Journal of Chromatography, 633 (1993) 135–142
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 769

Cyclodextrin stationary phases for the gas–solid chromatographic separation of light hydrocarbons

Evidence for multiple retention mechanisms

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(First received July 16th, 1992; revised manuscript received October 29th, 1992)

ABSTRACT

Cyclodextrin, bonded to silica gel and used as a gas–solid chromatographic (GSC) stationary phase provides a practical and efficient means for separating a wide variety of volatile C_1–C_7 hydrocarbons at ambient to elevated temperatures. Conditioning the columns at high temperature (300°C) for several hours increased efficiency and resolution. The adsorption of these light hydrocarbons involves multiple retention mechanismns. For unsaturated hydrocarbons, the cyclodextrin GSC column can act as a polar stationary phase analogous to silica gel. However, for saturated hydrocarbons, it acts as a non-polar phase. Evaluation of the columns and an analogous silica gel column with hydrocarbon standards is reported. Capacity factors and chromatograms are presented for compounds analyzed on these GSC stationary phases.

INTRODUCTION

Gas–solid chromatography (GSC) is a widely used technique for the separation of light hydrocarbons and a variety of other gases. Compared with gas–liquid chromatography (GLC), GSC stationary phases have comparatively larger surface areas [1] and strong adsorption properties which result in excessive retention times and band broadening for most large molecules. For the GLC separation of lower-molecular-mass hydrocarbons (C_1–C_4), small partition coefficients at room temperature make for necessarily long columns [2]. Packed columns, and more recently, porous-layer open-tubular (PLOT) or support-coated open-tubular (SCOT) [3–5] columns are preferred for the separation of a wide range of gaseous and volatile molecules. Molecular sieves [6,7], alumina and silica gel [8–11], porous polymers [12–16], charcoal [17–19] and other more novel GSC stationary phases, including charge-transfer complexes [20], ammonium tungstosilicate [21] and metal complexes (for a review, see ref. 22) have been cited as separating light hydrocarbons. Elution order for adsorption columns vary by stationary phase polarity [23]. Hydrocarbons are separated by boiling point on non-polar columns, while on polar stationary phases, compounds containing triple bonds are more strongly retained than compounds with double bonds, which, in turn, are more strongly retained than saturated compounds.

Smolková-Keulemansová [24] first used native and methylated cyclodextrins as stationary phase coatings for packed gas chromatographic columns. She found evidence for inclusion complex formation while focusing on somewhat higher boiling point hydrocarbons and geometric isomers. Presently, many researchers are reporting the use of amorphous derivatized cyclodextrins as chiral stationary phases for GLC [25–28]. Cyclodextrins are

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0021-9673/93/$06.00

cyclic oligosaccharides. They are composed of D(+)-glucopyranose units and are linked by α-(1,4) bonds. The three most common cyclodextrins, α, β and γ, are differentiated by the number of glucopyranose subunits (6,7 and 8, respectively). The cyclized glucopyranose units form a conical shaped structure, with secondary hydroxyls (12 for α-cyclodextrin) surrounding the wider end, and primary hydroxyls (6 for α-cyclodextrin) opposite. The top and bottom of the structure are polar, due to the hydroxyl groups, while the interior of the cavity is apolar. The internal diameter of α and β-cyclodextrin's cavities are approximatley 4.5 and 7 Å, respectively, and molecules with appropriate sizes can form a host/guest inclusion complex.

Mechanistic studies involving cyclodextrins [29,30] and derivatized cyclodextrins [31] have cited multiple retention mechanisms. Dipersive forces are responsible for the separation of aliphatic hydrocarbons [32]. Inclusion complexes of α-cyclodextrin and many lower hydrocarbons (methane, ethylene, propane and butane) in solution are formed when high positive pressures of these gases are maintained over an aqueous solution of cyclodextrin [33]. The crystalline complexes are very stable for long periods of time and contain 0.6–1.2 mol of gas per mol of cyclodextrin. Similiarly, crystalline complexes are formed for the noble gases krypton and xenon (0.34 and 0.85 mol of gas per mol of cyclodextrin, respectively) [34]. Lower noble gases (helium, neon and argon) do not to form inclusion complexes with α-cyclodextrin.

EXPERIMENTAL

Instrumentation

A Hewlett-Packard (Avondale, PA, USA) 5890 Series II gas chromatograph equipped with a packed column injection port, flame ionization detector, and a liquid nitrogen cryogenic coolant system was utilized in this study. The injector and detector were set at 200°C. The oven temperature program was 30°C for 2 min, then increasing at 7.5°C/min to 200°C. The program was terminated with the last eluting peak. Data collection was accomplished with a Hewlett-Packard 3396B Series II integrator. Helium was used as the carrier gas for all separations, with a flow-rate of approximately 10 ml/min. The dead (or void) time for the columns was measured with repetitive injections of hydrogen (150 μl). This large volume of hydrogen appeared to give a small peak before methane even with a flame ionization detector. Hamilton gas-tight syringes were used for all injections.

Stationary phases

Stationary phases were obtained from Advanced Separation Technologies (Whippany, NJ, USA). All separations were accomplished on 40-μm silica supports (preparative HPLC supports). The stationary phases were: Cyclobond I (CBI), Cyclobond I Acetylated (CBI AC), Cyclobond III (CBI-II), Cyclobond III Acetylated (CBIII AC), silica gel, silica gel containing the 6–10 atom epoxy-terminated linkage [35,36] used to bond cyclodextrin to silica gel (Epoxy) and β-cyclodextrin directly bonded to silica gel (contains a higher stationary phase loading than CBI) (HIGH). In the case of HIGH, there was no epoxy-terminated linkage chain. The modified β-cyclodextrin was directly attached to the silica via a "Si–O–C" linkage. All bonded stationary phases were made from the same base silica gel to which the epoxy-terminated linkage chain had been attached. The only exception to this, as noted above, was for "HIGH" which used the same silica gel, but no linkage chain. The acetylated stationary phases were made by taking a portion of the native cyclodextrin bonded phase and reacting them with acetic anhydride. Consequently the size, pore distribution and surface area of the different stationary phases were as close as experimentally feasible. Stationary phases were packed into 91 cm × 0.21 cm inner diameter (I.D.) stainless-steel tubing (Supelco, Bellefonte, PA, USA). All columns were dry packed, while tapping or vibrating the column to ensure tight packing. Approximately 1.5 g of stationary phase were packed into each column.

The stationary phases were activated at 280–300°C for several hours before testing commenced. Conditioning removes water and any residual solvent remaining from the cyclodextrin/epoxy bonding procedure. It was observed that better efficiency occurred after conditioning (Fig. 1).

Chemicals

Reagents were obtained from Aldrich (Milwaukee, WI, USA): 1,3-butadiene, 1-butene, *cis*-2-butene, cyclopentane, 2,2-dimethylbutane, 2,3-di-

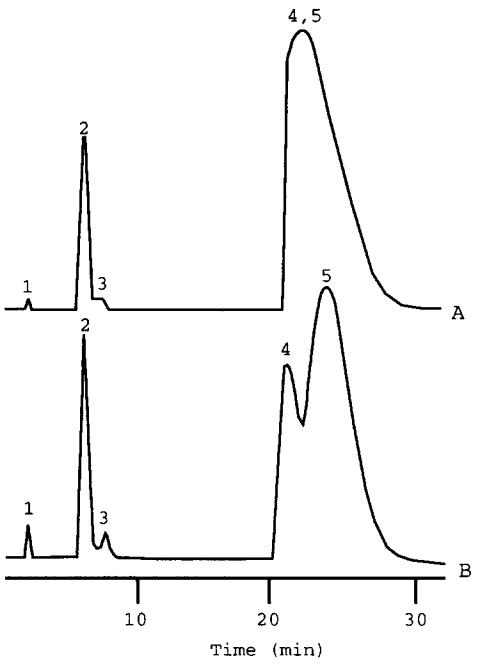

Fig. 1. Chromatogram of gas from a butane lighter. Column is 30 cm × 0.21 cm I.D. packed with 20-μm β-cyclodextrin stationary phase. (A) chromatogram prior to temperature conditioning; (B) same column conditioned at 300°C for several hours. Temperature is 50°C. Peaks: 1 = ethane; 2 = propane; 3 = propene; 4 = isobutane; 5 = butane.

methylbutane, 2,3-dimethylpentane, 2-methylpentane, 2-methylpropene (or isobutylene) and *trans*-2-butene; Matheson Gas (East Rutherford, NJ, USA): propylene; Phillips Petroleum (Bartlesville, OK, USA): 2,2-dimethylpropane; Scott Specialty Gases (Plumsteadville, PA, USA): (1000 ppm C_1–C_6 *n*-alkanes (can mix 236), 100 ppm C_2-C_6 olefins (can mix 222), 10 ppm C_2-C_4 alkynes (can mix 30), 10 ppm branched paraffins (can mix 2), 10 ppm, C_4 + isomers (can mix 55) and hydrogen (can 108). Liquids were sampled via headspace analysis, and gases were sampled directly from containers or gas sampling bulbs. Approximately 2 μl of headspace above liquids were injected into the gas chromatograph. Gas mixture injection volumes varied with the concentration of the blend. Successively lower amounts of the above alkane, olefin and alkyne mixtures were injected (until the detection limit was reached) to verify that there was no significant effect of concentration on retention at the analyte levels used in this study.

RESULTS AND DISCUSSION

Six GSC stationary phases, along with silica gel (for comparison), were evaluated in terms of retention and separation characteristics of light hydrocarbons. The stationary phases consisted of three native and two derivatized (acetylated) cyclodextrins in addition to silica gel covered with the epoxy terminated linkage chain but no cyclodextrin.

In general, native cyclodextrin columns produced longer retention times (larger capacity factors, k') than the analogous acetylated cyclodextrin columns, with the directly bonded β-cyclodextrin (HIGH) having the largest capacity factors. Every solute tested had a longer retention time on the directly bonded β-cylodextrin column than any other stationary phase. The data in Table I (k' values, arranged by stationary phase and by each component's boiling point) indicates that compounds are not always eluted in order of their boiling points. Table II lists three series of analytes composed of n-alkanes, 1-alkenes and 1-alkynes. Table II shows that for all columns, compounds in a family (*i.e.*, ethane, ethylene, acetylene) containing triple bonds are retained longer than those with double bonds, which, in turn are adsorbed more strongly than compounds with only single bonds (*i.e.*, the elution order for this series of compounds is the same when analyzed on either cyclodextrin or silica gel columns). The trend observed when comparing the data from the silica gel column to the cyclodextrin phases is the silica gel column had the smallest capacity factors for saturated compounds, but the k' between silica gel and the directly bonded β-cyclodextrin columns became similar as unsaturation was introduced into a compound series (*i.e.*, propane, propene and propyne). This is indicated in Table III (also Figs. 2 and 3) which lists the ratio of capacity factors between silica gel and directly bonded β-cyclodextrin stationary phases (HIGH) for a series of compounds. Figs. 2 and 3 plot the capacity factors of *n*-alkanes, 1-alkenes and 1-alkynes for the silica gel and directly bonded β-cyclodextin stationary phases. Figs. 2 and 3 show the capacity factors for three families of compounds. Fig. 4 gives a comparison of the *n*-alkane capacity

TABLE I

COMPARISON OF LIGHT HYDROCARBON CAPACITY FACTORS (k') BY STATIONARY PHASE AND BOILING POINT (°C)

Hydrocarbons	B.p. (°C)	k'						
		Silica	Epoxy[a]	CBIII[b]	CBIIIAC[c]	CBI[d]	HIGH[e]	CBIAC[f]
Hydrogen	−252.8	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Methane	−161.4	0.69	0.70	0.85	0.83	0.85	0.92	0.76
Ethene	−103.7	7.03	5.20	5.90	5.33	6.12	8.33	4.68
Ethane	−88.6	3.87	4.12	5.37	5.13	5.43	6.42	4.67
Acetylene	−84.0	11.58	8.85	9.20	8.77	9.35	12.01	7.70
Propene	−47.7	15.28	12.96	14.27	13.28	14.47	17.25	12.37
Propane	−42.1	9.68	10.15	12.35	11.79	12.47	14.29	11.18
Propyne	−23.2	23.26	19.27	19.87	18.77	20.06	23.55	17.29
Isobutane	−11.7	14.99	15.45	17.91	17.37	18.10	20.15	16.56
Isobutylene	−6.9	21.86	19.11	20.65	19.85	20.86	24.14	18.68
Butene	−6.3	20.78	18.47	20.65	19.85	20.86	23.47	18.68
1,3-Butadiene	−4.4	22.68	19.57	21.40	20.71	21.72	25.32	19.45
Butane	−0.5	15.90	16.46	19.02	18.25	19.23	21.55	17.55
trans-2-Butene	0.9	22.20	19.64	21.32	20.54	21.52	24.56	19.36
cis-2-Butene	3.7	22.20	19.64	21.32	20.54	21.52	24.56	19.36
1-Butyne	8.1	27.45	23.48	24.35	23.47	24.55	28.41	22.06
2,2-Dimethylpropane	9.5	19.29	19.59	22.05	21.60	22.24	24.28	20.69
2-Butyne	27.0	31.78	27.22	27.84	26.63	27.99	32.29	24.97
2-Methylbutane	27.9	20.61	21.18	23.85	23.25	24.10	26.62	22.32
1-Pentene	30.1	24.86	23.39	25.45	24.52	25.70	28.93	23.55
Pentane	36.1	21.23	21.87	24.59	23.76	24.87	27.56	22.98
Cyclopentane	49.3	21.34	22.15	24.89	24.47	25.07	27.09	23.69
2,2-Dimethylbutane	49.7	24.59	25.04	27.70	27.24	27.93	30.37	26.24
2,3-Dimethylbutane	58.0	25.06	25.65	28.45	27.89	28.73	31.44	27.02
2-Methylpentane	60.3	25.25	25.93	28.74	28.16	29.02	31.96	27.15
3-Methylpentane	63.3	25.25	25.93	28.74	28.16	29.02	31.96	27.15
Hexene	63.5	29.01	27.86	30.13	29.25	30.43	34.80	28.25
Hexane	69.0	25.79	26.55	29.40	28.58	29.72	32.94	27.75
2,3-Dimethylpentane	89.8	29.20	29.87	33.12	32.50	33.52	38.01	31.45

[a] Epoxy-terminated 6–10 atom linkage connecting cyclodextrin (CD) to silica gel.
[b] CBIII is native α-CD bonded to silica gel.
[c] CBIIIAC is acetylated α-CD bonded to silica gel.
[d] CBI is native β-CD bonded to silica gel.
[e] HIGH is a high-density surface coverage of β-CD directly bonded to silica gel (2–3 times more coverage than CBI).
[f] CBIAC is acetylated β-CD bonded to silica gel.

factors. Due to similar retention characteristics between the cyclodextrin and silica gel columns, it would appear that under these separation conditions, the underivatized cyclodextrin stationary phases tested can be considered polar (at least for unsaturated compounds).

A compound-by-compound comparison of stationary phases shows that alkanes are not as strongly retained on silica gel columns as on cyclodextrin stationary phases (Tables I and III). In fact, the retention of saturated compounds on the silica gel column was less than any other column tested. This retention behavior is in contrast to that for unsaturated analytes. When cyclodextrin is bonded to sil-

TABLE II

COMPARISON OF LIGHT HYDROCARBON CAPACITY FACTORS (k') BY FAMILY

See Table I or text for indications of phases.

Hydrocarbons	B.p. (°C)	k'						
		Silica	Epoxy	CBIII	CBIIIAC	CBI	HIGH	CBIAC
Ethane	−88.6	3.87	4.12	5.37	5.13	5.43	6.42	4.67
Ethene	−103.7	7.03	5.20	5.90	5.33	6.12	8.33	4.68
Acetylene	−84.0	11.58	8.85	9.20	8.77	9.35	12.01	7.70
Propane	−42.1	9.68	10.15	12.35	11.79	12.47	14.29	11.18
Propene	−47.7	15.28	12.96	14.27	13.28	14.47	17.25	12.37
Propyne	−23.2	23.26	19.27	19.87	18.77	20.06	23.55	17.29
Butane	−0.5	15.90	16.46	19.02	18.25	19.23	21.55	17.55
1-Butene	−6.3	20.48	18.56	20.29	19.31	20.51	23.47	18.38
1-Butyne	8.1	27.45	23.48	24.35	23.47	24.55	28.41	22.06

ica gel, the retention times of non-polar non-polarizable saturated hydrocarbons increase. When the cyclodextrin density on the surface of the silica gel is increased (as with the directly bonded β-cyclodextrin stationary phase), the retention times of these alkanes show a further increase. The interaction of alkanes with cyclodextrin must involve a non-polar portion of the stationary phase and that interaction very likely occurs in the cyclodextrin's cavity.

From the previously discussed results, it appears that there may be two different retention mechanisms for light hydrocarbons on cyclodextrin stationary phases in GSC. Clearly the retention of unsaturated compounds, particulary those with triple bonds, are nearly identical on the directly bonded β-cyclodextrin column (HIGH) and silica gel column. When the linkage chain and cyclodextrin are bonded to silica gel, the number of free silanol

TABLE III

RATIO OF CAPACITY FACTORS FOR COMPOUNDS CHROMATOGRAPHED ON DIRECTLY BONDED β-CD AND SILICA GEL STATIONARY PHASES

HIGH is a high-density surface coverage of β-CD directly bonded to silica gel (2–3 times more coverage than CBI).

Hydrocarbons	B.p. (°C)	$\frac{k'_{HIGH}}{k'_{silica\ gel}}$
Ethane	−88.6	1.66
Ethene	−103.7	1.18
Acetylene	−84.0	1.04
Propane	−42.1	1.48
Propene	−47.7	1.13
Propyne	−23.2	1.01
Butane	−0.5	1.36
1-Butene	−6.3	1.15
1-Butyne	8.1	1.04

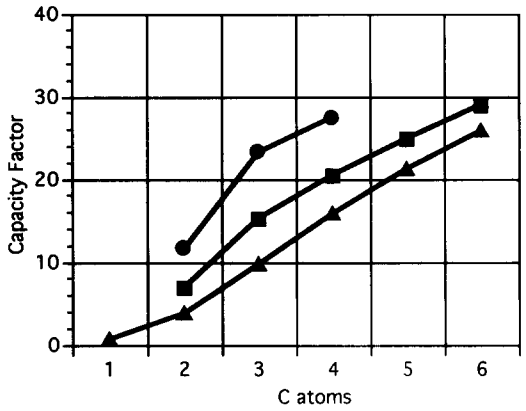

Fig. 2. Comparison of *n*-alkane (▲), 1-alkene (■) and 1-alkyne (●) capacity factors on a silica gel column by degree of unsaturation and number of carbon atoms in a compound. Temperature program: 30°C for 2 min, ramp at 7.5°C/min to 200°C. Column is 91 cm × 0.21 cm I.D. packed with 40-μm stationary phase.

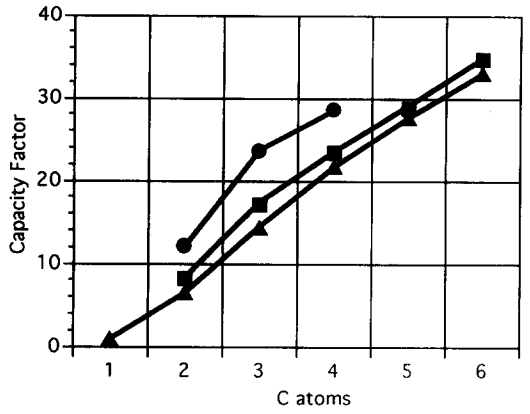

Fig. 3. Comparison of *n*-alkane (▲), 1-alkene (■) and 1-alkyne (●) capacity factors on a directly bonded β-cyclodextrin column by degree of unsaturation and number of carbon atoms in a compound. Temperature program: 30°C for 2 min, ramp at 7.5°C/min to 200°C. Column is 91 cm × 0.21 cm I.D. packed with 40-μm stationary phase.

groups is greatly reduced. Indeed, the stationary phase that retained unsaturated compounds the least was the one that had only the linkage chain attached to the silica gel (*i.e.*, "Epoxy" in Tables I and II). However, native cyclodextrins have a plethora of free hydroxyl groups. It is likely that the retention of unsaturated compounds on the native cyclodextrin phases is due to the cyclodextrin-hydroxyl groups, just as in the silica gel case, it is through the silanol groups. However, in the retention of saturated hydrocarbons, an option exists with the cyclodextrin phases that does not exist with silica gel. Retention in a relatively apolar cavity is the most likely explanation for the enhanced retention of saturated hydrocarbons on cyclodextrin stationary phases. No analogous retention mechanism exists on underivatized silica gel.

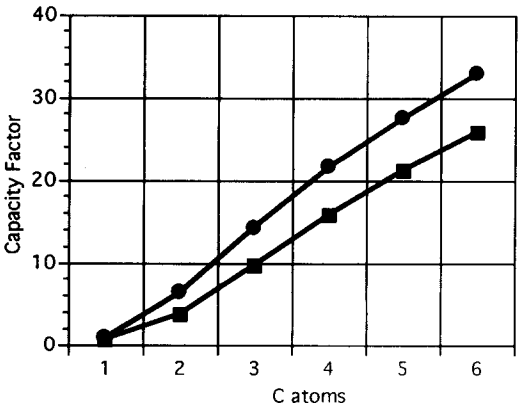

Fig. 4. Comparison of *n*-alkane capacity factors on directly bonded β-cyclodextrin (●) and silica gel (■) columns. Temperature program: 30°C for 2 min, ramp at 7.5°C/min to 200°C. Columns are 91 cm × 0.21 cm I.D. packed with 40-μm stationary phase.

Smolková *et al.* [30] reported the measurement of a wide range of sorbates from 50 to 80°C on α- and β-cyclodextrin. Two compounds, *n*-pentane and *n*-hexane are common to this study. Smolková *et al.* reported a 50–100 factor increase in the adjusted retention time of *n*-pentane on α-cyclodextrin over β-cyclodextrin. This was attributed to the tighter inclusion complex formed in α-cyclodextrin's cavity. Under the conditions of this study, there was little difference in retention times for compounds tested on α and β-cyclodextrin stationary phases. At the higher elution temperatures of this study, a tight inclusion complex may play a less dominant role in retention. Berthod *et al.* [31] reported a strong mechanistic temperature dependence in derivatized cyclodextrin liquid stationary phases. Indeed, the same compound could have different retention mechanisms at different temperatures, and these mechanisms are determined on a case-by-case basis.

Smolková-Keulemansová *et al.* [29] reported large differences in the retention times of isomers (branched versus straight chained compounds) on α-, but not β-cyclodextrin. This was attributed to the cavity size; the branched isomer was prohibited by size from entering α-cyclodextrin's cavity, and hence was less retained than the straight chain isomer, which could form an inclusion complex. In our studies, the elution order of branched and straight-chain aliphatic isomers occurred by boiling point. The elution order of these isomers on silica gel and non-polar stationary phases are also by boiling point. However, our studies were done at considerably higher temperatures and generally with smaller analytes. Despite these differences, we arrived at essentially the same conclusion as Smolková-Keulemansová *et al.* [29] for the saturated hydrocarbons, particularly at lower temperatures (*i.e.*, that inclusion complexation plays a significant role in retention).

In the present study, acetylating cyclodextrins re-

sulted in a decreased stationary phase polarity (by derivatizing hydroxyl groups) compared to native cyclodextrin. Compounds chromatographed on acetylated cyclodextrin stationary phases had shorter retention times than the same compound analyzed on the analogous native cyclodextrin phase. Table IV lists the capacity factor ratios for compounds analyzed on native and acetylated cyclodextrin stationary phases.

The bonding of the epoxy-terminated linkage to silica gel support could modify the support in two ways. First, the epoxy linkage should decrease the silica gel support's polarity (modification of a polar surface with a less polar appendage). For saturated hydrocarbons, the elution time is slightly higher on the epoxy column than on the silica gel support, but the retention times are still smaller than those obtained on any cyclodextrin stationary phase. If one assumes that alkanes are retained more on non-polar phases and less on polar stationary phases, under these experimental conditions, then the epoxy phase would appear to have a polarity between that of the silica gel and the cyclodextrin-bonded stationary phases.

Bonding cyclodextrin to the polar silica gel support modifies the silica gel's surface polarity. This modification of the surface polarity changes adsorption behavior. The phenomenon of differing adsorption between cyclodextrins and silica gel leads to gas mixtures separable on cyclodextrin but not on silica gel. Fig. 5 shows chromatograms obtained on the directly bonded β-cyclodextrin and silica gel stationary phases. The directly bonded β-cyclodextrin phase separates C_1–C_6 *n*-alkanes

TABLE IV

RATIO OF CAPACITY FACTORS FOR COMPOUNDS CHROMATOGRAPHED ON NATIVE AND ACETYLATED CYCLODEXTRIN STATIONARY PHASES

See Table I or text for indications of phases.

Hydrocarbons	$\frac{k'_{\alpha\text{-CD}}}{k'_{\text{AC-}\alpha\text{-CD}}}$	$\frac{k'_{\beta\text{-CD}}}{k'_{\text{AC-}\beta\text{-CD}}}$
Methane	1.02	1.12
Ethane	1.05	1.16
Propane	1.05	1.12
Butane	1.04	1.10
Pentane	1.03	1.08
Hexane	1.03	1.07
Ethylene	1.11	1.31
Propylene	1.07	1.17
1-Butene	1.05	1.12
1-Pentene	1.04	1.09
1-Hexene	1.03	1.08
Acetylene	1.05	1.21
Propyne	1.06	1.16
1-Butyne	1.04	1.11
2-Butyne	1.05	1.12
2,2-Dimethylpropane	1.02	1.08
2-Methylbutane	1.03	1.08
2,2-Dimethylbutane	1.02	1.06
2-Methylpentane	1.02	1.07
3-Methylpentane	1.02	1.07
Isobutane	1.03	1.10
Isobutylene	1.04	1.12
trans-2-Butene	1.04	1.11
cis-2-Butene	1.04	1.11
1,3-Butadiene	1.03	1.12
Cyclopentane	1.02	1.06
2,3-Dimethylbutane	1.02	1.06
2,3-Dimethylpentane	1.02	1.07

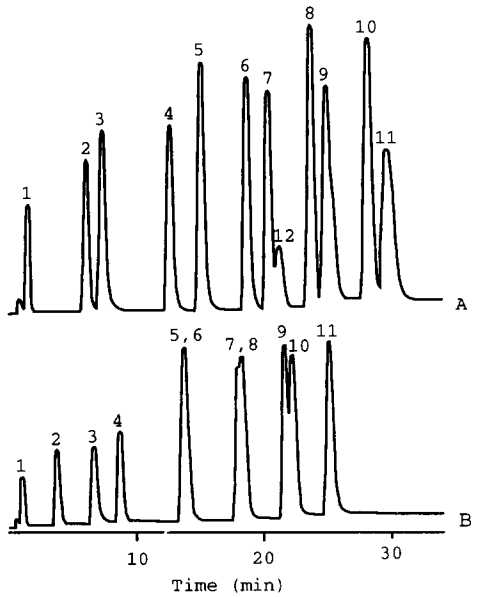

Fig. 5. Chromatogram of C_1–C_6 *n*-alkanes and C_2–C_6 1-alkenes. Temperature program: 30°C for 2 min, ramp at 7.5°C/min to 200°C. Columns are 91 cm × 0.21 cm I.D. packed with 40-μm stationary phase. (A) With the directly bonded β-cyclodextrin stationary phase; (B) with a silica gel stationary phase. Peaks: 1 = methane; 2 = ethane; 3 = ethene; 4 = propane; 5 = propene; 6 = butane; 7 = butene; 8 = pentane; 9 = pentene; 10 = hexane; 11 = hexene; 12 = impurity.

from C_2–C_6 1-alkenes but an analogous silica gel column does not completely resolve all peaks.

Cyclodextrin bonded to silica gel allows for different adsorption behaviors in regard to light hydrocarbons. A dual retention mechanism seems to be a factor in the separation of these compounds. Alkanes appear to be retained through an interaction with the apolar cavity, while unsaturated molecules can interact with the cavity and/or through the hydroxyl groups on the top and bottom of the cyclodextrin molecules. Separation of geometric isomers is inadequate at the high temperature and conditions of this study. However, these compounds are effectively resolved by GLC on the derivatized cyclodextrin phases [27]. New approaches are being tested to improve the generality and selectivity of the cyclodextrin columns for the GSC separation of other volatile compounds and gases.

ACKNOWLEDGEMENT

Support of this work by the Department of Energy, Office of Basic Science (DE FG02 88ER13819) is gratefully acknowledged.

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