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SHAPE-SELECTIVE SORPTION OF MONOMETHYLALKANES BY SILICALITE, A ZEOLITIC FORM OF SILICA

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SUMMARY

The complete isolation of monomethylalkanes from complex hydrocarbon mixtures is demonstrated. The technique is based on the molecular sieve properties of silicalite, a recently synthesized zeolite. Silicalite provides a direct isolation, *ca.* 40% pure, of the monomethylalkanes, which are sorbed by silicalite but, unlike the *n*-alkanes, are excluded from Linde 5A molecular sieve. The use of these two sieves thus provides a shape-selective window, approximately 1 Å wide. The final purification to *ca.* 98% or more is obtained using bidimensional preparative gas chromatography (GC). Based on the findings, a new and more rapid method for *n*-alkane determination is now possible. The high selectivity, reversibility and high thermal stability of silicalite are major advantages. Column chromatography with silicalite separates the 2-, 3- and 4-methylalkane isomers with sample loads 100,000-fold higher than capillary GC.

INTRODUCTION

The isolation of monomethylalkanes from complex hydrocarbon mixtures, a problem of longstanding difficulty, is described in this paper. These biogenic compounds persist in ancient petroleums, bitumens and sedimentary rocks because they are not easily altered and escape the carbon cycle[1]. The 3-methylalkanes may be formed by direct biosynthesis or derived from asymmetric, precursor fatty acids and alcohols of algae and bacteria[2,3]. Because of the problems of isolation and identification, the questions of asymmetry persistence over geological lengths of time, and the effects of geothermal stress on methyl migration, have not been explored. Such studies are now possible due to the shape-selective properties of silicalite, a recently synthesized zeolitic form of silica.

Very large numbers of compounds with varied configurations comprise the saturated hydrocarbon fraction obtained from biological or geological samples. To

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illustrate, one gram of petroleum might contain 300–600 mg of saturated hydrocarbons with a relatively high proportion of *n*-alkanes, and 0.2 mg of the monomethyl-branched group[4]. A key aspect is that the normal and monomethyl-branched alkanes possess the narrowest cross-sectional dimension among the set of rodlike paraffin structures. This suggests the use of shape-selective sorptive effects for their separation. Previous attempts have been made to do this using molecular-shape-selective urea adduction[5]. This concentrates the monomethylalkanes, but they generally remain as a small proportion of the urea clathration mixture. The present study was begun on finding that the pore size of silicalite allows permeation by normal and monomethylalkanes and by relatively few other compounds. Multiply methylated alkanes such as the isoprenoid, pristane, are totally excluded.

Silicalite is a zeolitic form of silicon dioxide with discrete pores in its crystal structure. Its intersecting bent-orthogonal channels are precisely formed with two similar cross-sectional geometries: circular, 6 Å in diameter, and elliptical, 5.1–5.7 Å on the major axes[6].

Silicalite offers the next currently available zeolitic pore size up from Linde 5A molecular sieve. The latter zeolite sorbs rodlike hydrocarbon molecules no larger in kinetic diameter, based on molecular cross section, than the *n*-alkanes. Silicalite sorbs both *n*-alkanes and the monomethyl-branched isomers as well as a limited number of single-ring compounds[7].

It is well known that zeolites, having fixed pore size, exhibit extremely sharp molecular size-selectivity. Without exception, rodlike molecules whose kinetic diameter exceeds the available pore size are totally excluded. Molecules only a fraction of an Ångström smaller in kinetic diameter are able to permeate[8]. It is of interest that molecules whose kinetic diameter closely approaches the available pore size will also be absorbed. However, as observed by nuclear magnetic resonance spectrometry with ZSM-5, these "just fit" molecules display striking diffusional stagnation[9]. Since ZSM-5 and silicate both have the same crystalline pore structure[10], silicalite should be permeated by molecules up to the size of *m*-xylene, including the *n*-alkanes. Silicalite inclusion, combined with exclusion by molecular sieve 5A, provides a narrow window for the isolation of rodlike molecules ranging between 5 and 6 Å of kinetic diameter, a class that now excludes the *n*-alkanes. The exact breadth of this window may be narrowed by time or temperature optimizzation for molecular diffusion effects in the pores.

Key operational aspects of silicalite are as follows. Silicalite does not have an appreciable number of silanol groups; it is strongly lipophilic, and it is also hydrophobic. Most zeolites have hydrophilic ionogenic sites, so the use of their lipophilic effects must be guarded by anhydrous conditions in order to avoid water sorption and consequent pore plugging. This effect, along with notoriously slow diffusion effects, have made conventional zeolites of limited interest for analytical separations[11] except as drying agents[12] and for small-molecule gas chromatography (GC)[13]. Silicalite is essentially oblivious to water, as suggested by a reported patent on the use of water as a carrier from which small molecules can be reversibly sorbed in the liquid chromatographic (LC) mode[14].

EXPERIMENTAL

Silica gel column chromatography

Silica gel was stored in an oven at 200°C until needed. Sample loads of 1% or less were used for column elution in hexane. This procedure provides the weakly sorbed saturated hydrocarbon fraction from mixtures.

Linde molecular sieve 5A

This molecular sieve was vacuum dried overnight at 300°C at pressures less than 0.01 atm (1 atm = 101 kPa), stored in a dessicator. *n*-Alkane sorption into the 5A sieve from boiling toluene was carried out overnight with sample loads less than 10% of the pore volume. For analytical purposes the *n*-alkanes were isolated by dissolution of the sieve in concentrated hydrofluoric acid, followed by solvent extraction and vacuum evaporation of the solvent (see Fig. 5).

Silicalite in batchwise sorption

Silicalite was obtained from Union Carbide Corporation (Danbury, CT, U.S.A.). Silicalite, as received, was calcined at 500°C in air to yield an organic-free material. Sorption of permeable hydrocarbons was readily obtained from toluene or cyclohexane solvents. Contact times of 2 h were used because silicalite sorbs at rates at least ten-fold faster than the 5A sieve. Even shorter times are possible, since preliminary experiments[15] at low sample loads showed that sorption may be complete within several minutes.

Desorption from silicalite was carried out in several ways: (1) batchwise desorption with a hot displacing *n*-alkane, such as *n*-octane (see Fig. 1); (2) column elution with a displacing *n*-alkane solvent (see Fig. 3), and (3) complete dissolution of the silicalite in concentrated hydrofluoric acid.

Dry-column chromatography with silicalite

Experiments were carried out with silicalite, dry-packed in a 30 × 0.8 cm I.D. stainless-steel column. Samples were injected in 1 ml of toluene. After a sorption period of 1 h, column elution was begun with step-wise feed switching from *n*-hexane to *n*-heptane to *n*-octane. The flow-rate was 2 ml/min at room temperature. Twenty fractions of 10 ml each were collected to a total of 60 fractions and 600 ml of eluate volume. The fractions were vacuum-evaporated. Sample residues were analyzed by GC (see Figs. 3 and 4) and GC–mass spectrometry (MS). The residual hydrocarbon composition was unchanged after batch-wise desorption by *n*-octane displacement at 100°C. This result indicates the reversibility of sorption in both the batch and column chromatographic modes.

The use of silicalite with liquid carrier for dry-column chromatography was successful even though the largest particle size was 2 μm. The porous stainless-steel column end-fittings did not pass nor get plugged by the fine particles. This suggests that the particles, though originally a free-flowing (respiratory irritant) powder, were highly aggregated. In a few experiments, suddenly diminished column permeability was observed if a critical flow-velocity were exceeded. This suggests the possibility of column compaction at excessive flow-rates.

Glass capillary gas chromatography. A Perkin-Elmer Model 900 GC, fitted with

a 60 m × 0.25 mm I.D. fused-silica open tubular column, coated with a 0.25-μm film of DB-5 bonded phase (J & W. Scientific, Rancho Carboda, CA, U.S.A.) was used. The same column was used in a Finnegan 4500 GC–MS and an Incos 2300 data system. A 20-μg sample mixture was injected by the Scientific Glass (Palo Alto, CA, U.S.A.) solids injector, after a 20:1 direct split. Temperature was programmed from 100–300°C at 2.5°C/min while 2.0 atm column head pressure was maintained. The column effluent was fed directly into the ion source without an intervening helium separator.

Electron-impact mass spectra readily distinguish the isomers of monomethyl substituted alkanes. Given that P is the mass of the parent ion, then the 2-methyl, 4-methyl and 5-methyl isomers have P–43, P–57 and P–71, respectively, as major fragment ions. The 3-methyl isomer is exceptional in that it yields a major fragment ion at P–29.

Preparative GC. A 3 m × 4.8 mm I.D. column of 3% Dexsil 300 coated on Chromosorb W support was used. Milligram sizes of sample were dissolved in hexane solvent and injected. Individual monomethyl alkane fractions were collected manually. High-resolution GC–MS showed that these fractions contained cyclic or naphthene contaminants, specifically alkylcyclopentanes.

The individual fractions were then re-chromatographed using a similar column geometry with 5% free fatty acid phase (FFAP) on Chromosorb W. The slightly more polar naphthenes were more strongly retained and, therefore, easily separated. The entire set of re-chromatographed fractions, consisting of highly purified individual monomethylalkane homologues, were then reconfirmed by GC (see Fig. 2) and by GC–MS.

RESULTS

The conventional procedure for isolation of hydrocarbon fractions has been reviewed by Eglinton[16]. The chromatography of oil or shale extract with silica gel gives the non-retained saturated hydrocarbon fraction. Further treatment with the 5A molecular sieve removes the *n*-alkanes which can then be recovered for analytical purposes. The branched-cyclic fraction is excluded in this step.

Treatment of the branched-cyclic fraction with silicalite was found to give highly concentrated branched-paraffin hydrocarbons that were sorbed by the silicalite. The monomethylalkanes at this point were approximately 40% of the isolated branched-paraffin mixture. Distinctly similar isolations were obtained by using silicalite sorption of the branched-cyclic fraction, or by evaporating the collected hexane, heptane and octane dry-column eluates. An illustrative chromatogram of the silicalite permeable branched-paraffin group is shown in Fig. 1.

A striking feature of the chromatogram in Fig. 1 is the reversal from the high prominence of *n*-alkanes in the typical crude petroleum-bearing samples (see ref. 1). In the branched-paraffin fraction the monomethyl isomers of the *n*-alkanes are the predominant feature. Approximately half-way between the labeled positions of the 2-methyl isomers are impurities that correspond to the elution positions of the *n*-alkanes.

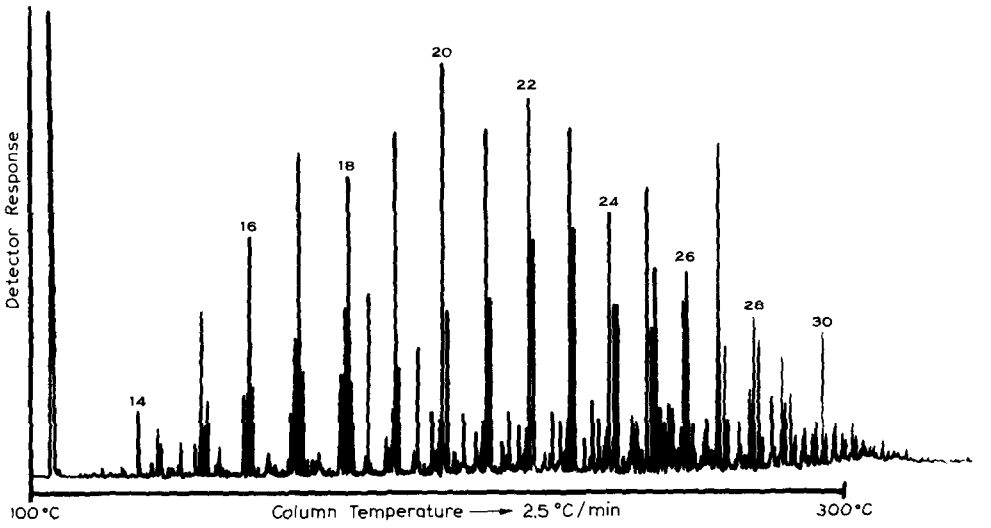

Fig. 1 Capillary GC of the total monomethyl-branched hydrocarbon fraction obtained from a Miocene-aged petroleum from the Los Angeles basin. The sample corresponds to No. 26 described by Phillipi[17]. Saturated hydrocarbons, isolated by silica gel chromatography, were first treated with molecular sieve 5A to remove the *n*-alkanes. The excluded portion was then treated with silicalite in boiling toluene to adsorb the branched (methyl, dimethyl and naphthene) paraffins. These compounds, shown resolved in the chromatogram, were desorbed by hot *n*-octane. The number at each cluster indicates the total carbon number including the methyl branch of the compounds in the group.

Purified monomethyl-branched paraffins

The use of GC–MS showed that the branched-paraffin fraction contains two types of impurities. The minor impurities that are eluted near the virtual *n*-alkane positions include dimethylalkanes. These were removed by a boiling point separation on a non-polar preparative GC column. Within the monomethyl alkane clusters were the naphthenic interferences. These cyclic compounds were easily separated due to their higher retention in the preparative GC step with the polar FFAP phase.

The result of the two-step sequential preparative GC isolation yielded individual groups of monomethylalkanes. The within-group variation was at the methyl position. When these fractions were combined in their entirely, the entire suite of purified monomethyl alkanes was obtained. The result was the chromatogram shown in Fig. 2. This shows that the present five-stage procedure, a liquid–solid sorptive sequence of silica, 5A molecular sieve and silicalite, followed by the dual preparative GC separation, provides an effective isolation of the sought-for monomethyl alkanes.

Preparative liquid chromatography

A sample of the branched-paraffin fraction was chromatographed by the dry-column chromatographic procedure and a series of fractions were collected. Each successive fraction contained only a few dominant compounds, such as shown in Fig. 3. By studying the pattern of elution it became clear that very strong selectivity effects were operating.

The elution order is that retention increases markedly with hydrocarbon chain

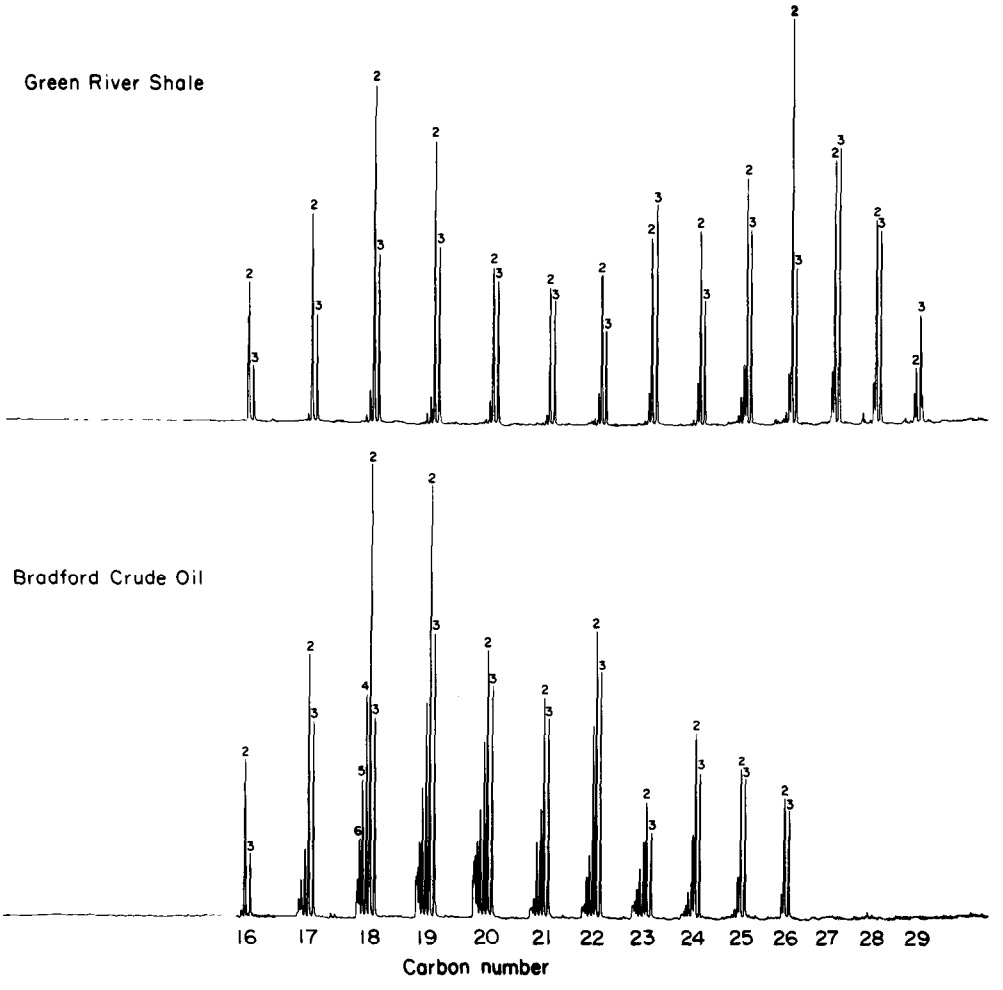

Fig. 2. Capillary GC analysis of the estimated ⩾ 98% pure monomethyl, acyclic alkanes, isolated from an extract of the Green River Oil shale and from crude oil from the Bradford, Pennsylvania field. The samples had initially been treated by the procedure described in Fig. 1. They were subsequently purified by two-stage preparative GC on polar and non-polar substrates. The position of methyl substitution is indicated by the numbers at the tops of the peaks. The carbon number indicates the total number of carbon atoms in the molecules forming the chromatographic peaks including the methyl substituent.

length for a particular type of alkane isomer. This is a major effect. The choice of lower *n*-alkane eluents of serially increasing size and displacement strength for the dry-column elution chromatography was based on this.

It was evident from the GC–MS on a number of the fractions that dry-column chromatography provided strong selectivity according to the methyl group location in the chain. The peaks are relatively broad, and collected fractions, *ca.* 30 ml in volume, were needed to encompass any particular alkane or isomer. Attempts were not made to reduce the bandspread which we assume to be the result of diffusion in the silicalite pore structure.

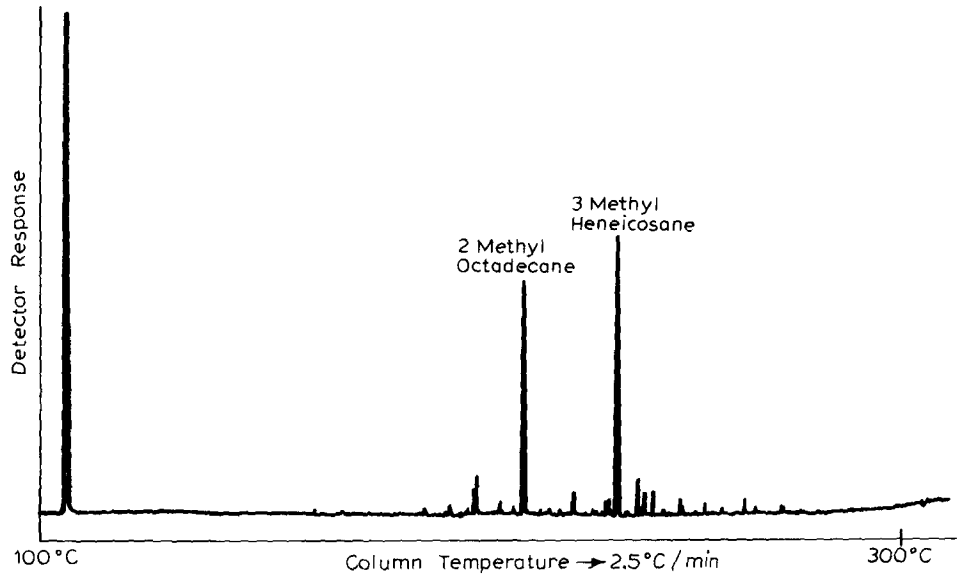

Fig. 3. Capillary GC of one of the liquid chromatographic fractions, isolated from the total branched hydrocarbon mixture shown in Fig. 1, by dry-column chromatography on silicalite. The fraction shown was eluted in the interval of 110–115 ml of hexane. Identification was made by capillary GC–MS.

Since silicalite is a high-capacity material, 0.2 cm^3/g, a preparative-scale experiment was carried out on 10 mg each of standard samples of 2-, 3-, and 4-methyloctadecane. The result is shown in Fig. 4. The same separation can be accomplished by capillary gas chromatography, but a 100,000-fold smaller sample load would be required.

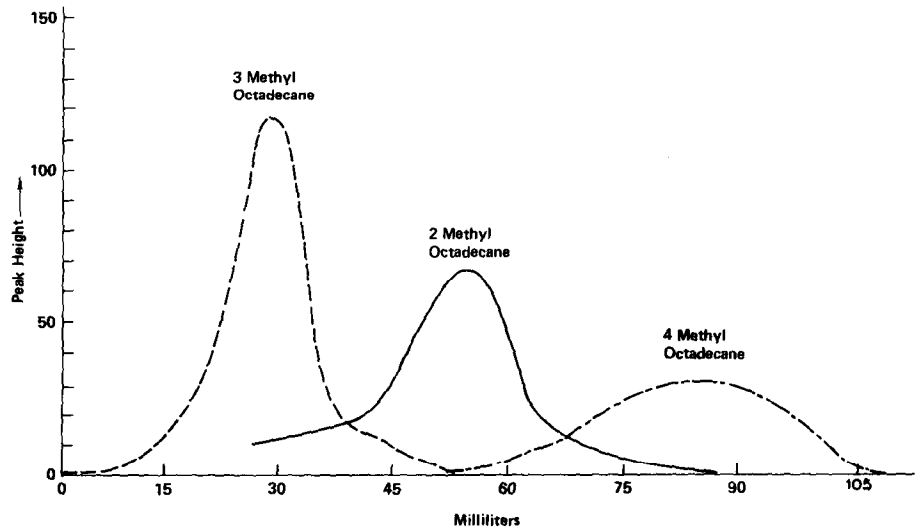

Fig. 4. Separation of 2-methyl-, 3-methyl- and 4-methyloctadecane by dry-column liquid chromatography on silicalite using *n*-hexane as the eluent. Fractions of 5 ml were collected, and the composition of each was measured by capillary GC.

A new procedure for n-alkane determinations

The foregoing observations show that silicalite occludes most of the impurities that would contaminate major *n*-alkane components during gas chromatographic analysis.

A test was made to determine whether silicalite isolation could be used to replace the ten-fold slower molecular sieve 5A sorption of *n*-alkanes. Measurements were made of *n*-alkane distributions in capillary gas chromatograms of hydrocarbons; sorbed batchwise from toluene by silicalite, followed by toluene wash and final displacement with hot *n*-octane. The results from analyses of the following samples were intercompared: (a) crude petroleum, (b) the saturated hydrocarbon fraction, and (c) the *n*-alkanes, isolated from the saturated hydrocarbon fraction using 5A. The results are shown in Fig. 5.

Starting with $n = 18$, the normalized abundances in Fig. 2 show precise agreement. *n*-Alkanes with $n = 15$–17, the more volatile end group, show larger fluctuations that might be reduced by refining the technique. It should be noted that while these results were obtained with silicalite sorption from toluene, the choice of solvent may not be critical.

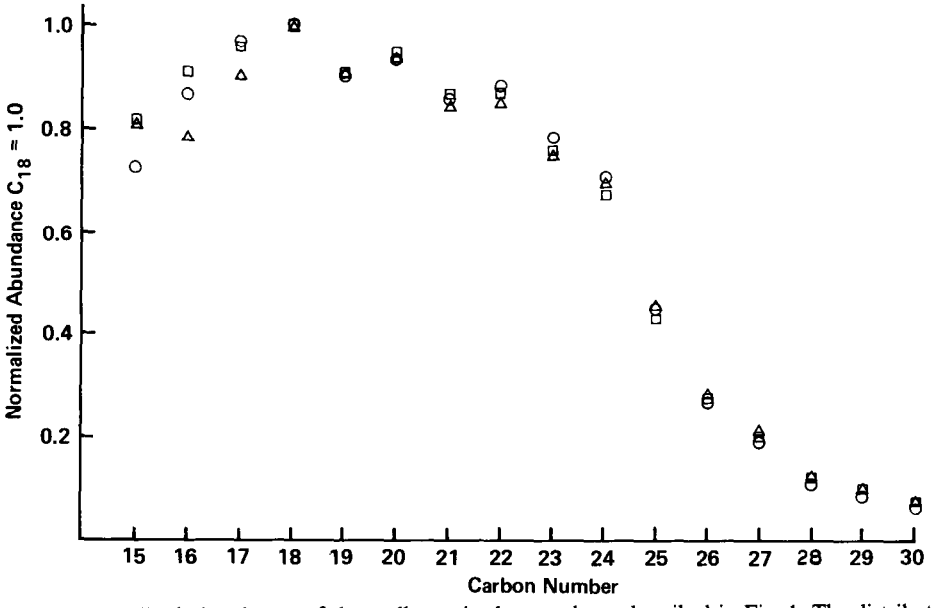

Fig. 5. Normalized abundances of the *n*-alkanes in the petroleum described in Fig. 1. The distributions were measured in three ways: The first, indicated by squares, is by sorption into molecular sieve 5A from the hexane eluate of silica gel chromatography. The *n*-alkanes were then isolated by dissolution of the sieve in concentrated hydrofluoric acid. The second method, indicated by circles, is by sorption of the hexane eluate into silicalite, followed by desorption by hot *n*-octane. The third, described by the triangles, is by silicalite sorption on the original crude petroleum without the initial silica gel chromatography. The much faster direct isolation on silicalite is a sufficient basis for the *n*-alkane determination. The possibility of such precise agreement is consistent with the few impurities that would interfere with *n*-alkane elution, based on analysis of results for which Fig. 1 is typical.

CONCLUSIONS

The present success in isolating the branched alkanes places silicalite in a class by itself. It provides a combination of ultraselective sieving when used alone or in combination with the 5A molecular sieve. The performance in the dry-column mode, including that exhibited with the $C_{19}H_{40}$ standards in Fig. 4, suggests silicalite offers a combination of high-load capacity, chemical reversibility, and pronounced shape selectivity. It can logically be placed first in a sorptive sequence for isolation of nearly straight-chain structures.

Preliminary experiments showed that silicalite causes tetrahydrofuran to polymerize at room temperature, forming a gum in several days. This effect was suppressed in the presence of 1% dibutylamine. It is not possible to assess the extent of such side effects at this point, except to alert the reader to the possibility and to the need to make the necessary tests.

The dry-column chromatography conditions are probably not the only ones that will work well with silicalite. Unlike many other sorbents, but typical of zerolites, silicalite sorption and desorption of paraffins involve a diffusion component that is temperature-activated. A stopped-flow period after conventional LC column injection can be tried, and time and temperature optimization remain to be demonstrated.

The present results show that shape-selective separations can be based on the molecular sieve properties of silicalite. This new sorptive, lipophilic, and ultra-stable material offers improved separation properties that merit further study.

REFERENCES

1 W. G. Meinschbein, in G. Eglinton and M. T. J. Murphy (Editors), *Organic Geochemistry*, Springer, New York, 1969, Ch. 13.
2 K. Stransky, M. Streibl and F. Storm, *Collect. Czech. Chem. Commun.*, 33 (1967) 416–424.
3 N. Polgar, in F. D. Gunstone (Editor), *Topics in Lipid Chemistry*, Wiley-Interscience, New York, Toronto, 1971.
4 T. C. Hoering, *Annual Report 1979–1980 of the Director*, Geophysical Laboratory, Carnegie Institution, 1980, pp. 399–403.
5 M. T. J. Murphy, in G. Eglinton and M. T. J. Murphy (Editor), *Organic Geochemistry*, Springer, New York, 1969, Ch. 3.
6 E. M. Flanigan, J. M. Bennett, R. W. Grose, J. P. Cohen, R. L. Patton, R. M. Kirchner and J. V. Smith, *Nature (London)*, 271 (1978) 512–516.
7 R. M. Dessau, in W. H. Flank (Editor), *Absorption and Ion Exchange with Synthetic Zeolites, ACS Symposium Series No. 135*, Washington, 1980, pp. 123–135.
8 R. M. Barrer, in *Hydrothermal Chemistry of Zeolites*, Academic Press, New York, 1982, p. 25.
9 J. B. Nagy, E. G. Derouane, H. A. Resing and G. R. Miller, *J. Phys. Chem.*, 87 (1983) 833–837.
10 D. M. Bibby, N. B. Milestone and L. P. Aldridge, *J. Phys. Chem.*, 280 (1979) 664.
11 B. J. Mair, *Anal. Chem.*, 30 (1958) 276–279.
12 D. R. Burfield, G.-H. Gan and R. H. Smithers, *J. Appl. Chem. Biotechnol.*, 28 (1978) 23–39.
13 B.-M. Karlsson, *Anal. Chem.*, 38 (1966) 668–669.
14 T. P. J. Izod, *U.S. Patent* 4,375,568 (1983).
15 D. H. Freeman, *Annual Report 1980–1981 of the Director*, Geophysical Laboratory, Carnegie Institution, 1981, pp. 414–415.
16 G. Eglinton, in G. Eglinton and M. T. J. Murphy (Editors), *Organic Geochemistry*, Springer, New York, 1969, Ch. 2.
17 G. T. Phillipi, *Geochim. Cosmochim. Acta*, 29 (1965) 1021–1049.