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CYCLODEXTRIN STATIONARY PHASES FOR THE GAS-SOLID CHROMATOGRAPHIC SEPARATION OF HYDROCARBONS

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ABSTRACT

Cyclodextrin, bonded to silica gel and used as a gas-solid chromatographic stationary phase provides a practical and efficient means for separating a wide variety of 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 a multiple retention mechanism. Evaluation of the columns and an analogous silica gel column with hydrocarbon standards is reported. Capacity factors and chromatograms are presented for these GSC stationary phases.

INTRODUCTION

Gas-solid chromatography (GSC), introduced in 1941 by Martin and Synge [1] is a widely used technique for the separation of light hydrocarbon and permanent gases. Compared with gas-liquid chromatography (GLC), GSC stationary phases (GSC SPs) have a comparatively larger surface area [2] and this results in excessive retention times for large molecules. For lower molecular weight compounds, GLC has little selectivity, and is seldom used. For separation of these low molecular weight molecules, packed columns, and more recently, porous layer open tubular (PLOT) or support coated open tubular (SCOT) [3][4][5] columns are the main choices. Many GSC stationary phases have been cited as separating light hydrocarbons, including molecular sieves [6][7], alumina and silica gel [8][9][10], porous polymers [11][12][13][14][15] and charcoal [16][17][18]. Elution order for adsorption columns vary by stationary phase polarity [19]. Compounds are separated by boiling point on non-polar columns, while on polar stationary phases, in an analogous series, triple bonded compounds are retained stronger than double bonds which are retained stronger than saturated compounds.

A GSC SP used for separating higher boiling compounds along with geometric isomers is composed of cyclodextrin on an inert support [20]. Presently, many researchers are reporting the use of derivatized cyclodextrins as GLC chiral SPs for the separation of enantiomers, diastereomers, and geometric isomers [21][22][23][24]. Cyclodextrins are cyclic oligosaccharides; D(+)-glucopyranose units linked alpha (1,4). The three most common CDs are the alpha, beta and gamma (α, β and γ), which 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-CD) surrounding the wider end and primary hydroxyls (6 for α-CD) opposite. The top and bottom of the structure are polar, due to the hydroxyl groups, while the interior of the cavity is apolar.

The alpha and beta-cyclodextrin cavities are on the order of 4.5 and 7 Å, respectively, and molecules with appropriate sizes can form a host/guest inclusion complex. Mechanistic studies involving CDs [25][26] and derivatized CDs [27] have cited multiple retention mechanisms. These studies were done on compounds (hydrocarbons, chlorocarbons, aromatics, etc.) in which a tight fitting host/guest complex could be obtained. For aliphatic hydrocarbons, dispersive forces are responsible for inclusion. With these forces, a guest in close proximity to the CD is required since the dispersive force diminishes with the reciprocal of the sixth power of distance. Inclusion complexes of α-CD and lower hydrocarbons (methane, ethylene, propane, butane) in solution are formed when the gases are held at a high pressure for several days[28]. The crystalline complexes are very stable for long periods of time and contain 0.6-1.2 mole of gas per mole of CD. Similarly, lower noble gases (helium, neon and argon) do not to form an inclusion complex with α-CD, where the larger members of the group (krypton and xenon) do form inclusions under high pressure [29]. Acetylated cyclodextrins have much steric bulk, and inclusion is difficult to obtain .

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 minutes, then increasing at 7.5°C/minute 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/minute. The void retention time for the columns was measured with repetitive injections of (150 µL) hydrogen. Hamilton gas tight syringes

were used for all injections.

Stationary Phases

Stationary phases were obtained from Advanced Separation Technologies, Inc. (Whippany, NJ). All separations were accomplished on 40 μm silica supports (preparative HPLC supports). The SPs were: Cyclobond I (CBI), Cyclobond I Acetylated (CBI AC), Cyclobond III (CBIII), Cyclobond III Acetylated (CBIII AC), silica gel, silica gel containing the 6-10 atom epoxy terminated linkage [30][31] used to bond cyclodextrin to silica gel (Epoxy) and CBI with a high stationary phase density (HIGH). Cyclobond I is β-cyclodextrin and Cyclobond III is α-cyclodextrin. SPs were packed into three foot by one eighth inch OD (3'x1/8"), 2.1 mm ID stainless steel tubing (Supelco, Bellefonte, PA). All columns were prepared by dry packing, using tapping or vibrating to ensure tight packing. Approximately 1.5 grams of stationary phase was packed into each three foot column.

Chemicals

Reagents were obtained from Aldrich Chemical Company, Inc. (Milwaukee, WI): 1,3-butadiene (29,503-5), 1-butene (29,505-1), cis-2-butene (29,507-8), cyclopentane (15,476-8), 2,2-dimethyl butane (D15,140-8), 2,3-dimethyl butane (D15,160-2), 2,3-dimethyl pentane (D17,320-7), 2-methyl pentane (M6,580-7), 2-methyl propene (or isobutylene) (29,546-9) and trans-2-butene (29,508-6); Matheson Gas Company, Inc. (East Rutherford, NJ): propylene; Phillips Petroleum Company (Bartlesville, OK): 2,2-dimethyl propane; Scott Specialty Gases (Plumsteadville, PA): (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 in their headspace, and gases were sampled directly or from gas sampling bulbs. Approximately 2 μL of headspace above liquids was injected into the GC. Gas mixture injection volumes varied with the concentration of the blend.

RESULTS AND DISCUSSION

Six gas-solid chromatographic stationary phases, along with silica gel as a comparison, were evaluated in terms of retention and separation characteristics of light hydrocarbons. The GSC SPs evaluated were based upon cyclodextrin (CD), either alpha or beta. These phases consisted of three native and two derivatized CD phases along with the hydrolitically stable epoxy terminated linkage which connects CD to the silica gel. SPs were attached to 40 μm (325/400 mesh) spherical silica gel.

The stationary phases were activated at 280-300°C for several hours before testing commenced. Conditioning of the SP removed water and any residual solvent remaining

from the CD bonding step. It was observed that better efficiency occurred after conditioning. Table 1 lists the capacity factors for the compounds by SP. Hydrogen was used as the dead (void) time for all calculations. Native CDs have longer retention times (larger capacity factors, k') than acetylated CDs, with the high surface density β CD (HIGH) having the largest k' values. HIGH had the longest retention times for every compound tested. The data in Table II (K' values, arranged by compound boiling point) indicates that triple bonds are adsorbed stronger than double bonds, which are adsorbed stronger than single bonded materials (like the silica gel SP), and not eluted by boiling point. The trend observed when comparing the data from the silica gel column to the CD phases is the silica gel column had the lowest k' values for saturated compounds, but the k' ratio between silica gel and HIGH significantly decreased as unsaturation was introduced into a compound series (i.e. propane, propene and propyne); CD columns retained unsaturated compounds to a lesser extent then the silica gel column. The SPs tested thus can be considered moderately polar.

Alkanes are not tightly adsorbed on silica gel, and their retention times are minimal. When CDs are bonded to silica gel, the retention times of these non-polar, non-polarizable molecules increase. When the CD density on the surface of the silica gel is increased, the retention time of the alkanes also increases. The interaction of alkanes with CDs must involve a non-polar region, therefore that interaction must dominantly occur in the cavity.

Unsaturated compounds are heavily retained on silica gel SPs. The mechanism involves the acidic silanol groups and the sorbate's polarizable π-bonds. CD SPs bonded to silica gel reduce or eliminate accessible silanol groups, but, alcohol groups are added. Alcohols are less acidic and do not polarize π-bonds as strongly as silanols do and unsaturated compounds are not retained as strongly on CDs as silica gel. The elution order of alkanes, alkenes and alkynes on CD indicates a polar SP, therefore, the retention mechanism of these unsaturated compounds may involve an inclusion process, but also involves the CD's polar alcohol groups.

Smolkova et al. (1982) reported the measurement of a wide range of sorbates from 50 to 80°C on alpha and beta-CD. Two compounds (n-pentane and n-hexane) are in common. Differences in our experiments need be noted : 1) supports - chromosorb W at 60/80 mesh (250 - 177 μm) versus silica gel at 325 mesh (40 μm), 2) coated versus bonded phase, and 3) isothermal versus temperature programming. Hence for pentane, Smolkova et al. reports elution at an adjusted retention time (t_r') of 496 seconds at 80°C, while in this paper the acetylated beta CD (used for comparison since it had the shortest retention time of all the CD phases), had an t_r' of 1100 seconds and elution occurred at approximately 160°C. Berthod et al. (in press)

TABLE I. COMPARISON OF LIGHT HYDROCARBON CAPACITY FACTORS (K') BY STATIONARY PHASE.

Hydrocarbons	BP(°C)	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
Ethane	-88.6	3.87	4.12	5.37	5.13	5.43	6.42	4.67
Propane	-42.1	9.68	10.15	12.35	11.79	12.47	14.29	11.18
Butane	-0.5	15.90	16.46	19.02	18.25	19.23	21.55	17.55
Pentane	36.1	21.23	21.87	24.59	23.76	24.87	27.56	22.98
Hexane	69.0	25.79	26.55	29.40	28.58	29.72	32.94	27.75
Ethene	-103.7	7.03	5.20	5.90	5.33	6.12	8.33	4.68
Propene	-47.7	15.28	12.96	14.27	13.28	14.47	17.25	12.37
1-Butene	-6.3	20.48	18.56	20.29	19.31	20.51	23.47	18.38
1-Pentene	30.1	24.86	23.39	25.45	24.52	25.70	28.93	23.55
1-Hexene	63.5	29.01	27.86	30.13	29.25	30.43	34.80	28.25
Acetylene	-84.0	11.58	8.85	9.20	8.77	9.35	12.01	7.70
Propyne	-23.2	23.26	19.27	19.87	18.77	20.06	23.55	17.29
1-Butyne	8.1	27.45	23.48	24.35	23.47	24.55	28.41	22.06
2-Butyne	27.0	31.78	27.22	27.84	26.63	27.99	32.29	24.97
Isobutane	-11.7	14.99	15.45	17.91	17.37	18.10	20.15	16.56
2,2-Dimethyl propane	9.5	19.29	19.59	22.05	21.60	22.24	24.28	20.69
2-Methyl butane	27.9	20.61	21.18	23.85	23.25	24.10	26.62	22.32
2,2-Dimethyl butane	49.7	24.59	25.04	27.70	27.24	27.93	30.37	26.24
2-Methyl pentane	60.3	25.25	25.93	28.74	28.16	29.02	31.96	27.15
3-Methyl pentane	63.3	25.25	25.93	28.74	28.16	29.02	31.96	27.15
Isobutane	-11.7	14.98	15.44	17.90	17.37	18.10	20.16	16.53
N-butane	-0.5	15.94	16.45	19.04	18.41	19.26	21.56	17.54
Isobutylene	-6.9	21.86	19.11	20.65	19.85	20.86	24.14	18.68
1-Butene	-6.3	20.78	18.47	20.65	19.85	20.86	23.47	18.68
Cis 2-butene	3.7	22.20	19.64	21.32	20.54	21.52	24.56	19.36
Trans 2-butene	0.9	22.20	19.64	21.32	20.54	21.52	24.56	19.36
1,3-Butadiene	-4.4	22.63	19.57	21.40	20.71	21.72	25.32	19.45
1-Butyne	8.1	28.01	23.37	24.32	23.44	24.55	28.38	22.03
Cyclopentane	49.3	21.34	22.15	24.89	24.47	25.07	27.09	23.69
2,3-Dimethyl butane	58.0	25.06	25.65	28.45	27.89	28.73	31.44	27.02
2,3-Dimethyl pentane	89.8	29.20	29.87	33.12	32.50	33.52	38.01	31.45

[a]Epoxy terminated 6-10 atom linkage connecting 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 β-CD on silca gel (2-3 times more coverage than CBI). [f]CBIAC is acetylated β–CD bonded to silica gel.

reported a strong mechanistic temperature dependence in derivatized CD liquid SPs; the same compound could have different retention mechanisms at different temperatures, and these mechanisms are determined case by case. Smolkova et al. reports a factor of 50-100 difference for t_r' on alpha (larger t_r') and beta-CD for

TABLE II. COMPARISON OF LIGHT HYDROCARBON CAPACITY FACTORS (K') BY STATIONARY PHASE AND BOILING POINT (°C).

Hydrocarbons	BP(°C)	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	22.63	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-Dimethyl propane	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-Methyl butane	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-Dimethyl butane	49.7	24.59	25.04	27.70	27.24	27.93	30.37	26.24
2,3-Dimethyl butane	58.0	25.06	25.65	28.45	27.89	28.73	31.44	27.02
2-Methyl pentane	60.3	25.25	25.93	28.74	28.16	29.02	31.96	27.15
3-Methyl pentane	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-Dimethyl pentane	89.8	29.20	29.87	33.12	32.50	33.52	38.01	31.45

[a]Epoxy terminated 6-10 atom linkage connecting 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 β-CD on silca gel (2-3 times more coverage than CBI). [f]CBIAC is acetylated β-CD bonded to silica gel.

pentane, and attributes this to the tighter inclusion complex formed in alpha-CD rather than beta-CD. With the conditions operative in this study, little difference in retention times was observed for compounds tested on alpha and beta-CD. At the higher elution temperatures of this study, a tight inclusion complexation may play a minimal role in retention. The SP polarity (apolar cavity) may be a more dominant mechanism than the actual inclusion complex mechanism.

Smolkova-Keulemansova et al. (1985) reported large differences in the retention times of isomers (branched versus straight chained) on alpha, but not beta CD. This again was attributed to the cavity size; the branched alkane was prohibited by size from entering the alpha-CD's cavity, and was less retained than the straight chain alkane which could form an inclusion complex. Smolkova-Keulemansova et al. found that branched nonanes eluted before n-heptane, even though the nonanes had a higher boiling point. In our studies, the elution time of branched versus straight chained aliphatic isomers occurred by boiling point (silica gel and none polar SPs have the same trend). Smolkova-Keulemansova et al. partially methylated (66%) CDs, and found that the large differences in retention times between branched and linear hydrocarbons was diminished. Steric effects of the methyl groups, thereby decreasing cavity accessibility, was used to explain this decreased separation.

Acetylating CDs decreases the accessibility of the cavity and decreases the SP polarity. Acetylated CDs have shorter retention times than native CDs. This can be explained by steric effects for alkanes (decreasing accessibility will decrease non-polar/non-polar interactions and result in a decreased retention time. The unsaturated compounds retention times were also decreased. Again, a decreased accessibility to the cavity can be a factor, but also a decrease in the number of alcohol groups (π-interactions) can be important in the overall mechanism.

Bonding the epoxy chain to the CD results in two factors. First, for the alkanes, the epoxy group decreases SP polarity, so, compared with the silica gel column, alkanes are adsorbed stronger. This decrease in SP polarity is still minimal compared with the apolar CD cavity and the retention times on the Epoxy column are considerably shorter than the retention times on the native CD columns. Secondly, the epoxy group decreases the number and accessibility of the silanol groups, which makes the unsaturated compounds elute faster then they would on the silica gel column.

Bonding CD to the polar silica gel support decreases that supports polarity. This modification of the surface polarity changes adsorption strengths and hence column selectivities vary. This phenomena of differing selectivities between CDs and silica gel leads to gas mixtures separable on CDs but not on silica gel. Figures 1 and 2 show this selectivity difference where HIGH (Figure 1) separates C_1-C_6 paraffins from C_2-C_6 1-alkenes but an analogous silica gel (Figure 2) column does not completely resolve all peaks.

CD bonded to silica gel allows for differing selectivities in regards to lower hydrocarbons. A dual retention mechanism is a factor in the separation of these compounds. Alkanes are retained through an interaction with the apolar cavity, while unsaturated molecules can interact with the cavity and/or through the alcohol groups

on the CDs. Separation of geometric isomers is inadequate, which should be a CD strength. New approaches are being tested to improve the generality and selectivity of the CD columns.
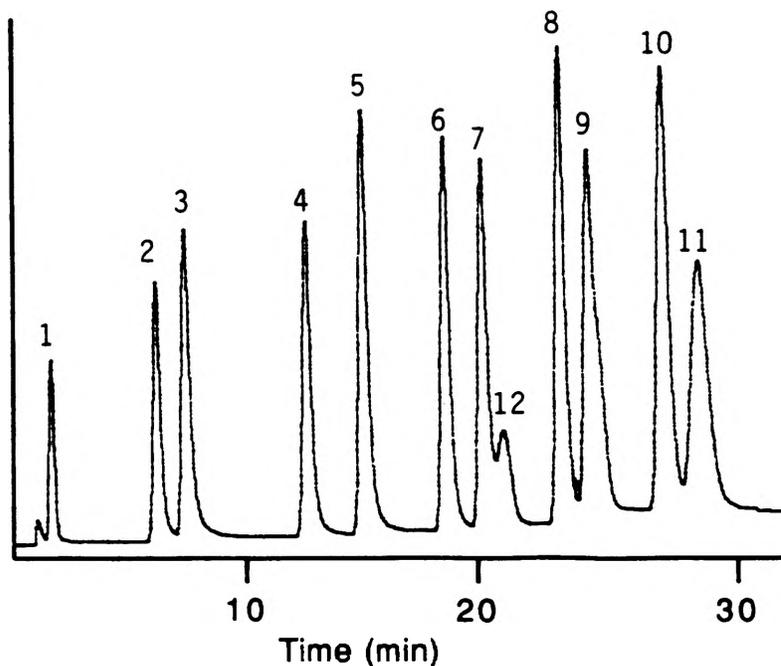

Figure 1. Chromatogram of C_1-C_6 n-alkanes and C_2-C_6 1-alkenes on HIGH. Temperature program : 30°C for 2 minutes, ramp at 7.5°C/minute to 200°C. 1, methane; 2, ethane; 3, ethene; 4, propane; 5, propene; 6, butane; 7, butene; 8, pentane; 9, pentene; 10, hexane; 11, hexene; 12, impurity.
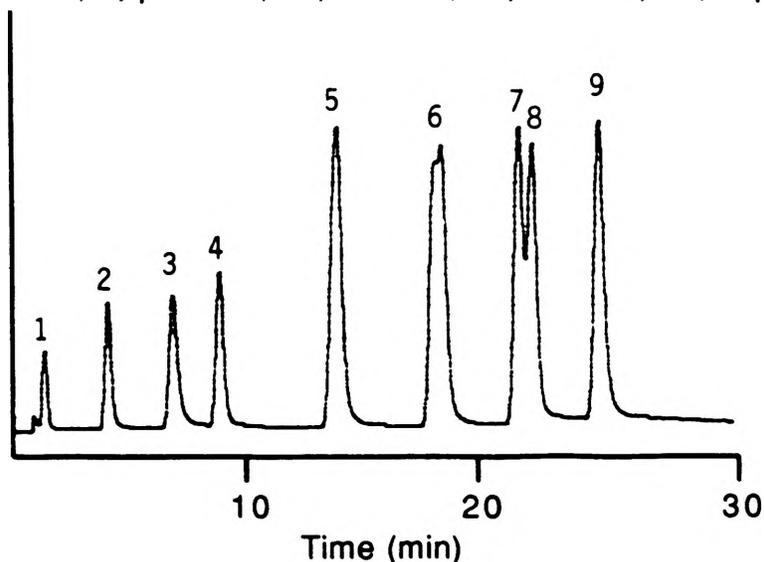

Figure 2. Chromatogram of C_1-C_6 n-alkanes and C_2-C_6 1-alkenes on Silica gel. Temperature program : 30°C for 2 minutes, ramp at 7.5°C/minute to 200°C. 1, methane; 2, ethane; 3, ethene; 4, propane; 5, propene/butane; 6, butene/pentane; 7, pentene; 8 hexane; 9, hexene.

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ACKNOWLEDGMENTS

REFERENCES

1   A.J.P. Martin and R.L. Synge, *Biochem. J.*, 35 (1941) 1358.

2   C.F. Poole and S.A. Schuette, *Contemporary Practice of Chromatography*, Elsevier Science Publishing Co., New York, 1984, p. 72.

3   L.S. Ettre and J.E. Purcell, *Adv. Chromatogr.*, 10 (1974) 1.

4   R.G. Mathews, J. Torres and R.D. Schwartz, *J. Chromatogr.*, 199 (1980) 97.

5   W. Schneider, J.C. Frohne and H. Bruderreck, *J Chromatogr,* 155 (1978) 311.

6   N. Brenner and V.J. Coates, *Nature*, 181 (1958) 1401.

7   B.T. Whitman, *Nature*, 182 (1958) 391.

8   S.A. Greene, M.L. Moberg and E.M. Wilson, *Anal. Chem.*, 28 (1956) 1369.

9   S.A. Greene and H. Pust, *Anal. Chem.*, 29 (1957) 1055.

10   H.N. Morrow and K.B. Buckley, *Petrol. Refiner.*, 36 (1957) 157.

11   O.L. Hollis, *Advances in Gas Chromatography 1965*, A. Zlatkis and L.S. Ettre, eds., Preston Technical Abstracts Co., Evanston, 1966, p. 56.

12   O.L. Hollis, *Anal. Chem.*, 38 (1966) 309.

13   O.L. Hollis and W.V. Hayes, *J. Gas Chromatogr.*, 4 (1966) 235.

14   W.F. Wilhite and O.L. Hollis, *J. Gas Chromatogr.*, 6 (1968) 84.

15   C.N. Jones, *Anal. Chem.*, 39 (1967) 1858.

16   H.W. Patton, J.S. Lewis and W.I. Kaye, *Anal. Chem.*, 27 (1955) 170.

17   S. Ohksoshi, Y. Fujita, and T. Kwan, *Shokubai*,15 (1958) 1.

18   N.H. Ray, *J. Appl. Chem.*,4 (1954) 21.

19   A.B. Littlewood, *Gas Chromatography Principles, Techniques, and Applications*, Academic Press, New York, 1970, p. 431.

20   E. Smolkova-Keulemansova, *J. Chromatogr.*, 251 (1982) 17.

21   W.Y. Li, H.L. Jin and D.W. Armstrong, *J. Chromatogr.*, 509 (1990) 303.

22   D.W. Armstrong, W. Li, A.M. Stalcup, J.I. Seeman, H.V. Secor, R.R. Izac, *Anal. Chim. Acta.*, 234 (1990) 365.

23   D.W. Armstrong, W. Li, C.D. Chang and J. Pitha, *Anal. Chem.*, 62 (1990) 914.

24   W.A. Konig, R. Krebber and P. Mischnick,*J. High Res. Chromatogr.*,12 (1989) 732.

25   E. Smolkova-Keulemansova, L. Feltl and S. Krysl, *J. Inclusion Phenomena,* 3 (1985) 183.

26   E. Smolkova, H. Kralova, S. Krysl and L. Feltl, *J. Chromatogr.*, 241 (1982) 3.

27   A. Berthod, W. Li and D.W. Armstrong, *Anal. Chem.*, In Press.

28   F. Cramer and F.M. Henglein, *Angew. Chem.,* 68 (1956) 649.

29   F. Cramer and F.M. Henglein, *Chem. Ber.,* 90 (1957) 2572.

30   D.W. Armstrong, US Patent No. 4,359,399 (1985).

31   D.W. Armstrong and W. Demond, *J. of Chromatogr. Sci.*, 22 (1984) 411.