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ENRICHMENT OF POLYCYCLIC TERPENOID, SATURATED HYDROCARBONS FROM PETROLEUM BY ADSORPTION ON ZEOLITE NaX

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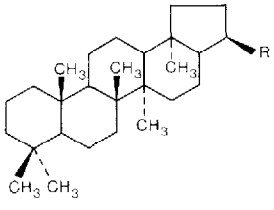
SUMMARY

A method for the isolation of hopane and tricyclic terpane concentrates from petroleum saturates is presented. These important biomarkers are selectively adsorbed onto a large-pore-size molecular sieve (zeolite NaX) from pentane solution. The procedure is optimized for quantitative recovery of the biomarkers and is a simple method suitable for routine analysis. Subsequent gas chromatographic analysis allows the quantitative determination of these biomarkers.

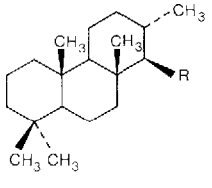
INTRODUCTION

Saturated hydrocarbons from petroleum and other geochemical sources can be fractionated by various, well established clathration procedures[1]. In the course of such an analysis consecutive adductions with 5A molecular sieve[2], urea[3] and thiourea[4] yield fractions of the *n*-alkanes, the *iso*- and *anteiso*-alkanes and the acyclic terpenoid alkanes, respectively. The remaining fraction, consisting of a highly complex mixture of polycyclic alkanes[5–7], usually shows mainly unresolved chromatograms with few significant peaks, even when high-resolution methods are used.

The saturated hydrocarbon fractions of heavily biodegraded crude oils show chromatograms similar to that of the bitumen of the Athabasca oil sand depicted in Fig. 1a. Therefore, this fraction of the Athabasca oil sand was chosen as the test sample for the present enrichment procedure. Among the few distinct peaks which appear on the chromatogram are members of the homologous series of the hopane (I) and the tricyclic cheilanthane type terpenoid hydrocarbon (II) biomarkers. Up to



I



II

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now the enrichment of these biomarkers from samples of geochemical sources has mainly been done by column chromatography on alumina[8–11]. In routine analysis this lengthy step, which is difficult to reproduce, is avoided and the analysis is usually done by costly gas chromatography mass spectrometry (GC–MS) techniques[12–14]. Despite their possible potential for such purposes, zeolites with larger pore sizes, *e.g.* zeolite NaX, CaX or ZSM-types, have rarely been used. To the best of our knowledge only one worker has used a molecular sieve method to concentrate hopanes from appropriate distillation cuts of a Nigerian crude oil[15]. As a clathrate-forming agent the molecular sieve X-10 was used, a zeolite which has since disappeared from the suppliers' catalogues. Thus, it appeared desirable to search for alternative and complementary methods for the fractionation of such samples.

Potential users of clathration methods with large-pore molecular sieves have possibly been deterred by the problems involved when it came to choosing a solvent system[1]. By analogy with the clathration of *n*-alkanes with 5A molecular sieve, it would be desirable to use a solvent with a larger molecular diameter than the pore size of the zeolite. For zeolite NaX this parameter is 9–10 Å (ref. 16), certainly too large for all common solvents. On the other hand, a study by Kiselev and Lopatkin[17] suggested that the heat of adsorption on zeolite NaX of molecules smaller than the pore size decreases with decreasing molecular size. In another study, by Breck and Flanigen[16], it was also demonstrated that the heat of adsorption of large molecules drops to virtually zero, when their cross-sectional diameter exceeds the pore diameter. Molecules of an intermediate size should therefore exhibit the highest adsorption energies. Preliminary experiments confirmed our expectations. Hopanes (I) and tricyclanes (II) were selectively adsorbed onto zeolite NaX from a pentane solution, yielding the zeolite adsorbate fraction (ZA fraction) and leaving behind most of the unresolved complex mixture in the remaining zeolite non-adsorbate fraction (ZNA fraction). (Reference to the separation process as adsorption rather than adduction or clathration is arbitrary since the precise nature of it is not known.)

We report here the optimization of these preliminary experiments. Our main concerns were to find optimal conditions for quantitative recovery of the biomarkers of interest and a simple procedure suitable for routine analysis. The resulting improvements lead to a simple method for concentrating the hopane and tricyclane biomarkers in a manner superior in several aspects to earlier procedures.

EXPERIMENTAL

Samples and materials

The Athabasca oil sand (AOS) used was from the Syncrude mine site near Fort McMurray, Alberta, Canada (government coordinates 1-2-93-11-W4, 18 m below the surface). The analysis of this sample yielded 12 wt-% of bitumen, 2.96 wt-% water and 85% mineral matter. Zeolite NaX (80–100 mesh, batch Nos. 063082 and 100182) was obtained through Chromatographic Specialties, Brockville, Canada, from Coast Engineering Lab., Gardena, CA, U.S.A., under the trade description Molecular Sieve X-13. Prior to use it was heated for 12 h at 250°C and for 36 h at 400°C and stored in sealed ampoules in portions of 3.5 and 7 g. The molecular sieve can be reused after reactivation without loss of activity.

Methods

For the adsorption experiments a purified, saturated hydrocarbon fraction from AOS bitumen was isolated as described earlier[9-11] and subjected to a final purification step by treating it with bromine in carbon tetrachloride in order to remove any unsaturates present. The saturates were recovered by thin-layer chromatography on silica gel using *n*-pentane as eluent.

A purified sample of *ca.* 50 or 100 mg was dissolved in 50 ml of *n*-pentane and 5.0 g of zeolite, *i.e.* half of the zeolite necessary for the desired zeolite: sample ratio, was added. The mixture was refluxed for 3 h, filtered and quickly washed four times with 150 ml of cold *n*-pentane (5°C). The filtrate was reduced *in vacuo* and dissolved in 50 ml of *n*-pentane. The rest of the zeolite (5.0 g) was added and the mixture again refluxed for 3 h. Filtration and washing as above yielded the ZNA fraction. The two fractions of zeolite were Soxhlet-extracted with isooctane for 36 h. The extract, reduced *in vacuo* and filtered through silica with Skelly B, yielded the ZA fraction. In some instances, the zeolite was subsequently dissolved in hydrofluoric acid and extracted with Skelly B. The individual fractions were weighed, the recovery calculated and the samples were subjected to gas chromatographic (GC) analysis.

Qualitative GC analysis of the samples was performed on a Hewlett-Packard (Model 5830A) apparatus equipped with a capillary inlet system, a flame ionization detector and an integrating GC terminal (Model 18850A). A pyrex glass capillary column (20 m × 0.25 mm I.D.), deactivated by silylation[18] and statically coated with SE-30, was used with a hydrogen carrier gas flow-rate of 50 cm/sec. Film thickness (0.075 μm) and separation efficiency ("Trennzahl", TZ = 45) were determined by the Grob test[19]. The samples (0.7 μl of a 5% solution in isooctane) were injected at an injector temperature of 300°C with a preset split ratio of 1:20 with the column at 30°C. The column was kept at this temperature for 1.5 min, then heated to 60°C at a rate of 30°C/min, then at 2.5°C/min to 290°C. Compounds were identified by comparison with authentic samples[9-11,20] from the same source.

For quantitative GC analysis, known quantities of three internal standards (androstane, *n*-C_{28} and *n*-C_{36}) were added in isooctane solutions. The splitless injection technique was used (1.5 μl sample as 0.1% solution in isooctane) with a splitless period of 1.5 min[21]. To improve sample transfer onto the column the carrier gas flow-rate was increased to 70 cm/sec and the temperature program rate to 3.5°C/min. The use of three internal standards of different retention times allowed us to check each injection for minimum discrimination. Concentrations were calculated from the peak areas assuming a response factors equal to 1 for the flame ionization detector, but compensating for the remaining discrimination by establishing curves for sample transmission *versus* retention time from peak areas and amounts of the internal standards added.

RESULTS AND DISCUSSION

Typical chromatograms for the ZA fractions are shown in Fig. 1b and c, respectively, illustrating the pronounced enrichment of biomarkers I and II in the ZA fraction.

Our efforts in optimizing our preliminary experiments were directed toward a simple procedure suitable for quantitative analysis. Our emphasis was therefore put

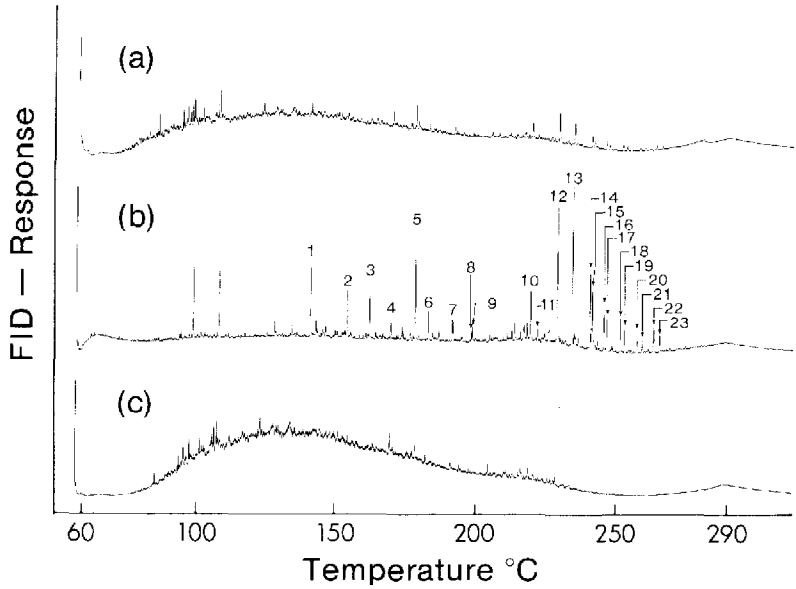


Fig. 1. Chromatograms of saturated fractions from Athabasca oil sand: (a) total saturates; (b) ZA fraction (zeolite: sample ratio = 100:1); (c) ZNA fraction (zeolite: sample ratio = 100:1). For GC conditions see Experimental and for peak assignment see Table I.

on quantitative recovery of the biomarkers in both the adsorption and desorption step, while keeping the number of manipulations as low as possible.

Complete desorption is achieved by exhaustive extraction with isooctane as verified by dissolution of the extracted zeolite in hydrofluoric acid. Total sample recoveries by weight are better than 95%. Short extraction times and the use of lower boiling Skelly B lead to incomplete and discriminative desorption, causing incomplete recovery of the C_{29}, C_{30} and the 22*R*-C_{31-35} hopanes (peaks 12, 113, 15, 17, 19, 21, 23).

Complete adsorption is mainly dependent on the zeolite:sample ratio. The influence of this parameter was therefore studied more thoroughly. As the ratio increased, an increasing portion of the sample was recovered in the ZA fraction (Fig. 2, broken curve). The curve is steep at low zeolite:sample ratios and gradually becomes shallower as the ratios increases, but never becomes horizontal. Similar curves for the recovery of individual biomarkers follow a similar trend, but their slopes approach zero at zeolite:sample ratios between 140:1 and 280:1 (Fig. 2, solid curves for selected tricyclanes).

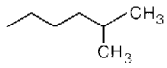
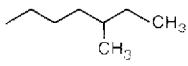
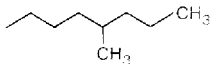
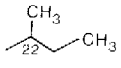
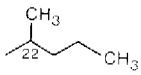
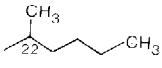
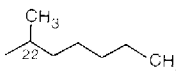
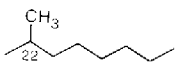
The discrepancy in curve shape between the curve for the total ZA fraction *versus* zeolite:sample ratio and the curves for individual biomarker recovery *versus* zeolite:sample ratio is caused by the adsorption of an increasing portion of unresolved, complex mixture (the "hump" in the chromatogram) with increasing zeolite:sample ratio.

The flattening of the curves for the individual biomarkers indicates complete recovery of the individual biomarkers from the sample. The differences in curve shape within the individual biomarkers recoveries are probably due to differences in adsorption energies of the corresponding compounds.

TABLE I

BIOMARKER CONCENTRATION IN ATHABASCA OIL SAND DETERMINED BY QUANTITATIVE ANALYSIS OF THE ZA FRACTION BY GC

Zeolite:sample ratio = 280:1. For GC conditions see Experimental.

Peak No.	*Structure*			*Molecular formula*	*Concentration in*		*Systematic error (%)**
	No.	*R*	*Configuration*		*Saturated fraction (ppm)*	*Oil sand (ppm)*	
1	II	CH_3		$C_{19}H_{34}$	298	7.6	10
2	II	C_2H_5		$C_{20}H_{36}$	236	6.0	2
3	II	n-C_3H_7		$C_{21}H_{38}$	255	6.5	<1
4	II	n-C_4H_9		$C_{22}H_{40}$	166	4.2	<2
5	II	n-C_5H_{11}		$C_{23}H_{42}$	744	19.0	12
6	II			$C_{24}H_{44}$	208	5.3	27
7	II		**	$C_{25}H_{46}$	190	4.8	n.d.
8	II		***	$C_{26}H_{48}$	46	1.2	n.d.
9	II		§		64	1.6	n.d.
10	I	H		$C_{27}H_{46}$	791	20.1	5
11	I	CH_3		$C_{28}H_{48}$	187	4.8	n.d.
12	I	C_2H_5		$C_{29}H_{50}$	1667	42.4	1
13	I	i-C_3H_7		$C_{30}H_{52}$	1967	50.1	*ca.* 0
14	I		22*S*§§	$C_{31}H_{54}$	1209	30.8	*ca.* 0
15	I		22*R*		837	21.3	<1
16	I		22*S*	$C_{32}H_{56}$	673	17.1	<1
17	I		22*R*		532	13.5	<1
18	I		22*S*	$C_{33}H_{58}$	542	13.8	<1
19	I		22*R*		368	9.4	<1
20	I		22*S*	$C_{34}H_{60}$	357	9.1	<1
21	I		22*R*		230	5.9	<2
22	I		22*S*	$C_{35}H_{62}$	483	12.3	<1
23	I		22*R*		339	8.6	<2

* n.d. = Not determined.
** Two isomers eluting together.
*** Earlier eluting isomer.
§ Later eluting isomer.
§§ Ref. 22.

For high zeolite:sample ratios the necessary amount of zeolite cannot be suspended properly in the 50-fold sample volume of solvent. Therefore the adsorption was carried out in a two-step procedure, adsorbing the sample consecutively onto two portions of zeolite. This sequence was maintained in all cases for reasons of uniformity and for averaging the effects of the solvent-washing of the zeolite after the removal of the ZNA fraction.

In some instances high zeolite:sample ratios lead to lower concentration values for some of the biomarkers. We attribute this to the increased presence of "hump", which causes a lower signal-to-noise ratio and therefore lowers the precision of the GC analysis. With such samples we also encountered difficulties in obtaining a sufficient sample transfer at the high-boiling end of the chromatogram during splitless injections. Use of the cold on-column injection technique could improve on this.

For the sample used, a zeolite:sample ratio of 280:1 seems to be a good compromise between completeness of biomarker recovery and avoiding too much "hump" in the chromatogram. The resulting biomarker concentrations are reported in Table I.

To account for the systematic errors the ZNA fraction was adsorbed a second time onto zeolite NaX. Quantitation of the residual biomarker concentrations revealed that with the given sample and a zeolite:sample ratio of 280:1 the systematic errors due to incomplete adsorption are negligibly small for the hopanes (I) and the tricyclanes (II) up to C_{23} (Table I, last column).

Tetracyclic steroidal alkanes are also present in the saturate fraction of the Athabasca bitumen[23] (the small unassigned peaks in Fig. 1b) but their separation was not explored in the present study.

CONCLUSIONS

The adsorption of hopanes and tricyclanes onto zeolite NaX provides a useful method for the enrichment of these biomarkers. Subsequent GC analysis allows their quantitative determination with negligible systematic errors in most cases.

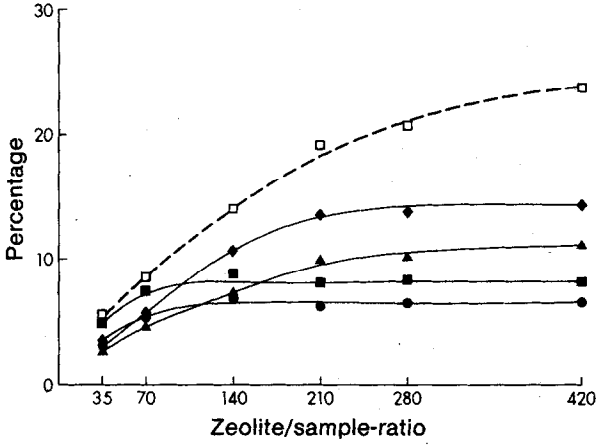


Fig. 2. Broken line: percentage (mg/mg) absorbed *versus* zeolite:sample ratio from saturates of Athabasca oil sand. Solid lines: recovery of selected tricyclanes (I) *versus* zeolite:sample ratio (▲ = C_{19}; ● = C_{20}; ■ = C_{21}; ◆ = C_{23}; arbitrary scale on abscissa).

This method offers practical advantages over previous ones in several aspects. It uses commercially available zeolite NaX, yields a concentrate of the important biomarkers in one fraction, avoids the use of toxic hydrofluoric acid for releasing these compounds, allows recycling of spent molecular sieve and obviates difficult chromatography steps. It may also obviate the need for costlier GC–MS analysis in screening for these biomarkers.

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