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GAS-LIQUID CHROMATOGRAPHIC-MASS SPECTROMETRIC STUDIES ON EXTRACTS AND DISTILLATES FROM POSIDONOMIA SHALES

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SUMMARY

Solvent extraction and distillation of Posidonomia shales from Dotternhausen formation (G.F.R.) delivered various hydrocarbon fractions which were analyzed by means of gas-liquid chromatography in combination with mass spectrometry. Main components found were *n*-alkanes ranging from C₁₀ to C₂₆ (maximum between C₁₅ and C₁₉). Isoprenoid compounds identified were 2,6,10-trimethyltridecane, 2,6,10,14-tetramethylpentadecane, 2,6,10-trimethylpentadecane and 2,6,10,14-tetramethylhexadecane. Numerous cyclic low-molecular-weight hydrocarbons, mainly derivatives of cyclohexane, were present. Several alkylbenzene derivatives as well as alkyl-naphthalene derivatives were identified. In addition, thin-layer chromatography of extracts showed presence of anthracene, phenanthrene and pyrene. Results are discussed as regards to straining of sediments by temperature and pressure.

INTRODUCTION

Investigations were made of the contents and compositions of hydrocarbons in samples of Posidonomia Shales [Lias epsilon (Toarcien)] obtained from the Dotternhausen formation (G.F.R.). The impetus for this work was the observation that Dotternhausen oil shales contain relatively large amounts of low-molecular-weight hydrocarbons, and in this respect they differ from other sediments of the same geological age found at Reutlingen and Metzingen (G.F.R.). In general, the total organic matter content varies between 10% and 17% at the sites mentioned, as determined by combustion analysis¹. The aim of the investigation was to study the composition of different hydrocarbon fractions and to find a possible correlation between the contents and geological history of these sediments.

EXPERIMENTAL

Material was collected from freshly exposed surfaces revealed by explosives (performed at a local cement works for the production of oil shale cement). Samples were crushed to small chips with a hammer and ground to analytical grade by ball milling in water-cooled steel beakers. To obtain the organic material, solvent extraction was used, as this is the preferred method for obtaining low-molecular-

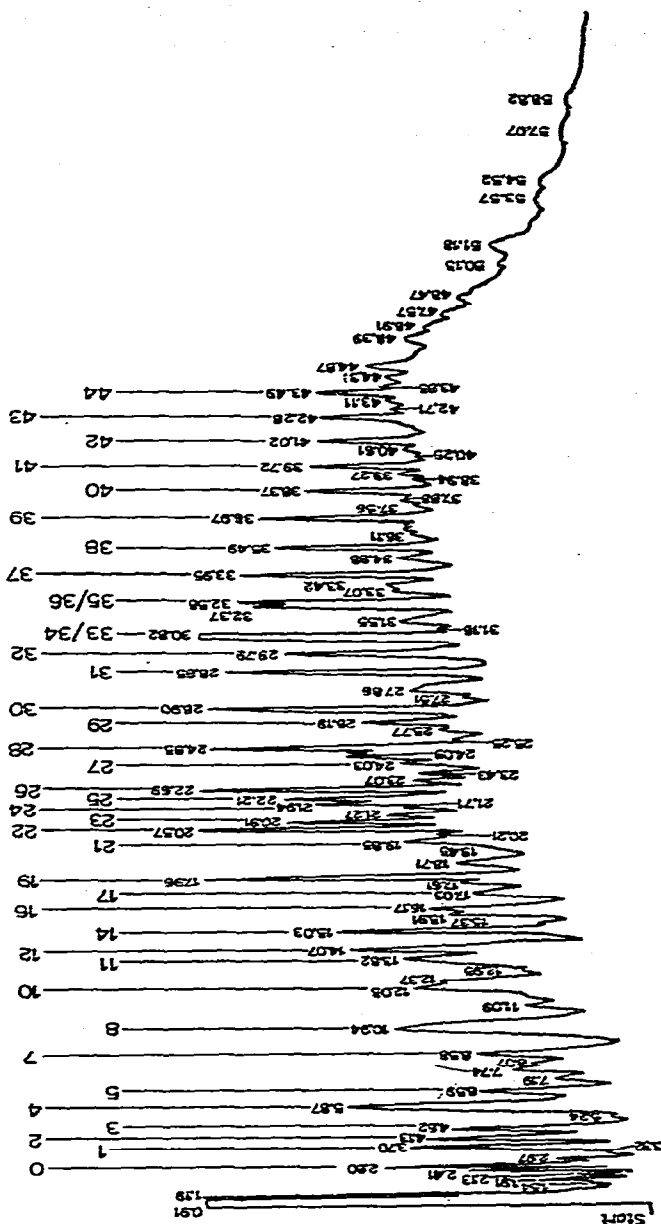


Fig. 1. GLC of Dotterhausen oil shale extract. Extraction with dichloromethane for 72 h. Column: 6 ft. x 2 mm I.D. glass, packed with 3% UCCW. Temperature programme: 4 min at 40°, then up to 250° at 2°/min and held there for 30 min. For identification of peaks, see Table I.

weight compounds. A degreased, pre-extracted Soxhlet apparatus was used, and the extraction time was reduced to 48 and 72 h in order to minimize the thermal strain on the material. Longer extraction times enhance the risk of resin formation in the oil shale extracts. The solvent used was dichloromethane. The extracts were evaporated in a rotary evaporator under normal pressure to a final volume of about 2 ml. The solutions were analysed without further pre-fractionation.

In order to exclude the possibility of contamination, the samples of oil shales were distilled *in vacuo* in a closed all-glass apparatus, which consisted of a 250-ml round-bottomed flask containing about 50 g of material and connected to two wide-mouthed cooling traps. Relatively mild conditions were chosen: the shales were heated for 5 h at 90° (*ca.* 133 Pa) and the vapour was frozen out with liquid nitrogen. Subsequently, the distillate was washed out with 2 ml of dichloromethane and used directly for analysis.

Survey gas-liquid chromatographic (GLC) runs were performed with an HP 5830 A instrument. For GLC-mass spectrometric (MS) analysis an HP 5710 A gas chromatograph coupled to an HP 5980 A mass spectrometer was used.

RESULTS

The extraction technique proved to be superior to distillation. Distillation gave the same qualitative analysis as extraction, but had the disadvantage of poor yields and a high water content of the distillates. Typical gas-liquid chromatograms of oil shale extracts are shown in Figs. 1 and 2. Dichloromethane proved to be the best solvent for the range of compounds studied.

Four groups of hydrocarbon compounds were found in all stratifications of the Dotternhausen oil shales investigated: *n*-alkanes, isoprenoid hydrocarbons, cycloalkanes and aromatic compounds. *n*-Alkanes were identified according to their

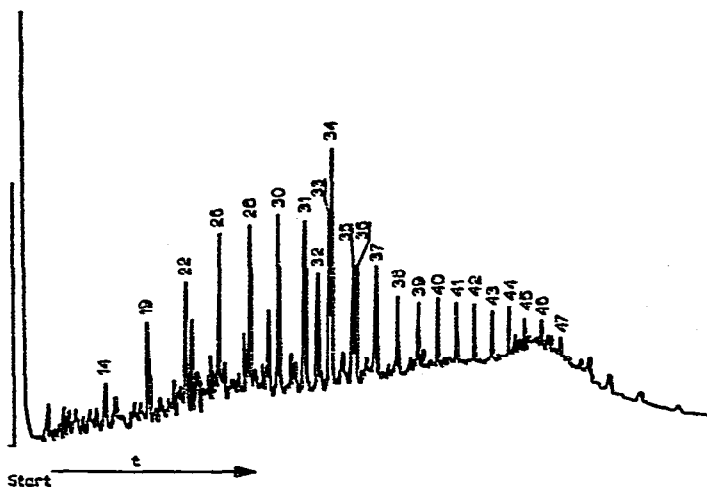


Fig. 2. GLC of Dotternhausen oil shale extract. Extraction with dichloromethane for 48 h. Column: 6 ft. \times 2 mm I.D. steel, packed with OV-1. Temperature programme: 4 min at 70°, then up to 270° at 6°/min and held there for 12 min. For identification of peaks, see Table I.

characteristic fragmentation patterns. Molecular ions of higher *n*-alkanes (e.g., *n*-C₁₉ to *n*-C₂₆), however, could not be identified unambiguously because of the background caused by temperature programming of the GLC column. In case of uncertainties, chemical ionization (methane) helped to establish the position of the molecular ion². Also, if *n*-hexane was used as the solvent for extraction, the background was lower than that with the more polar dichloromethane. The range of *n*-alkanes started at *n*-nonane and extended to *n*-nonacosane (see Table I). Qualitative analysis showed a maximum distribution between *n*-C₁₅ and *n*-C₁₉. No preferential distribution towards odd-carbon-numbered alkanes was found. Isoprenoid compounds gave highly characteristic peaks at the branching points. Four members of this class of compound were identified: 2,6,10-trimethyltridecane (C₁₆H₃₄), 2,6,10-trimethylpentadecane (C₁₈H₃₈), 2,6,10,14-tetramethylpentadecane (pristane) (C₁₉H₄₀) and 2,6,10,14-tetramethylhexadecane (phytane) (C₂₀H₄₂). In this instance too, identification of the molecular ion was much easier if chemical ionization was used. The separations of pristane-*n*-C₁₇ and of phytane-*n*-C₁₈ were incomplete on columns packed with OV-1 or UCCW, but could be enhanced by using SE-30 instead.

Numerous alkylcyclohexanes could be identified by comparison with published spectra. The series started with dimethylcyclohexane immediately after the solvent peak and consisted of trimethylcyclohexane (presumably with 1,1,3-positioning of the side-groups) (Fig. 3, spectrum 1), methylethylcyclohexane, isopropylcyclohexane and methylpropylcyclohexane. Methyleneethylcyclopentane could also be identified.

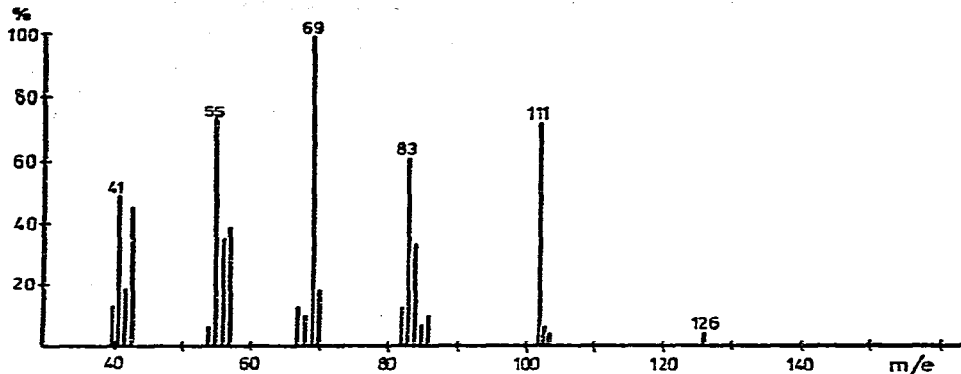
Two alkylbenzene derivatives were found. A low-boiling alkylbenzene was observed between *n*-nonane and *n*-decane in the chromatogram. The structure could not be derived from mass spectral data, except for the formula C₉H₁₂. Positioned between *n*-decane and *n*-undecane, 1-methyl-4-isopropylbenzene was identified by comparison with published spectra (Fig. 3, spectrum 2). Separate solvent extraction of fossilized wood (gagat) found in Dotternhausen oil shales with dichloromethane and GLC-MS analysis showed the presence of further alkylbenzenes. In this material, the presence of large amounts of aromatic compounds as compared with *n*-alkanes was established, including ethylbenzene, propylbenzene, methylethylbenzene and *tert*-butylbenzene.

Higher-molecular-weight aromatic compounds identified in Dotternhausen oil shales extracts were 1-methylnaphthalene, 2-methylnaphthalene, dimethylnaphthalene and partly reduced derivatives, e.g., dimethyltetrahydronaphthalene (Fig. 3, spectrum 3). As we presumed the presence of condensed ring aromatic compounds also, the extraction time for some samples was extended to 7 days, and the dichloromethane extracts were analysed by two-dimensional thin-layer chromatography on alumina using the method of Hellmann³. By comparison with reference substances, anthracene, phenanthrene and pyrene were identified. The thin-layer chromatograms also showed the presence of naphthalene derivatives, giving fluorescent spots which sublimed rapidly after the chromatograms had been dried.

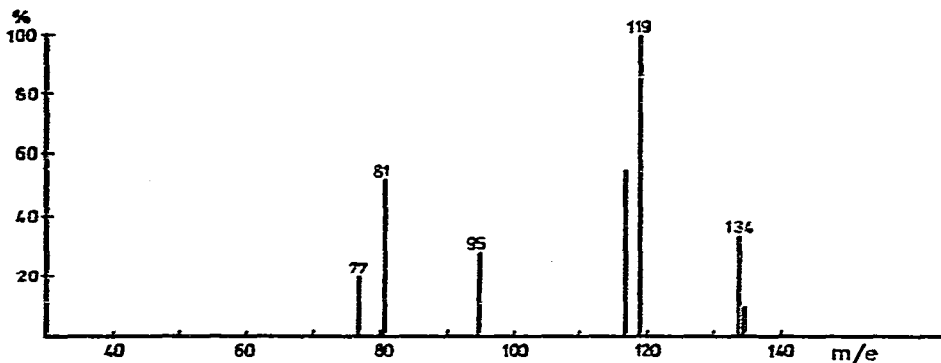
DISCUSSION

The distribution of *n*-alkanes and the qualitative analysis of oil shale extracts clearly confirm that the Dotternhausen sediments are of marine origin. As regards *n*-alkanes in the range C₁₂ to C₂₆, there is no difference in the qualitative analytical

Spectrum 1



Spectrum 2



Spectrum 3

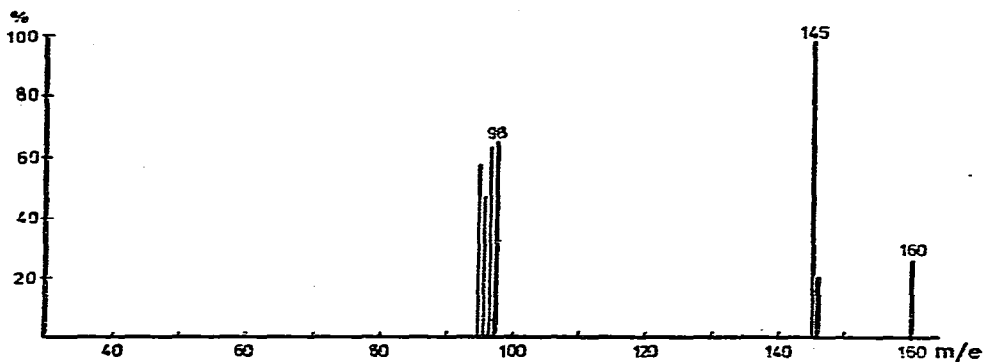


Fig. 3. Selected mass spectra, obtained by GLC-MS. Spectrum 1: trimethylcyclohexane (corresponds to peak No. 4, Fig. 1), M^+ 126. Spectrum 2: 1-methyl-4-isopropylbenzene (corresponds to peak No. 17, Fig. 1), M^+ 134. Spectrum 3: dimethyltetrahydronaphthalene (corresponds to peak No. 23, Fig. 1), M^+ 160. GLC column: 6 ft. glass, packed with 3% UCCW. Temperature: programmed from 50° to 260° at 4°/min and held there for 8 min. Carrier gas (helium) flow-rate: 30 ml/min. Mass spectral data: 70 eV; a.m.u. span 40-300; scan speed 100-340 a.m.u./sec; registered at maximum of GLC peak.

TABLE I
SUBSTANCES IDENTIFIED IN DOTTERNHAUSEN OIL SHALE EXTRACTS

Peak No.*	Substance	Peak No.*	Substance
0	Contaminant = diethylmethylsilane	23	Dimethyltetrahydronaphthalene
1	Dimethylcyclohexane	24	1-Methylnaphthalene
2	Methylethylcyclopentane	25	2-Methylnaphthalene
3	Contaminant in solvent = tetrachloroethene	26	Tridecane
4	Trimethylcyclohexane	27	Dimethylnaphthalene
5	Methylethylcyclohexane	28	Tetradecane
7	1-Methyl-4-ethylcyclohexane	29	2,6,10-Trimethyltridecane (C ₁₆ H ₃₄)
8	Nonane	30	Pentadecane
10	Isopropylcyclohexane	31	Hexadecane
11	Alkylbenzene (C ₉ H ₁₂)	32	2,6,10-Trimethylpentadecane (C ₁₈ H ₃₈)
12	Methylpropylcyclohexane (C ₁₀ H ₂₀)	33	Pristane
14	Decane	34	Heptadecane
17	1-Methyl-4-isopropylbenzene	35	Phytane
19	Undecane	36	Octadecane
21	Contaminant = silane derivative	37	Nonadecane
22	Dodecane	38	Eicosane
		39-47	<i>n</i> -C ₂₁ - <i>n</i> -C ₂₉

* See Figs. 1 and 2.

results compared with the analysis of oil shales from Reutlingen or Metzingen². Extensive diagenetic processes have taken place as no preferential occurrence of odd-carbon-numbered hydrocarbon compounds was found. In contrast, sediments of more recent origin, *e.g.*, Green River Shales (Colorado, age 70 million years), contain larger amounts of odd-carbon-numbered hydrocarbons. Also, the maturation of the sediments is shown by the abundant presence of C₁₆-C₂₀ isoprenoid hydrocarbons, in this respect agreeing with the analysis of Creveney (France) oil shales which are similar in age (180 million years).

The high contents of low-molecular-weight cyclic hydrocarbons also suggest extensive diagenetic processes. As the oil shale deposits at Reutlingen and Metzingen do not contain this fraction in corresponding amounts, although they are of the same age, the presence of large amounts of low-molecular-weight cyclic alkanes found in the Dotternhausen sediments may be indicative of tertiary volcanic activity at the latter location. Small dislocations within shale formations might support this hypothesis. The thermal strain thus being applied to the sediments presumably enhanced the production of cyclic and aromatic compounds from precursors such as squalene and carotene.

Also, the presence of large amounts of low-molecular-weight cycloalkanes might be taken as a direct consequence of currents in the ocean during the period of formation of sediments leading to local concentrations of material from higher terrestrial plants. Terpenes are known to be precursors of cyclic and aromatic compounds. Interestingly, oil shales obtained from the location of Holzmaden also contain larger amounts of low-molecular-weight hydrocarbons than the oil shales at Reutlingen and Metzingen. This agreement with the Dotternhausen oil shales also extends to large amounts of fossil woods found and fossil content in general.

CONCLUSIONS

Investigations were made of the contents and compositions of hydrocarbons in samples belonging to Lias epsilon (Toarcien) obtained from the Dotternhausen formation (G.F.R.). The shales are 150 million years old. The total organic matter determined by combustion analysis varies between 10% and 17%. Extracts were prepared using a degreased pre-extracted Soxhlet apparatus; samples of powdered oil shales were distilled under reduced pressure in a closed all-glass apparatus. The compositions of the extracts and distillates were investigated using gas-liquid chromatography in combination with mass spectrometry.

The main components were *n*-alkanes ranging from C₁₀ to C₂₆, with a maximum between C₁₅ and C₁₉. Isoprenoid hydrocarbons such as 2,6,10-trimethyltridecane, 2,6,10-trimethylpentadecane, 2,6,10,14-tetramethylpentadecane and 2,6,19,14-tetramethylhexadecane were present. Numerous cyclic low-molecular-weight hydrocarbons such as dimethylcyclohexane, methylethylcyclopentane, trimethylcyclohexane and 1-methyl-4-ethylcyclohexane could be identified. Aromatic compounds present included several alkylbenzene derivatives, several alkylnaphthalene derivatives and dimethyltetrahydronaphthalene. Results obtained with the distillates and extracts agreed in qualitative composition. In addition, thin-layer chromatography of the extracts showed the presence of anthracene, phenanthrene and pyrene.

The presence of *n*-alkanes in the range from C₁₀ to C₂₆ without the preferential occurrence of odd-carbon-numbered hydrocarbons clearly established the fact that the oil shale deposits at Dotternhausen are mature sediments where extensive diagenesis of hydrocarbons from long-chain fatty acids and waxes has taken place. In contrast, immature sediments such as Green River Shales (Colorado, age 70 million years) show a higher content of odd- than even-carbon-numbered hydrocarbons. Also, maturation of the sediments is shown by the abundant presence of C₁₆-C₂₀ isoprenoid hydrocarbons, and in this respect is in agreement with the analysis of Creveney (France) oil shales, which are similar in age (180 million years).

Strikingly high contents of low-molecular-weight cyclic hydrocarbons suggest straining of sediments by pressure and temperature, thus causing extensive diagenetic processes. The precursors of cyclic alkanes and aromatic hydrocarbons compounds are terpenes from higher plants and unsaturated compounds such as squalene or carotene.

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