coals and their pyridine extracts has already been described (10) using this novel technique. About 100 micrograms of ground coal sample was heated in the high vacuum of a combined e.i./f.i./f.d. ion source of a double-focusing mass spectrometer (Finnigan MAT 731, Bremen, FRG). The sample was heated at a constant rate of 24 oC/min from 50 to 500 oC. The volatilization of the coal was 30 % daf. This end temperature had been selected in such way that the yield of volatilization of the coal in the mass spectrometer was comparable with the mobile phase content in the coal. The temperature also corresponds to a rapid decrease of volatilization that is shown in Figure displaying total ion current.

Forty spectra were recorded electrically in the whole temperature range. The f.i. signals of all the spectra were integrated, processed and plotted using the Finnigan Spectro-System 200 to give a summed spectrum. Five measurements of the sample were recorded and their averaged, summed spectrum was finally obtained which is reproducible and representative of the coal.

High mass resolution /h.r./ f.i. mass spectrography was carried

out using the same py. conditions as above. The photoplate (Q2, Ilford, England) was exposed to f.i. ions in the range m/z 60-500 for about 10 min. The resolution obtained was between 10,000 and 20,000 /50 % valley definition/ with an average mass accuracy of approximately 0.003 Dalton /3 mmu/. The photographic plate was evaluated with a Gaertner comparator. Mass measurements were calibrated using perfluorokerosene. The accurate mass determinations allow the calculation of the elemental composition of the f.i. ions.

RESULTS AND DISCUSSION

The volatilization of the coal pyrolysed in the mass spectrometer to 500 °C corresponds to 30 wt % daf which is in accord with the mobile phase content of the coal, 32 wt % org. mat.

The molecular weights of the volatilized components were in the range of 80 to 800 Daltons. However, most intense f.i. signals were found in the much narrower range from 230 to 430 Daltons; abundances above this range quickly decreased to negligible values. The f.i. mass spectrum in question is not displayed here, since a similar one from another coal has been shown elsewhere (10).

High resolution f.i. data are shown in the Table. They are related to the major components of the volatilized material; the data for species for which intensities on the photoplate were below 5 % are not included, nor are the data for species above 300 Daltons that could not be accurately measured under the selected experimental conditions. Thus, the Table shows elemental composition of the species that account for app. 50 wt % of the volatilized material.

The species represent all homolog series of hydrocarbons from C_nH_{2n} to C_nH_{2n-28} ; of compounds with one oxygen atom from $C_nH_{2n-2}O$ to $C_nH_{2n-30}O$; and with two oxygen atoms from $C_nH_{2n-6}O_2$ to $C_nH_{2n-26}O_2$. These formulae relate to compounds that contain one, two /such as naphthalene and indene/ and three aromatic rings /such as anthracene, cyclopentaphenanthrene and benzoacenaphthene/ as well as four aromatic rings /such as pyrene, chrysene/ and five aromatic rings as in benzopyrene. There are from 1 to 8 carbon atoms in the alkyl substituents on the aromatic rings. It is worthy of note that the alkyl substituents are not long. Even if one assumes all alkyl carbons form one alkyl substituent on a ring, a substituent cannot be longer than C_8 for indenenes, C_7 for acenaphthenes, fluorenes and anthracenes and C_6 for benzenes and naphthalenes. Essentially the same applies to alkyl oxygen compounds.

Under the same py.-f.i.m.s. experimental conditions, compounds with normal and branched alkyl chains up to C_{32} were easily detected in natural waxes (13). Thus, the present results indicate that long alkyl compounds are not major constituents of the coal and discussing the FID signals of coal in terms of its "polyethelene structures" (B.C. Gerstein in reference 8) is not correct for the coal studied and may be not correct for other coals.

In summarizing, the following statements can be made:

- Py.-f.i.m.s. of coal can provide information on chemical nature of species that most likely, contain protons detected by n.m.r. experiments as mobile protons.
- The results for a low rank bituminous coal show a high diversity of molecular weights for such compounds, from 80 to 800 Daltons.
- The high resolution f.i. data, although limited to major components, also show diverse structures: the number of aromatic rings is from 1 to 5; the number of carbon atoms in alkyl substituents is in the range from 1 to 8.
- This structural diversity must account for the wide range of rotational mobilities of the components of the mobile phase.

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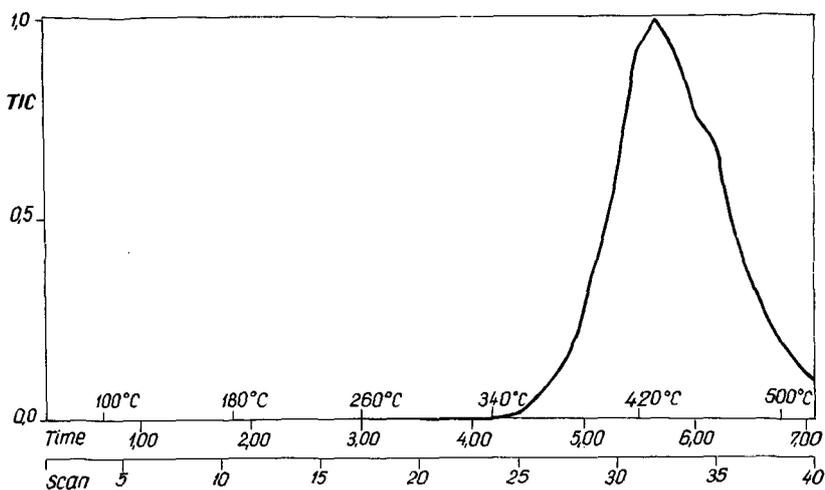
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Table. ELEMENTAL COMPOSITION OF F.I. MASS SIGNALS DETECTED FOR A LOW RANK BITUMINOUS COAL, 78 % daf

homolog series $C_n H_{2n} O$ and proposed structure	elemental composition of ions									
$C_n H_{2n}$; olefins/monocyclic alkanes	$C_6 H_{12}$	$C_7 H_{14}$	$C_8 H_{16}$	$C_9 H_{18}$	-	-	-	-	-	-
$C_n H_{2n-2}$; diolefins/dicycloalkanes	$C_6 H_{10}$	$C_7 H_{12}$	$C_8 H_{14}$	$C_9 H_{16}$	-	-	-	-	-	-
$C_n H_{2n-2} O$;	$C_6 H_{10} O$	$C_7 H_{12} O$	-	-	-	-	-	-	-	-
$C_n H_{2n-4}$; triolefins/tricycloalkanes	$C_6 H_8$	$C_7 H_{10}$	$C_8 H_{12}$	$C_9 H_{14}$	$C_{10} H_{16}$	-	-	-	-	-
$C_n H_{2n-4} O$;	$C_6 H_8 O$	$C_7 H_{10} O$	$C_8 H_{12} O$	$C_9 H_{14} O$	-	-	-	-	-	-
Number of carbon atoms in alkyl substituents										
	C_0	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	
$C_n H_{2n-6}$; benzenes	$C_6 H_6$	$C_7 H_8$	$C_8 H_{10}$	$C_9 H_{12}$	$C_{10} H_{14}$	$C_{11} H_{16}$	$C_{12} H_{18}$	-	-	-
$C_n H_{2n-6} O$; hydroxy benzenes	$C_6 H_6 O$	$C_7 H_8 O$	$C_8 H_{10} O$	$C_9 H_{12} O$	$C_{10} H_{14} O$	$C_{11} H_{16} O$	$C_{12} H_{18} O$	-	-	-
$C_n H_{2n-6} O_2$; dihydroxy benzenes	$C_6 H_6 O_2$	$C_7 H_8 O_2$	$C_8 H_{10} O_2$	-	$C_{10} H_{14} O_2$	$C_{11} H_{16} O_2$	-	-	-	-
$C_n H_{2n-10}$; indenenes	$C_9 H_8$	$C_{10} H_{10}$	$C_{11} H_{12}$	-	$C_{13} H_{16}$	$C_{14} H_{18}$	-	$C_{16} H_{22}$	$C_{17} H_{24}$	-
$C_n H_{2n-10} O$;	$C_9 H_8 O$	$C_{10} H_{10} O$	-	$C_{12} H_{14} O$	$C_{13} H_{16} O$	$C_{14} H_{18} O$	$C_{15} H_{20} O$	-	$C_{17} H_{24} O$	-
$C_n H_{2n-10} O_2$;	-	$C_{10} H_{10} O_2$	-	$C_{12} H_{14} O_2$	$C_{13} H_{16} O_2$	$C_{14} H_{18} O_2$	-	$C_{16} H_{22} O_2$	-	-
dihydroxyindenenes	-	-	-	-	-	-	-	-	-	-

	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈
C _n H _{2n-12} :naphthalenes/ -tetrahydrofluorenes	C ₁₀ H ₈	C ₁₁ H ₁₀	C ₁₂ H ₁₂	C ₁₃ H ₁₄	C ₁₄ H ₁₆	C ₁₅ H ₁₈	C ₁₆ H ₂₀	-	-
C _n H _{2n-12} ⁰ :hydroxy- naphthalenes/ -tetrahydrofluorenes	-	C ₁₁ H ₁₀ ⁰	C ₁₂ H ₁₂ ⁰	C ₁₃ H ₁₄ ⁰	-	C ₁₅ H ₁₈ ⁰	C ₁₆ H ₂₀ ⁰	C ₁₇ H ₂₂ ⁰	C ₁₈ H ₂₄ ⁰
C _n H _{2n-12} ⁰ :dihydroxy- naphthalenes/ -tetrahydrofluorenes	C ₁₀ H ₈ ⁰	-	C ₁₂ H ₁₂ ⁰	C ₁₃ H ₁₄ ⁰	C ₁₄ H ₁₆ ⁰	C ₁₅ H ₁₈ ⁰	C ₁₆ H ₂₀ ⁰	-	-
C _n H _{2n-14} :acenaphthenes	C ₁₂ H ₁₀	C ₁₃ H ₁₂	C ₁₄ H ₁₄	C ₁₅ H ₁₆	C ₁₆ H ₁₈	C ₁₇ H ₂₀	C ₁₈ H ₂₂	C ₁₉ H ₂₄	-
C _n H _{2n-14} ⁰ : hydroxyacenaphthenes	C ₁₂ H ₁₀ ⁰	C ₁₃ H ₁₂ ⁰	C ₁₄ H ₁₄ ⁰	C ₁₅ H ₁₆ ⁰	C ₁₆ H ₁₈ ⁰	C ₁₇ H ₂₀ ⁰	-	-	-
C _n H _{2n-14} ⁰ : dihydroxyacenaphthenes	C ₁₂ H ₁₀ ⁰	-	C ₁₄ H ₁₄ ⁰	C ₁₅ H ₁₆ ⁰	-	C ₁₇ H ₂₀ ⁰	-	C ₁₉ H ₂₄ ⁰	-
C _n H _{2n-16} :fluorenes	C ₁₃ H ₁₀	C ₁₄ H ₁₂	C ₁₅ H ₁₄	C ₁₆ H ₁₆	C ₁₇ H ₁₈	C ₁₈ H ₂₀	C ₁₉ H ₂₂	C ₂₀ H ₂₄	-
C _n H _{2n-16} ⁰ :hydroxyfluore- nes	C ₁₃ H ₁₀ ⁰	-	C ₁₅ H ₁₄ ⁰	C ₁₆ H ₁₆ ⁰	C ₁₇ H ₁₈ ⁰	C ₁₈ H ₂₀ ⁰	C ₁₉ H ₂₂ ⁰	C ₂₀ H ₂₄ ⁰	C ₂₁ H ₂₆ ⁰
C _n H _{2n-16} ⁰ : dihydroxyfluorenes	-	C ₁₄ H ₁₂ ⁰	C ₁₅ H ₁₄ ⁰	-	C ₁₇ H ₁₈ ⁰	C ₁₈ H ₂₀ ⁰	C ₁₉ H ₂₂ ⁰	-	-
C _n H _{2n-18} :anthracenes	C ₁₄ H ₁₀	C ₁₅ H ₁₂	C ₁₆ H ₁₄	C ₁₇ H ₁₆	C ₁₈ H ₁₈	C ₁₉ H ₂₀	C ₂₀ H ₂₂	C ₂₁ H ₂₄	-
C _n H _{2n-18} ⁰ : hydroxyanthracenes	-	C ₁₅ H ₁₂ ⁰	-	C ₁₇ H ₁₆ ⁰	C ₁₈ H ₁₈ ⁰	C ₁₉ H ₂₀ ⁰	C ₂₀ H ₂₂ ⁰	-	-
C _n H _{2n-18} ⁰ : dihydroxyanthracenes	C ₁₄ H ₁₀ ⁰	C ₁₅ H ₁₂ ⁰	C ₁₆ H ₁₄ ⁰	-	C ₁₈ H ₁₈ ⁰	C ₁₉ H ₂₀ ⁰	-	-	-
C _n H _{2n-20} : cycloopenitaphenathrenes	C ₁₅ H ₁₀	C ₁₆ H ₁₂	C ₁₇ H ₁₄	C ₁₈ H ₁₆	C ₁₉ H ₁₈	C ₂₀ H ₂₀	-	-	-

	C ₀	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈
C _n H _{2n-20} ; hydroxycyclo-pentaphenanthrenes	-	C ₁₆ H ₁₂ ⁰	-	-	C ₁₉ H ₁₈ ⁰	-	-	-	-
C _n H _{2n-20} ⁰ ; dihydroxycyclo-pentaphenanthrenes	-	-	-	C ₁₈ H ₁₆ ⁰ ₂	-	-	-	-	-
C _n H _{2n-22} ; pyrenes/fluoranthenes	C ₁₆ H ₁₀	C ₁₇ H ₁₂	-	C ₁₉ H ₁₆	C ₂₀ H ₁₈	-	-	-	-
C _n H _{2n-22} ⁰ ; hydroxy- <i>pyrenes</i> / <i>fluoranthenes</i>	C ₁₆ H ₁₀ ⁰	-	-	-	-	-	-	-	-
C _n H _{2n-24} ; chrysenes	-	C ₁₉ H ₁₄	C ₂₀ H ₁₆	C ₂₁ H ₁₈	C ₂₂ H ₂₀	-	-	-	-
C _n H _{2n-24} ⁰ ; hydroxychrysenes	-	C ₁₉ H ₁₄ ⁰	-	C ₂₁ H ₁₈ ⁰	-	-	-	-	-
C _n H _{2n-24} ⁰ ₂ ; dihydroxychrysenes	C ₁₈ H ₁₂ ⁰ ₂	-	-	-	-	-	-	-	-
C _n H _{2n-26} ; cyclopentapyrene	C ₁₈ H ₁₀	C ₁₉ H ₁₂	C ₂₀ H ₁₄	C ₂₁ H ₁₆	C ₂₂ H ₁₈	-	-	-	-
C _n H _{2n-26} ⁰ ; hydroxycyclopentapyrenes	C ₁₈ H ₁₀ ⁰	-	C ₂₀ H ₁₄ ⁰	-	-	-	-	-	-
C _n H _{2n-26} ⁰ ₂ ; dihydroxycyclopentapyrenes	-	C ₁₉ H ₁₂ ⁰ ₂	-	-	-	-	-	-	-
C _n H _{2n-28} ; benzofluoranthenes	C ₂₀ H ₁₂	-	-	C ₂₃ H ₁₈	-	-	-	-	-
C _n H _{2n-28} ⁰ ; hydroxybenzofluoranthenes	-	C ₂₁ H ₁₄ ⁰	-	-	-	-	-	-	-
C _n H _{2n-30} ⁰ ; hydroxydibenzanthracenes	C ₂₂ H ₁₄ ⁰	-	-	-	-	-	-	-	-



TOTAL ION CURRENT TIC /arbitrary units/ VERSUS TEMPERATURE AND TIME OF HEATING /minutes/ THE SAMPLE IN THE DIRECT INTRODUCTION SYSTEM OF THE MASS SPECTROMETER, AND SCAN NUMBER