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ANALYSIS OF KEROGENS BY PYROLYSIS–GAS CHROMATOGRAPHY–MASS SPECTROMETRY USING SELECTIVE ION DETECTION

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SUMMARY

The analysis of coal maceral and sedimentary kerogens by pyrolysis–gas chromatography–mass spectrometry has been undertaken using the mass spectrometer as a selective ion detector. By monitoring one, or more, of the fragment ions with m/e values of 91, 105 and 141 information has been gained regarding differences in the content of alkylbenzene and alkylnaphthalene moieties in these kerogens. This kind of analysis may be useful for "typing" sedimentary kerogens thus providing a rapid assessment of their petroleum-producing potential.

INTRODUCTION

Organic matter is distributed throughout the Earth's crust occurring both in large concentrations as petroleum, coal, natural gas and bitumens, and also in a finely disseminated form in sedimentary rocks. The amount of this disseminated organic matter (90% of which is insoluble in common organic solvents and which is generally known as kerogen), considerably outweighs that accumulated in workable deposits and the living systems from which it is formally derived[1].

Kerogen, thought to be formed by the random polymerisation and condensation of monomers and oligomers of degraded biopolymers[2,3], is a complex heterogeneous substance which is considered to be the source material of petroleum and natural gas[4]. Kerogens have been characterised on the basis of their elemental analyses[5], which in turn define the low molecular weight products that may be produced during their geothermal alteration. Thus, kerogens rich in hydrogen (known as Type 1 kerogens) are thought to be primarily petroleum-producing whereas hydrogen-depleted kerogens (known as Type 3 kerogens), which include materials such as coals, are thought to generate gas with increasing burial[6]. It is important to try to understand the chemical structure of kerogens since from this it may be possible to predict its actual or potential petroleum-generating ability[6–8]. Some structural studies have involved chemical degradation of the polymer to more readily

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analysable fragments but many problems beset this approach; reviews have appeared[9,10] and a further, comprehensive work will appear shortly[11].

The analysis of kerogens separated from their rock matrix, and whole rocks, by pyrolysis coupled with gas chromatography (GC) and/or mass spectrometry (MS) is relatively new. Holden and Robb[12] used MS to analyse, directly, the low temperature pyrolysates of coals and noted the presence of many aromatic compounds. Since this early work the technique of pyrolysis–MS has progressed to the extent that characterisation of sedimentary kerogens is sometimes possible[13,14]. Pyrolysis–GC[15–18] (PGC) has been used in the study of bitumens[19,20], humic substances[21–23], other soil organic matter[24,25], kerogens and sediments[26–34]. The use of combined PGC–MS for the analysis of soil organic matter[25], and kerogens[13,34,35], has enabled the organic geochemist to analyse these complex materials with some success. Pyrolysis–hydrogenation–GC has also been used for the analysis of coals[36] and other kerogens[37]. A recent technique[38] for the characterisation of kerogens, and sediments, by pyrolysis has enabled their reliable "typing". Variation in the pyrolysis products of kerogens from different environments has been discussed[30,31] and methods of kerogen typing using PGC have been developed[34].

The complex nature of kerogen pyrolysates presents problems when analysing them for components that are present in low concentrations. One solution to this problem is to use specific ion detection MS (SID). Gallegos[35] has identified triterpane and sterane derivatives in the pyrolysate of Green River Shale kerogen by monitoring the characteristic fragment ions with values of m/e 191 and 217, respectively. Work in this laboratory, using PGC–MS in the SID mode has enabled steranes, and terpanes to be detected in many kerogen pyrolysates[14,39].

The application of this technique to the study of alkylated aromatic hydrocarbons in kerogen pyrolysates is the subject of this communication. Alkylbenzenes have been detected in many kerogen pyrolysates[14,34] with toluene and the C_8 alkylbenzenes being major constituents of, particularly, pyrolysates of kerogens from continental facies[30,31,34]. Previous results from this laboratory[34] have indicated that a study of alkylbenzenes might provide information regarding both the structure and petroleum generating potential of sedimentary kerogens. Furthermore alkylbenzenes found in kerogen pyrolysates might be related to those found naturally in petroleums. If so, an approach of this kind might, possibly, enable a correlation of petroleum and source-rock kerogen to be made. SID involves the monitoring of specific fragment ions to produce specific ion chromatograms, the mass spectrometer acting as an ion-specific detector. This method has been used to produce sterane and triterpane fingerprints in hydrocarbon-rich fractions extracted from source rocks[40]. Ions at m/e 91 and 105 are abundant in the mass spectra of monosubstituted and disubstituted alkylbenzenes, respectively[41], whereas an ion at m/e 141 is abundant in the spectra of alkylnaphthalenes[42]. Monitoring of these characteristic ions in kerogen pyrograms can thus produce specific ion pyrograms for these aromatic types. It should be noted, however, that a small fragment ion occurs at m/e 141 in the spectra of n-alkanes: the significance of this is discussed below. We believe that the specific ion pyrograms produced by this technique provide some information about kerogen structure and also provide a further novel method for kerogen characterisation.

EXPERIMENTAL

The apparatus consisted of a laboratory-built microfurnace pyrolyser coupled directly to a 20 or 25 m × 0.3 mm I.D. open tubular glass capillary column coated with OV-101 as stationary phase. The capillary column was connected directly to the ionisation chamber of a VG Micromass 12B mass spectrometer via an independently heated 30 cm × 0.20 mm I.D. deactivated glass capillary tube. The flow of helium, used as carrier gas, was maintained by applying a pressure of 0.12 atm at the pyrolyser inlet. (The pyrolyser has been much used in this laboratory and has been shown to give reproducible pyrograms with no evidence of secondary reactions[34].) The mass spectrometer was operated using a scan time of 0.5 sec, an electron impact energy of 70 eV, accelerating voltage of 4 kV and a source emission of 200 μA: integrated ion chromatograms were generally obtained by monitoring ions in the range from m/e 40 to 150.

Microgram quantities of solvent-extracted mineral-free kerogens were pyrolysed at 600° until no further decomposition occurred. Specific ion pyrograms were obtained by monitoring fragment ions with m/e values of 91, 105 and 141 in both SID and multiple ion detection (MID) modes. The latter facility enables the simultaneous production of two different SID traces but prevents the recording of mass spectra. SID scanning does allow mass spectra to be recorded though, as described below, the high sensitivity of the instrument in SID operation means that the spectra can be complex and not easily related to components in the specific ion trace.

By uncoupling the front end of the glass capillary column from the pyrolyser, and reconnecting it to a laboratory-built injector/splitter, the apparatus could be used for conventional GC–MS analyses. When used thus, the helium inlet pressure was 0.17 atm and the split ratio was *ca.* 1:10. Other GC conditions are noted in the figure legends.

RESULTS AND DISCUSSION

A criticism of SID work might be that fragment ions in a specific ion chromatogram do not necessarily represent one chemical type; for this reason care should be taken in the analysis of SID data. Thus the ion at m/e 141 occurs not only in the mass spectra of alkylnaphthalenes but also in those of *n*-alkanes. Despite this possible ambiguity, monitoring of this ion can still provide valuable information, since its intensity is much greater in alkylnaphthalene spectra than in alkane spectra[42]. Fig. 1A shows an integrated ion chromatogram and Fig. 1B a specific ion chromatogram (m/e 141) of a mixture of dodecane, tridecane, tetradecane, 1-methylnaphthalene and 2,6-dimethylnaphthalene. The concentration of each component in the mixture was identical but it can be seen in the SID chromatogram (Fig. 1B) that the detector response is much greater for the aromatic hydrocarbons.

Further confirmation of the applicability and validity of SID analysis for aromatic hydrocarbons in complex pyrolysates is illustrated in Fig. 2. This figure shows an integrated ion chromatogram (Fig. 2A) and also a mass chromatogram (Fig. 2B), obtained by monitoring the fragment ion at m/e 105 (characteristic of alkylbenzenes) in the chromatogram of a concentrated aromatic fraction. This fraction was obtained by pyrolysing a solvent-extracted alginite kerogen (torbanite; 200 mg) from room temperature to 500° at 16°/min in nitrogen and then separating the aromatic fraction
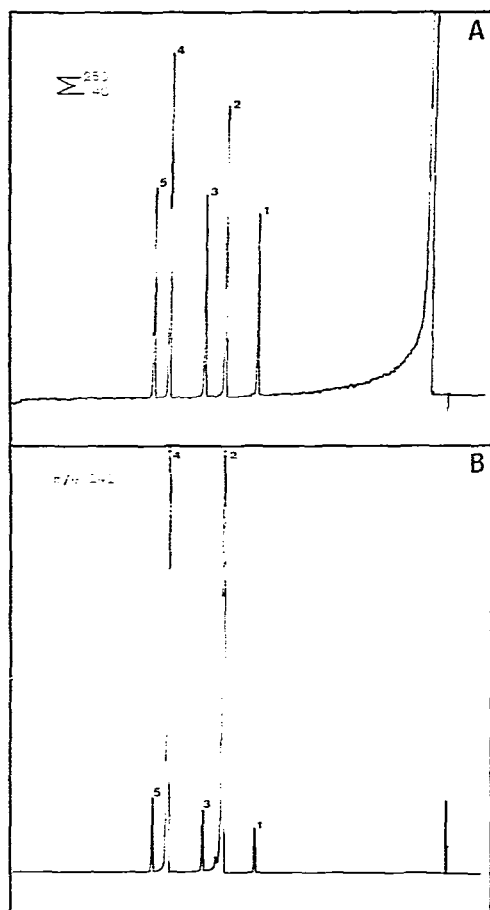
Fig. 1. Chromatographic analysis of a mixture of dodecane (1), methylnaphthalene (2), tridecane (3), 2,6-dimethylnaphthalene (4), tetradecane (5) using a V.G. Micromass 12B mass spectrometer as detector. A, Trace obtained by integrating the ion current produced by scanning from m/e 40–250; B, trace obtained by focussing the spectrometer on the m/e 141 fragment ion. Column conditions: 20 m × 0.3 mm I.D. glass capillary column coated with OV-101 programmed from 50° to 250° at a rate of 4°/min: split ratio, 1:10; helium, 0.17 atm.

from the pyrolysate by thin-layer chromatography. In the integrated ion chromatogram several homologous series of peaks are evident above a background "hump". The specific ion pyrogram (m/e 105; Fig. 2B) reveals a still complex, but much simpler, chromatogram which has been interpreted as evidence of a homologous series of alkylbenzenes containing at least two substituent alkyl groups. This interpretation is made on the basis that the ion at m/e 105 is a characteristic major fragment ion in the mass spectra of polysubstituted n-alkylbenzenes[31].

    Figs. 3–5 show multiple ion pyrograms of three typical coal maceral[*] kerogens.

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    [*] Macerals[43,44] are microscopically identifiable components of coal, considered analogous to the mineral constituents of rocks. Vitrinite is a maceral-group term which identifies the components of bituminous coals derived by anaerobic decomposition of ligno-cellulosic tissue of higher plants whereas sporinite, a member of the exinite maceral-group is derived from spore and pollen exines: alginite, another member of the exinite maceral-group is derived from algae.
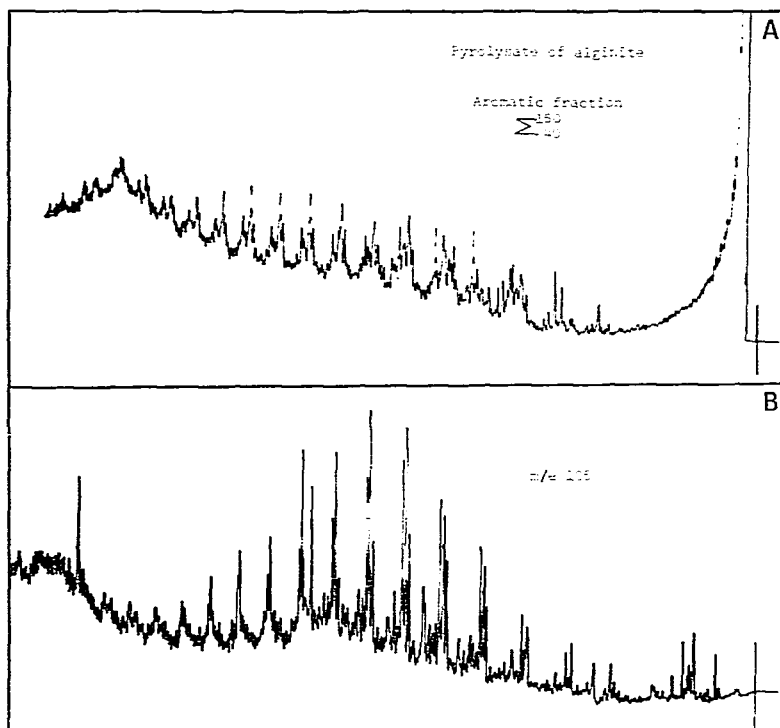
Fig. 2. Gas chromatographic analysis of the aromatic fraction separated from the pyrolysate of an alginite (torbanite, Permo-Carboniferous, Ermelo, S. Africa). GC and MS conditions as for Fig. 1 except that the ion current was integrated from m/e 40 to 150 and the column temperature was programmed at a rate of 2°/min.

The pyrograms were obtained at 600° and the ions monitored (m/e 91 and 141) were chosen as being characteristic of alkylbenzenes and alkylnaphthalenes as noted above. The three macerals studied namely alginite, sporinite and vitrinite are broadly analogous to the three main kerogen types I, II and III, respectively, as defined by Tissot et al.[6]. The atomic ratio of hydrogen to carbon in the three maceral types decreases in the sequence alginite, sporinite, vitrinite while the aromatic nature of the kerogen increases accordingly[45]. By comparing Figs. 3, 4 and 5 clear differences can be seen between the three kerogens when fragment ions at m/e 91 and 141 were monitored. Examination of the m/e 141 ion pyrogram for alginite (Fig. 3B) shows a homologous series of doublet peaks which have been identified by comparison with integrated ion pyrograms of alginite kerogens as a terminal n-alkene/n-alkane homology.

The sporinite pyrogram (m/e 141, Fig. 4B) contains, in addition to a weak aliphatic hydrocarbon homology, two large series of peaks. These have been identified, by comparison with integrated ion pyrograms of this kerogen from which mass spectral information was obtained, as methylnaphthalenes and dimethylnaphthalenes[14].

The vitrinite pyrogram (m/e 141) is dominated also by mono- and dimethylnaphthalenes (Fig. 5B) this result confirming the previously noted presence of abundant alkylnaphthalenes in vitrinite pyrolysates[34]. An increase in the proportions of
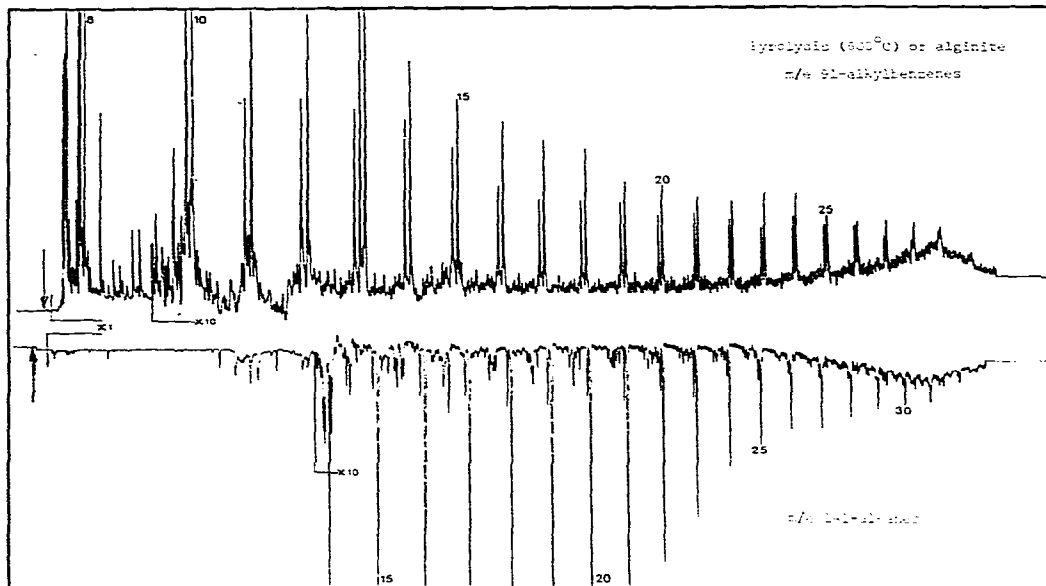
Fig. 3. Pyrolysis of alginite (torbanite, Ermelo, S. Africa) at 600°. The two traces represent pyrograms obtained by monitoring the fragment ions *m/e* 91 (upper) and 141 (lower) only. The virtual absence of methyl- and dimethylnaphthalenes is indicated since no large peaks appear in the C_{12}–C_{14} region (*cf.* following Figs. 4 and 5). Note pen offset, indicated by arrows at beginning of pyrograms. Chromatographic conditions as for Fig. 2 except that the column (25 m) was programmed from 30° to 250° at a rate of 2°/min; helium, 0.08 atm.
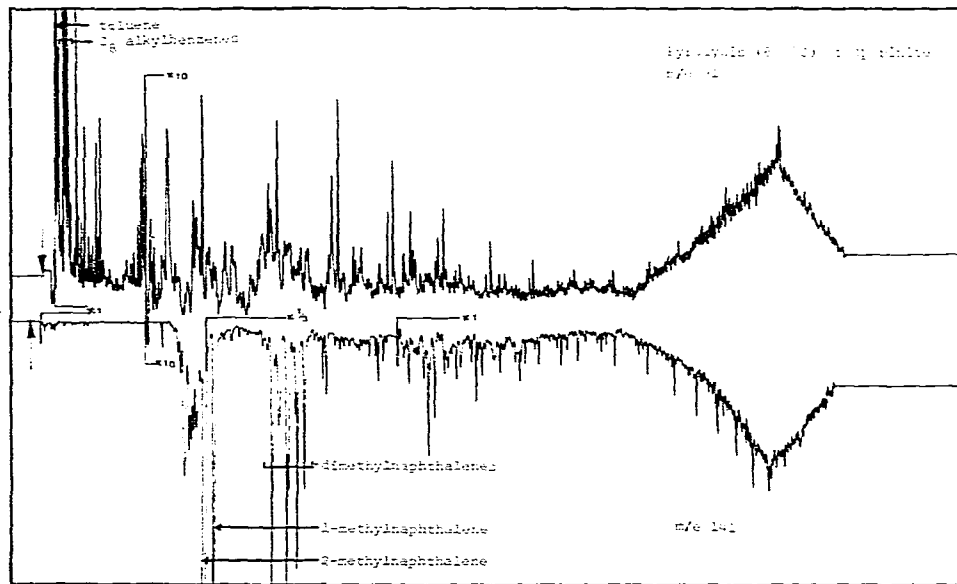

Fig. 4. Pyrolysis of sporinite, Carboniferous (Yorkshire) at 600°. Conditions as for Fig. 3.
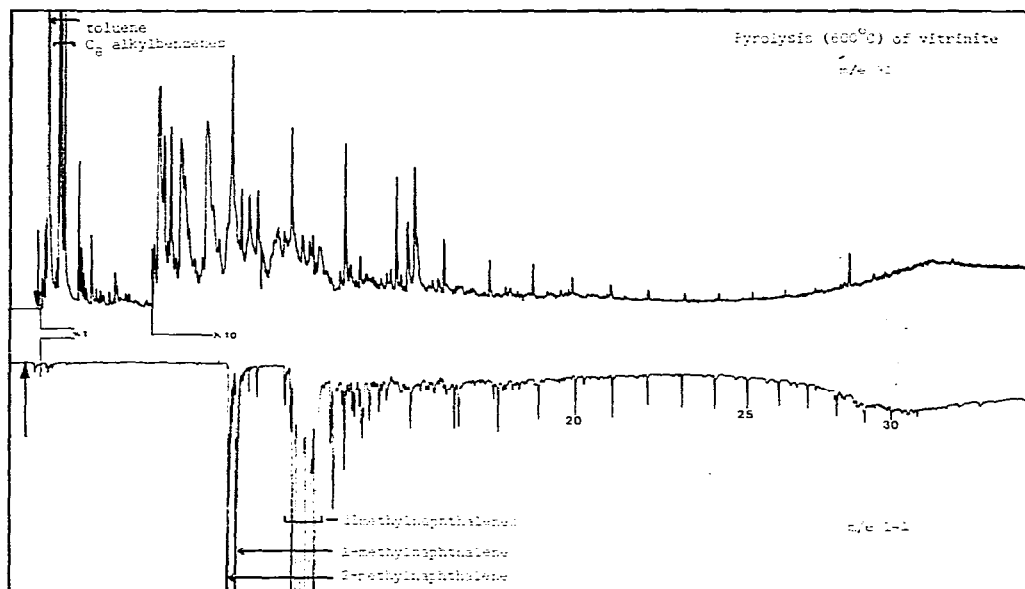
Fig. 5. Pyrolysis of vitrinite, Carboniferous (Yorkshire) (85.5% C dry ash free) at 600°. Conditions as for Fig. 3.

alkylnaphthalenes in the pyrolysates of the alginite, sporinite and vitrinite kerogens respectively is evident, confirming the results of conventional PGC and also agreeing with the increase in the aromatic content of the macerals in the above sequence[45].

Pyrograms of the three macerals in which the fragment ion at m/e 91 was monitored are again quite distinctive. All three pyrograms contain much toluene and the C_8 alkylbenzenes. Both the vitrinite and sporinite pyrograms contain a series of homologous peaks superposed on a background of other components. In contrast, the pyrogram of the alginite kerogen, whilst dominated by toluene and the C_8 alkylbenzenes, contains a homologous series of doublet peaks which decrease steadily in abundance. By inspection, it appears that this homology extends from C_7 to C_{31}. Comparison of the two alginite pyrograms (Fig. 3A, m/e 91 and Fig. 3B, m/e 141) confirms that the n-alkane/n-alkene homologies, represented in the m/e 141 ion pyrogram, have different retention times to the homologies present in the m/e 91 ion pyrogram. (Note pen offset of the two-pen recorder.) Examination of several hydrogen-rich kerogens (Type 1 kerogens) using PGC-specific ion MS confirmed that monitoring the m/e 91 ion revealed a well-defined doublet homology with retention times quite different from the alkene/alkane homologies which dominate normal pyrograms of such kerogens. Unfortunately, the mass spectra which were recorded of peaks in the m/e 91 ion pyrograms were poor, a consequence of the high sensitivity of the instrument when operated in SID mode. All spectra did have, however, a major fragment ion at m/e 91 which was often the base peak, suggesting that mono-subsituted n-alkylbenzenes were being produced during pyrolysis.

Fig. 6 shows the integrated ion pyrogram of Green River Shale kerogen and also the corresponding m/e 91 and 105 ion pyrograms. Green River Shale, deposited in a lacustrine basin (Eocene), represents one of the worlds largest deposits of work-

able oil shale. The kerogen is very rich in hydrogen (hydrogen–carbon atomic ratio 1.56) and is believed to be largely derived from the remains of algae[46]. The integrated ion pyrogram and conventional pyrograms of this kerogen are very similar[13,14], being dominated by a doublet homology of n-alkenes and n-alkanes. Interestingly, a major component with a retention index of ca. 1730 (OV-101) has been identified as a C_{19} isoprenoid alkene, probably prist-1-ene[47]. Both the m/e 91 and 105 ion pyrograms reveal that several homologies are present.
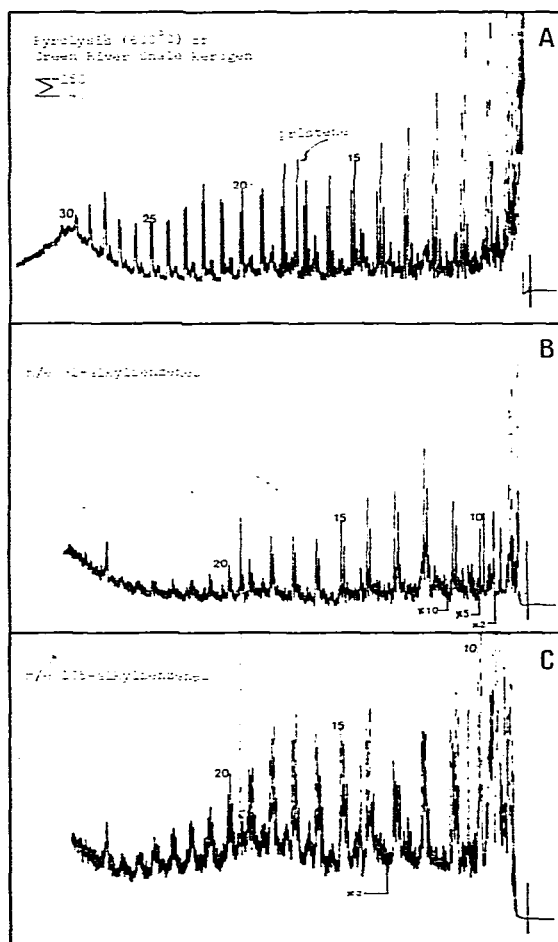

Fig. 6. Pyrolysis of oil-shale kerogen, (Eocene; Green River, Colo., U.S.A.) at 600°. Conditions as for Fig. 1 except that the GC column was programmed from 40° to 250° at a rate of 2°/min; helium, 0.12 atm.

The homologies of n-alkanes and n-alkenes which characterise the hydrocarbon fractions of many kerogen pyrolysates encourage the idea that the doublet homologies observed in the m/e 91 SID pyrogram (Fig. 6B) are n-alkenyl and n-alkylbenzenes: MS evidence (not shown) from other work concurs with this idea. The complex

homologies in the m/e 105 ion pyrogram (Fig. 6C) of this kerogen may represent long alkyl chains terminated with a tolyl group instead of a phenyl group. This more complex and varied distribution promises to be of more value for fingerprinting different kerogens than the simple doublet homologies due to n-alkanes/n-alkenes and n-alkyl/n-alkenylbenzenes. It is virtually impossible to estimate the quantitative contribution made to the integrated ion pyrogram (Fig. 6A) by the components shown in the specific ion pyrograms. Those with large fragment ions at m/e 105 do not appear to be major constituents and this is confirmed by the poor quality of their recorded mass spectra. The mass spectra do, however, contain an abundant ion at m/e 105 as would be expected from tolyl-terminated hydrocarbon chains[41]. Additionally, examination of kerogen pyrolysates by monitoring the fragment ions at m/e 119 and 133 also reveals homologous series of peaks which may be due to more highly substituted alkylbenzenes.

The results of SID analysis of some kerogen pyrolysates therefore suggest that long-chain alkylbenzenes, alkyltoluenes and possibly other polyalkylbenzenes are ubiquitous components of the more hydrogen-rich kerogens. An interesting and important consequence of this study has been to show that kerogens that are generally considered to be lipid-rich, and the least aromatic (*e.g.* alginites or Type 1 kerogens) in fact do contain potential alkylbenzenes that extend over a very wide carbon-number range. In contrast, the sporinite and vitrinite kerogens appear to have proportionately less long-chain alkylbenzenes but more mono- and dimethylnaphthalenes. The appearance of only abundant mono- and dimethylnaphthalenes, and not poly-methylnaphthalenes, in these SID pyrograms confirms similar findings from PGC–MS studies[34] and suggests that naphthalene nuclei are bound in these kerogens by only one, or two, chemical bonds. The implication of this in general kerogen studies will be discussed elsewhere. It has been shown that alkylbenzenes in petroleum do not contain several long substituent chains but rather one long alkyl (often n-alkyl) chain with methyl substituents on the benzene ring[48]. Since kerogen is considered to be the source of petroleum[4] it would appear possible that the alkylbenzenes produced by pyrolysis of the kerogen, under artificial conditions, will be related to those produced from the kerogen under conditions of natural geothermal alteration. Using specific ion detection PGC–MS it is now possible to obtain a fingerprint of the complex aromatic fractions produced when kerogens are pyrolysed and, in a similar manner, it would be possible to obtain alkylbenzene fingerprints from crude petroleums. Using this approach it may be possible to correlate a migrated petroleum directly with a source-rock kerogen or indeed one source-rock kerogen with another. Such would be of use in petroleum exploration studies and work towards this end is now being carried out in this laboratory.

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