

High Mass Compounds (up to 12 000 u) in Coal Tars

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The presence of high mass molecules (up to 12 000 u) in coal-derived material where previously the highest mass components detected did not exceed 1 or 2000 u is demonstrated for the first time by the use of laser desorption mass spectrometry.

Important recent developments and innovations in mass spectrometry have revolutionised the use and applicability of the technique. Molecular ions up to 300 000 u have been produced¹ from peptide molecules. For materials derived from coal by either gentle or severe pyrolysis or liquefaction methods however, mass spectrometric techniques have not hitherto identified molecular masses much greater than 1000–1500 u.² This is despite the fact that comparative measurements of molecular size or shape, such as size exclusion chromatography, have consistently indicated the presence of molecules of mass up to and greater than 10 000 u in such materials.³ Using laser desorption mass spectrometry, we have for the first time shown the presence of molecules of mass up to 12 000 u, the upper mass limit of the instrument used. These findings constitute the first independent confirmation of the presence of such large molecules in coal-derived materials identified by size exclusion chromatography.

If we know more about coal structure, we might be able to make better, cheaper synthetic fuels and chemical feedstocks from this abundant fossil fuel. The samples we have examined include products of high-temperature coking of coal (up to 1250 °C) and coal-liquefaction extracts under conditions where secondary reactions of the extract molecules were minimised. The high-temperature coking process involves

charging a hot (up to 1250 °C) oven with crushed coal at ambient temperature. In the absence of air, the rate of rise of temperature of the coal is rapid at the oven wall and slow at the centre of the oven. After 6 to 10 h, devolatilisation and coke formation are completed. The volatiles are continuously collected from above the oven and quenched by a spray of ammoniacal liquor. The non-aqueous hydrocarbon layer is the coal tar which is distilled to produce liquid products leaving pitch as the residue; the products are not simple distillates since thermal cracking occurs during the distillation.

The coal-liquefaction experiment⁴ takes place in a fixed-bed reactor where solubilized extract molecules are rapidly removed from the reaction zone and quenched, in order to minimise secondary reactions. Hence, they are likely to retain structural features of the original coal. These two types of coal-derived samples can be considered to represent extremes of severity of the preparation of liquids from coal.

These liquids were submitted to LD-MS analysis. Figs. 1–4 show the positive-ion mass spectra showing the mass regions 1000 to 12 000 u and 0 to 5000 u for a coal tar and from 1000 to 12 000 u and 0 to 1800 u for a liquefaction extract. These spectra are from single laser shots so are not of high intensity. Summation of spectra from repeated laser shots is not possible with the current instrument but is the object of further work.

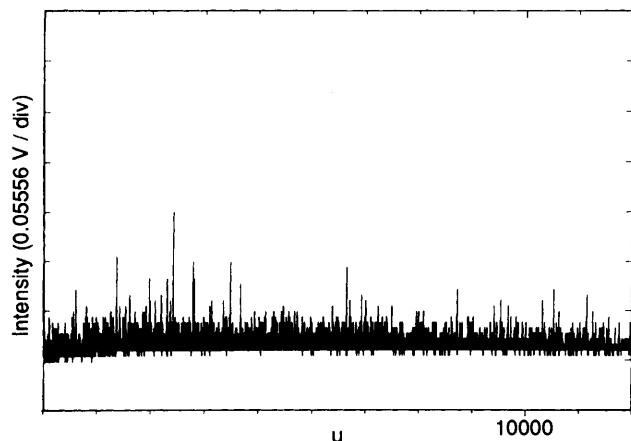


Fig. 1 Mass spectrum from 1000 to 12 000 u for a coal tar, showing ion intensity vs. mass number (m/z) in u

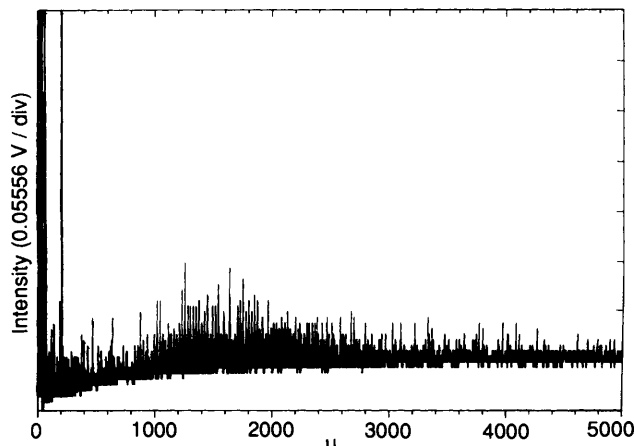


Fig. 3 Mass spectrum from 0 to 5000 u for a coal tar, showing ion intensity vs. mass number (m/z) in u

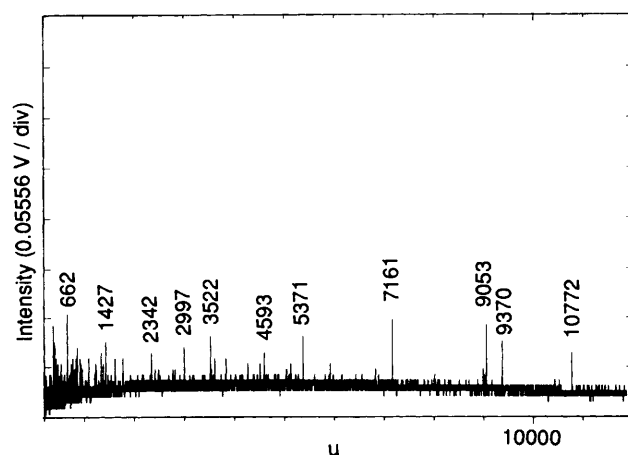


Fig. 2 Mass spectrum from 1000 to 12 000 u for a coal-liquefaction extract, showing ion intensity vs. mass number (m/z) in u

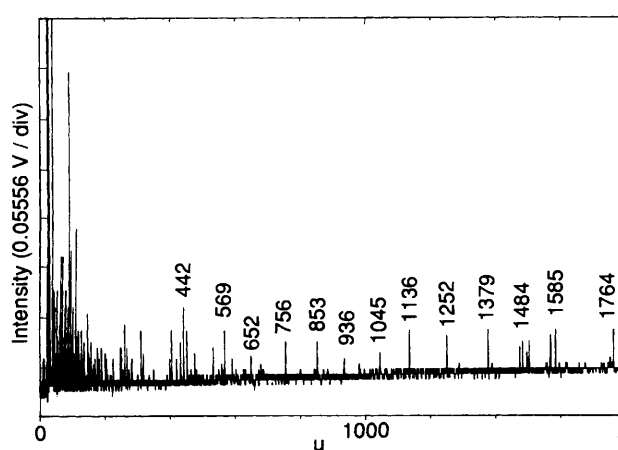


Fig. 4 Mass spectrum from 0 to 1800 u for a coal-liquefaction extract, showing ion intensity vs. mass number (m/z) in u

Mass peaks can be seen over the whole mass range, but an intensity peak is observed between 1000 and 3000 u for the tar. The separations between peaks in the tar spectra are characteristic of aromatic systems with 50 (a benzo group), 24 (an ethylene bridge) and 15 (a methyl group) mass unit gaps. For the liquefaction extract, mass separations between peaks are not so simply interpreted. The mass measurement is nominal only—to the nearest integer—and structures or atomic compositions cannot be derived without more detailed information.

However, with the atomic compositions of the samples involved, some conclusions can be reached on the mass spectrometric evidence. We have shown for the coal tar pitch⁵ that the components of the sample detected by gas chromatography-mass spectrometry and solids probe mass spectrometry correspond to a series of aromatics where the complexity of the molecules increases by the addition of successive benzo rings and ethylene bridges. The molecules correspond to polyaromatic hydrocarbons up to masses of 600 u and contain more than 95% carbon and less than 5% hydrogen with C/H ratios greater than 1.5. If we calculate the atomic compositions and possible structures of molecules with molecular mass greater than 1000 u using the same building blocks (*i.e.* extrapolate the GC-MS and probe-MS work), we find that the carbon content ranges from 95% to greater than 97%. The structures of these extrapolated molecules range

from relatively open aromatic systems to pieces of graphite ringed by hydrogen atoms.

However, the coal-derived liquids examined here have lower carbon contents (less than 90.5% C) and higher hydrogen contents (4 to 6%) than these hypothetical molecules. The implication is that the high mass material detected in either coke oven tar or the liquefaction product is less aromatic than expected from extrapolation of molecular types at low masses. The probable solution to this structural problem lies with the incorporation of heteroatoms, N, S and O into the large molecules as pyrrole, thiophene and furan rings. These structures are found at low masses in coal tar products by GC-MS and contain less than 90% carbon and between 4 and 5.5% hydrogen. This suggests a molecular structure made up of small atomic systems linked by heterocyclic systems rather than a graphite-like structure for the large molecules detected by laser desorption at masses between 1000 and 12 000 u. NMR spectroscopic studies of coal-derived material have indicated similar structures.⁶ We cannot draw firm conclusions regarding the difference between molecules in the high-temperature coal tar and the solvent extract. We expect the liquefaction extract to contain less highly condensed aromatic groupings and possibly fewer different types of molecules than the coal tar because of their different origins. The greater separation of peaks in the spectrum of the liquefaction extract sample, Fig. 2, com-

pared with the numerous peaks in the spectrum of the high-temperature coal tar, Fig. 1, may reflect this difference, however. More work is needed on this point.

Whilst we are not the first to use laser desorption-mass spectrometry to investigate molecular mass components of coal-derived liquids,⁷ we are the first to report such high masses in these materials. We believe the use of low laser power levels and the geometry of the instrument, with both incident radiation and ion collection normal to the target surface, have contributed to our success. High laser power levels lead to destruction of the sample and the large molecules, with formation of carbon clusters. We have observed the formation of carbon clusters in this work at low masses (up to C₂₉⁺); they are formed by the laser energy. Although the clusters are of intrinsic interest, they clearly have no significance as far as the structure of coal is concerned.

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