

Fig. 8. GC-ECD chromatogram of fraction III from the pyrenyl-silica HPLC column containing pentachloronaphthalenes with Halowax 1014 (trace A), non-*ortho* CBs (trace B) and a cleaned-up extract of cod liver oil (trace C), showing the separation by CP Sil 8 50 m \times 0.22 mm I.D., film thickness 0.22 μ m. Peaks: 1 = CB 77, 2 = CB 126, 3 = CB 169 and 4 = internal standard.

groups of similar or different structural classes of planar compounds which are present in the samples at very different concentrations. The separation can be tailored to isolate compounds that may be unresolved by capillary GC with either ECD or MS (or both). Most of these separations are highly reproducible and readily automated. The columns are robust and stable over long periods of operation provided that the samples have been through a rigorous clean-up procedure. One of the main reasons for the

longevity of the column is that it operates in the normal mode using simple non-polar solvents, as opposed to the reversed-phase mode where the water phase tends to dissolve the silica substrate. Where routine sample clean-up proves to be insufficient, the pyrenyl-silica column can be affected. Usually an incomplete clean-up, particularly involving lipids which have not been removed from biological tissue extract, will result in a decrease both in k' for each compound and a loss in resolution. Performance can be restored by flushing the column with ethyl acetate and then returning to the elution solvent, *n*-hexane. An improved stability and resolution is obtained for a number of separations, e.g. CB 138 and CB 163, if the pyrenyl-silica column is cooled to 0°C.

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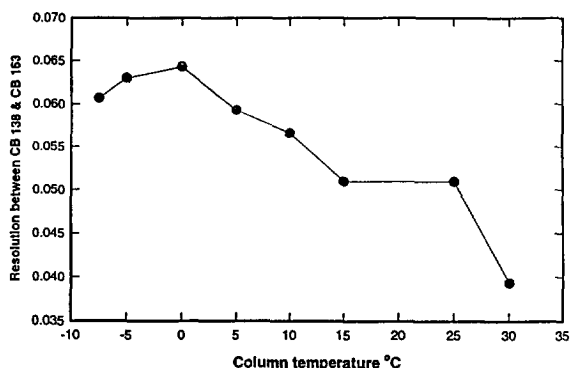


Fig. 9. Plot of the resolution between CB 138 and CB 163 on a pyrenyl-silica HPLC column, 250 \times 0.46 mm I.D., as a function of the column temperature. The maximum resolution occurs around 0°C. The column cooling was controlled by a solid-state Peltier heat pump.

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Gas chromatography of petroleum-derived waxes and high-molecular-mass linear alcohols and acids

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Abstract

Capillary gas chromatography procedures on a 15 m × 0.25 mm I.D. wall-coated open-tubular (WCOT) metal column have been developed to separate the components of microcrystalline waxes, paraffin waxes, Unilin® alcohols, or Unacid™ acids. For some microcrystalline waxes about 140 *n*-alkanes and non-normal, i.e., branched or cyclic, hydrocarbons with carbon numbers between 18 and 62 may be resolved. The peak-area percentages of the *n*-alkanes in microcrystalline or paraffin waxes are reproducible. In either underivatized Unilin® alcohols or Unacid™ acid methyl esters 20 to 24 homologs with carbon numbers between 14 and 60 are resolved from adjacent components and from *n*-alkane intermediates; their peak-area percentages are reproducible.

1. Introduction

Waxes of different compositions have been used for a variety of applications throughout the course of human civilization. Industrial waxes may be classified as natural waxes or synthetic waxes [1,2]. Waxes which are derived from petroleum may be subdivided into two classes on the basis of their physical properties and molecular masses: (1) paraffin waxes and (2) microcrystalline waxes. Paraffin waxes typically have average molecular masses ranging from about 360 to 420 and microcrystalline waxes have average molecular masses from about 580 to 700 [3]. Polywax® polyethylenes were introduced into the marketplace in 1970 by Petrolite (St. Louis, MO, USA), and are composed of polyethylene oligomers of molecular masses between

about 350 and 2000. Within the past decade, Unilin® alcohols and Unacid™ acids have become commercially available. These products, which are based on the technology used to produce Polywax® polyethylenes, are used as reactive intermediates, e.g. for non-ionic surfactants, and in personal-care products, adhesives, emollients, defoamers, coatings, moldings, and pulp and paper products. The physical properties of petroleum-derived waxes depend on the relative amounts of *n*-alkanes and non-normal hydrocarbons and on the molecular mass distributions of these compounds. The physical properties and chemical reactivities of Unilin® alcohols and Unacid™ acids depend on the molecular mass distribution of the alcohols or acids and on total quantity of reactive components.

It is the objective of the work reported herein to measure the molecular mass distributions of Unilin® alcohols, Unacid™ acids, paraffin

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waxes, and microcrystalline waxes using gas chromatography on a wall-coated open-tubular (WCOT) metal capillary column. The first chromatography of microcrystalline waxes on packed gas chromatography (GC) columns was reported many years ago [4]. About 40 *n*-alkane peaks of carbon numbers 20 to 70 in the urea-adducible fractions of four microcrystalline waxes with melting points from 60 to 80°C were resolved on a 2 ft. × 1/4 in. (0.61 m × 0.635 cm) O.D. stainless-steel column packed with 3% SE-52 on Chromosorb G [4]. Good resolution was also obtained for seven paraffin waxes. The unfractionated microcrystalline waxes, however, did not show satisfactory separation of normal alkanes from non-normal hydrocarbons on this short packed GC column. No well-defined peaks were seen for components with more than about 74 carbon atoms. This same column did give good resolution of about 40 *n*-alkanes in a Fisher–Tropsch wax [5].

When capillary GC columns were developed, much better resolution of *n*-alkanes from non-*n*-alkanes and elution of hydrocarbons of carbon numbers greater than 70 was achieved. For example, when aluminum-clad fused-silica WCOT capillary columns were introduced in 1986, there was a dramatic improvement in both resolution and the upper temperature limit of the column, thereby allowing peaks of at least 100 carbon atoms to be observed [6,7]. Since 1986, there have been numerous reports of high-temperature capillary gas chromatography of waxes and other compounds. Many of these results for petroleum-derived waxes and various synthetic waxes have been summarized recently by Philp [8] and Del Rio and Philp [9]. Barker [10,11] has published two excellent, very comprehensive, and thoughtful reviews of chromatographic analyses of refined and synthetic waxes. He clearly describes the problems of injection, column types, detection, and integration of gas chromatography peaks.

Another major improvement in capillary column technology took place about the start of this decade, namely the introduction of WCOT stainless-steel columns which were based on the work of Takayama and Takeichi [12] and Buyten et al.

[13]. Using this technology, Chrompack developed the Ultimet HT-SIMDIST-CB columns. Using a 15 m × 0.25 mm I.D. HT-SIMDIST-CB Ultimet column in this laboratory, GC procedures which are reported below have been developed to detect batch-to-batch variations in microcrystalline waxes, paraffin waxes, Unilin® alcohols, or Unacid^{RM} acids and to provide some information about composition.

2. Experimental

2.1. Reagents and materials

Be Square® 195 Amber microcrystalline wax, Victory® Amber microcrystalline wax, Unilin® alcohols, and UnacidTM acids are commercial products which are manufactured and sold by Petrolite Polymers Division (Tulsa, OK, USA). The fully refined paraffin wax of melting point 165°F (74°C) was obtained from another source.

The solvent 1,2-dichlorobenzene was purchased from Sigma–Aldrich (Milwaukee, WI, USA), catalog no. 27, 059-8, 99% HPLC grade.

To prepare known mixtures, the following chemicals, 98–99%, were purchased: *n*-tetracontane, *n*-pentacontane, and *n*-hexacontane from Fluka Chemika–Biochemika (Ronkonoma, NY, USA), and *n*-dotriacontane, *n*-tetracosane, *n*-C₁₄–C₂₄ alcohols, and *n*-C₁₄–C₂₄ fatty acid methyl esters from Alltech (Chicago, IL, USA).

Meth Prep II (5.3% *m*-trifluoromethylphenyl trimethyl ammonium hydroxide in methanol) is sold by Alltech (Chicago, IL, USA).

The 1-μl syringe with the sample contained in the needle was purchased from Hamilton (Reno, NV, USA), catalog no. 7001.

2.2. Instrumentation

The Model 8500 gas chromatograph with flame ionization detector and programmed temperature vaporizer (PTV) is produced by the Perkin-Elmer (Norwalk, CT, USA).

The Hewlett-Packard (Palo Alto, CA, USA) LDS with 5.24 software was used for peak-area integration and generation of the chromatograms

and figures. The horizontal baseline method, which is described by Barker [10], was used for peak integration of all waxes except Victory® Amber.

2.3. Procedure for microcrystalline wax

Column: 15 m × 0.25 mm I.D., WCOT Ulmetal, film thickness 0.15 μm, stationary phase HT-SIMDIST-CB, maximum operating temperature programmed 450°C, Chrompack International (Middelburg, Netherlands), catalog no. 99921 (custom made). This column still gives good separation after at least 250 injections. Carrier gas: helium (zero grade); flow-rate 41.3 ± 0.383 cm/s or 1.2 ml/min at initial oven temperature. Flow-rates combustion gases: hydrogen (zero grade), 40 ml/min; air (zero grade), 400 ml/min. Flame ionization detector (FID) temperature 430°C. Sensitivity: high. PTV events: -1.99 min: temperature 50°C; 0.01 min: temperature 425°C. Oven temperature program: initial oven temperature 170°C, hold 2 min; ramp 1 rate, 13°C/min to 300°C; ramp 2 rate, 10°C/min to 430°C, hold 5 min. Depth of injection into PTV liner, 50 mm. Injection volume, 0.5 to 1.0 μl. Split ratio, 25:1. Sample concentration in *o*-dichlorobenzene at ca. 60°C: 0.5–0.7 wt.%.

2.4. Procedure for Unilin® alcohols

The same 15 m × 0.25 mm I.D. HT-SIMDIST-CB column as for microcrystalline waxes was used. Carrier gas, helium (zero grade); flow-rate, 1.2 ml/min. Flow-rates combustion gases: hydrogen 40 ml/min; air 400 ml/min. FID detector temperature 435°C. Sensitivity: high. PTV events: -1.99 min: temperature 50°C; 0.01 min: temperature 385°C. Oven temperature program: initial oven temperature 90°C, hold 2 min; ramp 1 rate, 21°C/min to 180°C; ramp 2 rate, 16°C/min to 250°C; ramp 3 rate, 10°C/min to 430°C, hold 1 min. Depth of injection into PTV liner, 50 mm. Injection volume: 0.5 to 1.0 μl. Split ratio, 25:1. Sample concentration in *o*-dichlorobenzene at ca. 60°C: 0.5–0.7 wt.%.

2.5. Procedure for Unacid™ acids

The same 15 m × 0.25 mm I.D. HT-SIMDIST-CB column as for microcrystalline waxes was used. Carrier gas: helium; flow-rate, 1.2 ml/min. Flow-rates combustion gases: hydrogen 40 ml/min; air 400 ml/min. FID detector temperature, 435°C. Sensitivity, high. PTV events: -1.99 min: temperature 50°C; 0.01 min: temperature 420°C. Oven temperature program: initial oven temperature 140°C, hold 2 min; ramp 1 rate, 21°C/min to 180°C; ramp 2 rate, 16°C/min to 250°C; ramp 3 rate, 10°C/min to 435°C. Depth of injection into PTV liner, 50 mm. Injection volume: 0.5 to 1.0 μl. Split ratio, 25:1. Esterification procedure: weigh about 35 mg of Unacid™ acid in a 5-ml round-bottom flask. Add 3.0 ml *o*-dichlorobenzene and attach to a condenser. Heat at ca. 60°C until solid has dissolved. Add 1.0 ml of Meth Prep II (Alltech, Deerfield, IL, USA) through the top of the condenser. Heat 3 to 5 min until solution is homogeneous. Quickly transfer the solution to a 5 ml vial. Inject an aliquot of the warm (ca. 60°C) solution into the PTV.

3. Results and discussion

3.1. Petroleum-derived waxes

The chromatogram of Be Square® 195 Amber, a microcrystalline wax of melting point 93°C, is shown in Fig. 1. Certain peaks which elute at the same retention time as pure *n*-alkanes are marked. Based on proton NMR peak areas of CH₂ and CH₃ groups, the major peaks are presumed to be mostly *n*-alkane homologs. Hence these components are designated “*n*-alkanes” in Figs. 2 and 4, Table 1, and the following text. Peaks which contain hydrocarbons with 21 to 74 carbon atoms are shown in Fig. 1. *n*-Alkanes and non-normal hydrocarbons, which probably include branched and cyclic alkanes, co-elute if they contain more than 62 carbon atoms. In Fig. 2, the area-percents of *n*-alkanes are plotted as a function of their carbon numbers. The total amount of *n*-alkanes

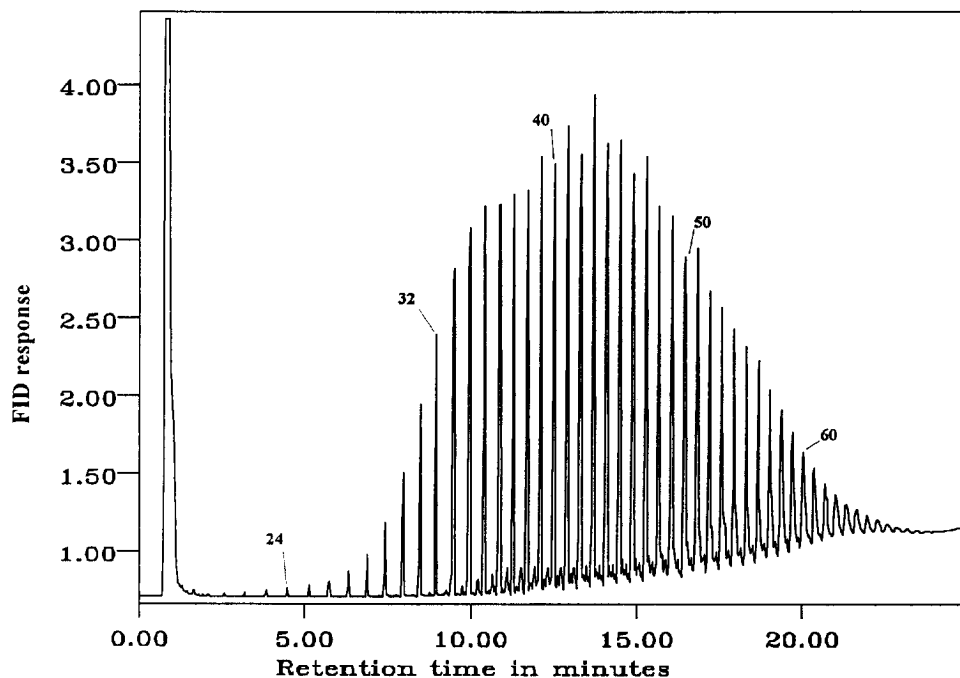


Fig. 1. Gas chromatogram of Be Square® 195 Amber microcrystalline wax.

with carbon numbers between C_{22} and C_{62} is 83 area-percent and the total amount of all hydrocarbons with carbon numbers between C_{63} and C_{73} is 4.2 area-percent. Hence this wax contains about 15% non-normal hydrocarbons. Barker [10] has reviewed the composition of petroleum-

derived waxes. He describes their complexity in detail.

The area-percents of the *n*-alkanes in the Be Square® 195 Amber are probably a good approximation of their weight-percents, since for known mixtures of several pure *n*-alkanes with 24 to 60 carbon atoms the area-percents and weight-percents are about equal, e.g. differing by ca. 1–2%.

The mean values of five replicate GC runs and their standard deviations of selected *n*-alkanes with carbon numbers between 22 and 60 are given in Table 1. From these values of the standard deviations, it may be concluded that the reproducibility of this GC procedure is good.

The chromatogram of Victory® Amber, a microcrystalline wax of melting point 79°C, is shown in Fig. 3. The distribution of *n*-alkanes is shown in Fig. 4. For components with more than 57 carbon atoms the *n*-alkanes and non-normal alkanes co-elute. The rather large rising “background” starting at about 34 carbon atoms probably is caused by incomplete resolution of *n*-alkanes and non-normal hydrocarbons of similar

Table 1

Mean values and standard deviations of the area-percents of selected *n*-alkanes in Be Square® 195 Amber and Victory® Amber

Carbon number	Be Square 195 Amber Mean \pm S.D. ($n = 5$)	Victory Amber Mean \pm S.D. ($n = 5$)
22	0.0469 \pm 0.0103	0.0488 \pm 0.00294
26	0.151 \pm 0.0147	0.232 \pm 0.00705
30	0.976 \pm 0.0182	0.616 \pm 0.0166
34	2.18 \pm 0.0517	1.63 \pm 0.0358
38	2.68 \pm 0.0568	2.26 \pm 0.0612
42	3.48 \pm 0.0418	2.03 \pm 0.0763
46	3.31 \pm 0.181	2.01 \pm 0.119
50	3.03 \pm 0.0202	1.60 \pm 0.0857
54	2.57 \pm 0.0243	1.11 \pm 0.0564
58	2.06 \pm 0.0213	1.18 \pm 0.0342

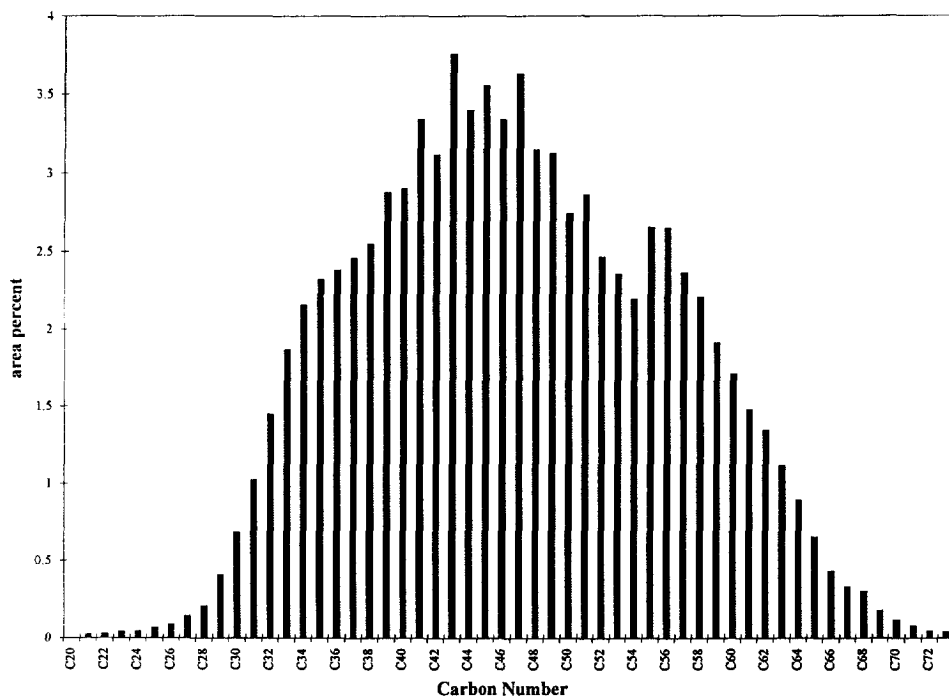


Fig. 2. Distribution of *n*-alkanes in Be Square® 195 Amber microcrystalline wax.

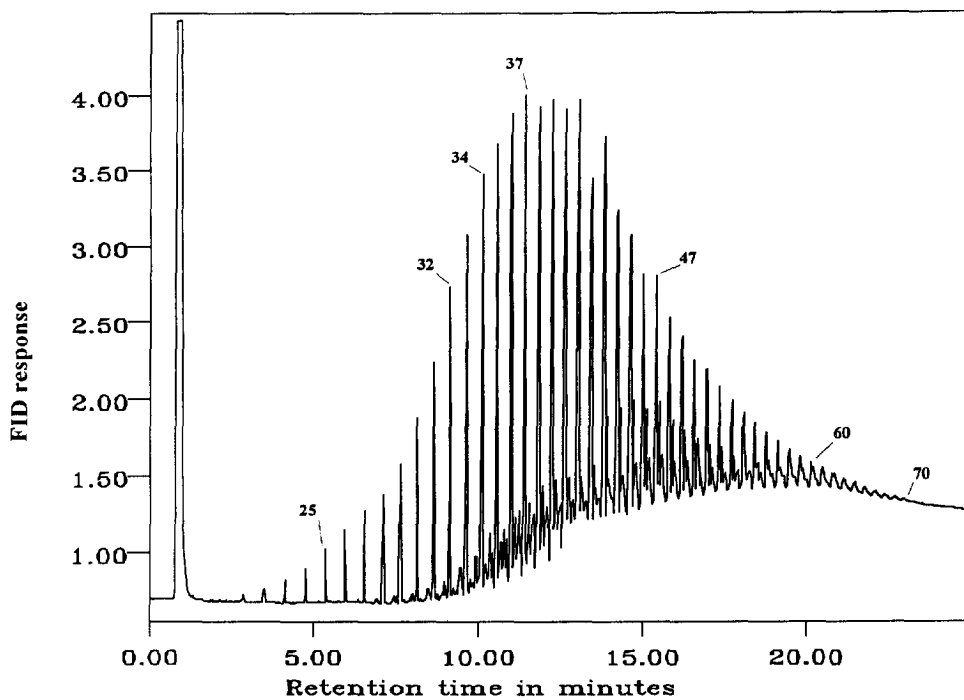


Fig. 3. Gas chromatogram of Victory® Amber microcrystalline wax.

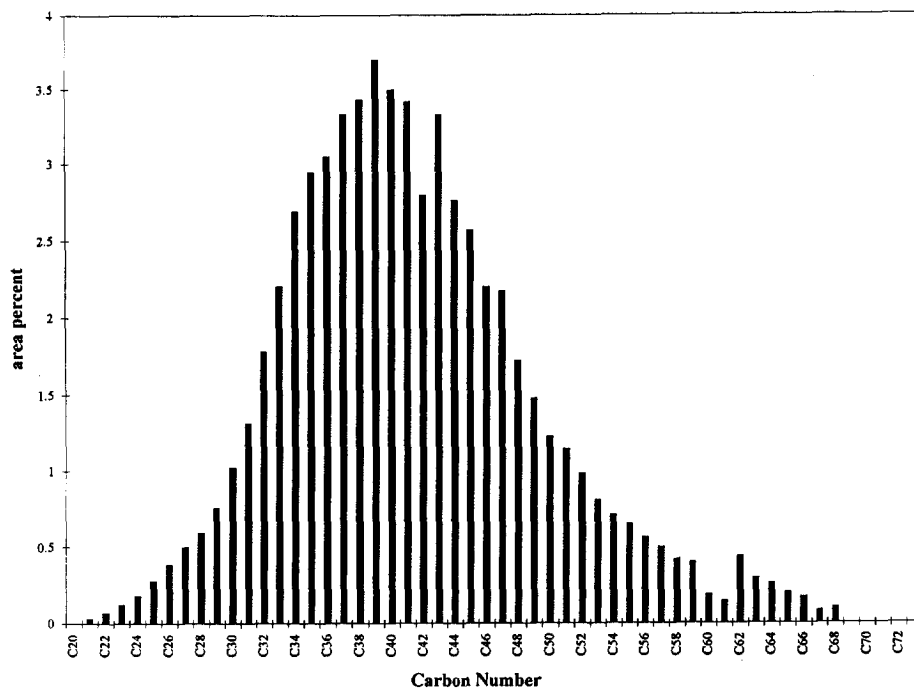


Fig. 4. Distribution of *n*-alkanes in Victory® Amber microcrystalline wax.

carbon numbers. The sum of the area-percents of the major peaks above the background using a modified horizontal background integration is 59% for components with 20 to 62 carbon atoms. The sum of the area-percents of peaks with 62 to 68 carbon atoms is only 1.1%. The mean values and standard deviations of the area-percents of selected *n*-alkane peaks between C₂₂ and C₆₀ are given in Table 1. Because of incomplete resolution and possible co-elution, the standard deviations tend to be larger than those of the major components of Be Square® 195 Amber. Nevertheless, gas chromatography appears to be a satisfactory means of detecting batch-to-batch variations in lower-melting-point microcrystalline waxes. Barker [10] has given a very thorough discussion of these problems of integration and resolution of components of microcrystalline waxes.

The GC procedure for microcrystalline waxes which is described in the Experimental section above for a 15-m long column, represents a

compromise between two diametrically opposite goals: (1) maximum resolution of *n*-alkanes from non-normal hydrocarbons, particularly in the 20 to 50 carbon number range, and (2) elution of the highest-molecular-mass hydrocarbons in the wax near the maximum operating temperature of the column and thermal stability of the hydrocarbons. As noted above, C₇₄, which elutes at 430°C after a 2 min hold, appears to be the last peak that can be integrated accurately. Three or four non-normal hydrocarbon peak areas are measured between *n*-alkane pairs of carbon numbers 32 and 48, while only two non-normal hydrocarbons are resolved between *n*-alkane pairs of carbon numbers 49 and 57. A larger column, e.g. 30 m, would give better resolution of the C₂₀–C₄₀ hydrocarbons, but then no components with more than possibly 55 carbon atoms would have peaks of reproducible areas or even be detected at all. Because microcrystalline waxes, particularly those with melting points less than about 85°C, probably contain at least sever-

al hundred chemical compounds, gas chromatography of the unfractionated waxes in a finite time to determine their exact compositions is not possible, but useful comparisons of waxes can still be made.

An appreciably different and much simpler chromatogram is obtained for a fully refined paraffin wax as is shown in Fig. 5. Here, the *n*-alkanes of carbon numbers C_{22} through C_{37} constitute 91% of the peaks which were integrated. The distribution of *n*-alkanes, i.e., area-percent versus carbon number, which is shown in Fig. 6, is much sharper than the distributions of the microcrystalline waxes, which are depicted in Figs. 2 and 4. For paraffin waxes it would be readily feasible to use a longer column to improve resolution of *n*-alkanes and non-normal hydrocarbons. The mean values and standard deviations of *n*-alkanes with 22 to 36 carbon atoms in this paraffin wax are presented in Table 2, demonstrating that the procedure has a very good reproducibility.

One key problem which must be addressed in high-temperature chromatography, is that of sample discrimination during the injection process, resulting in incomplete transfer of the higher-boiling-point compounds from the syringe into the injection part and onto the column. The use and optimization of the Perkin-Elmer programmed temperature vaporizer has been described [14–16]. Barker [10,11] has made extensive studies of injection techniques, especially PTV. Grob [17] recently has reviewed injection techniques in capillary GC. Although he concludes “today’s injection techniques often provide satisfactory results” he laments the lack of progress in solving “severe problems”. The results in Table 3 suggest that our PTV program is not causing discrimination of C_{50} or C_{60} in the mixture of pure *n*-alkanes–alkanes, since the theoretical weight-percents and measured area-percents differed by 2.3% and 1.3%, respectively. The author believes that use of the PTV injector and a syringe with sample in the needle

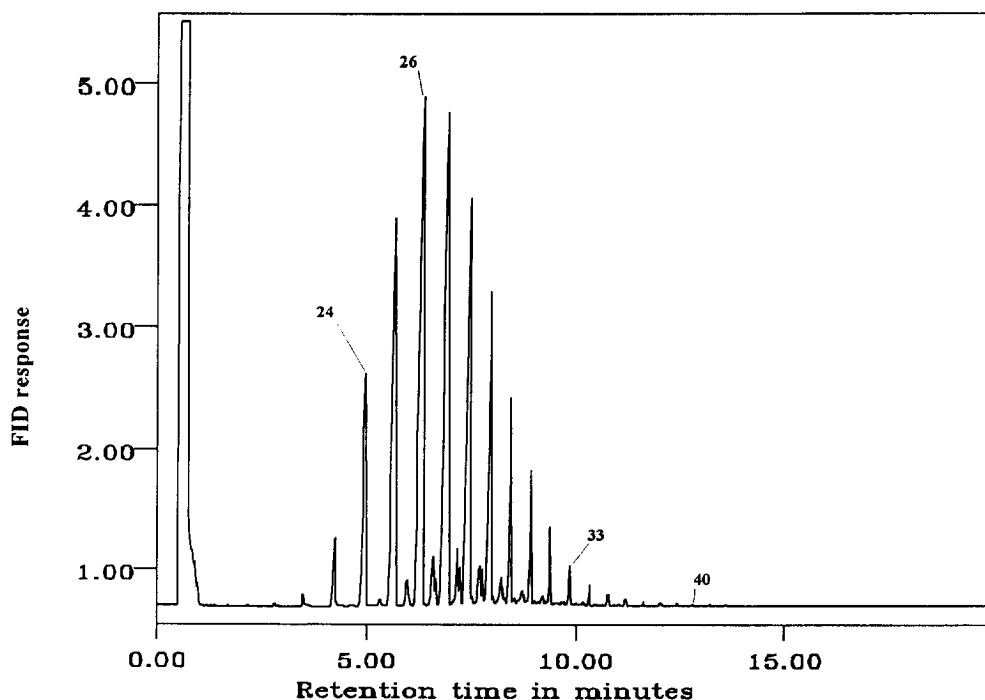


Fig. 5. Gas chromatogram of fully refined 165°F paraffin wax.

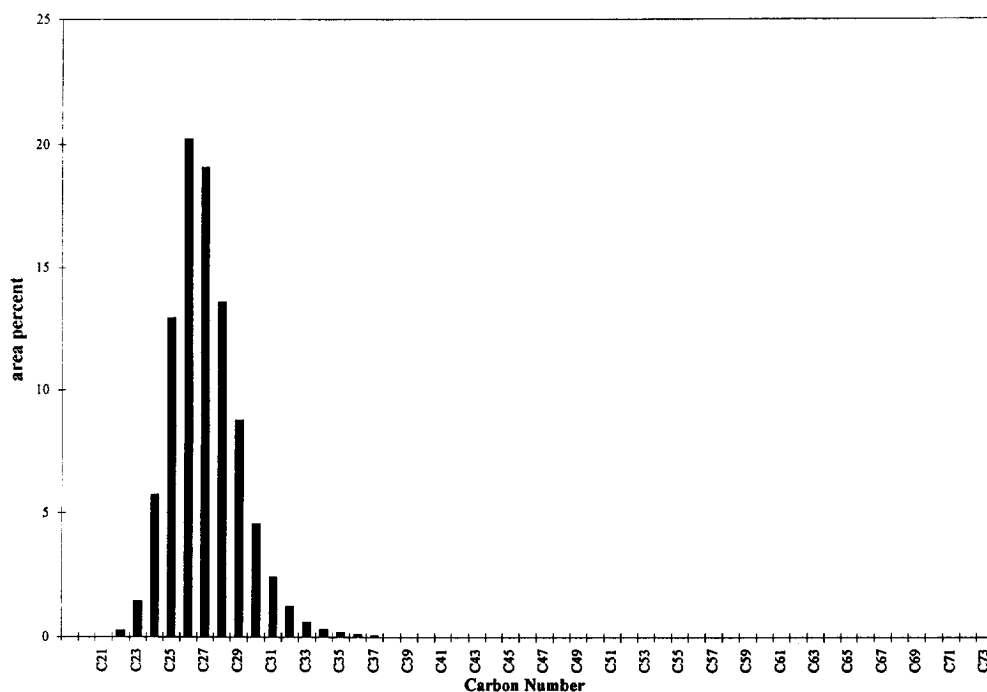


Fig. 6. Distribution of *n*-alkanes in fully refined 165°F paraffin wax.

is required for reproducible GC of microcrystalline waxes, Unilin® alcohols, and Unacid™ acids.

Table 2

Mean values and standard deviations of *n*-alkanes with 22 to 36 C atoms in a fully refined 165°F paraffin wax

Carbon number	Mean ± S.D. (<i>n</i> = 5)
22	0.248 ± 0.0175
23	1.46 ± 0.0693
24	5.81 ± 0.116
25	13.0 ± 0.0895
26	20.2 ± 0.144
27	18.9 ± 0.205
28	13.6 ± 0.243
29	8.67 ± 0.129
30	4.52 ± 0.0415
31	2.47 ± 0.0737
32	1.33 ± 0.0554
33	0.633 ± 0.0602
34	0.389 ± 0.0356
35	0.229 ± 0.0225
36	0.133 ± 0.0151

3.2. Unilin® alcohols

Unilin® alcohols of average molecular masses between 350 and 700 are commercially available. The chromatogram of one of these products, Unilin® 425, is shown in Fig. 7. About 55 components in all are resolved. The major peaks are *n*-alkanols of carbon numbers 14 to about 66,

Table 3

Comparison of weight-percents in a known mixture of *n*-alkanes with measured GC area-percents

Carbon no. of <i>n</i> -alkane	Weight-percent theory	Measured area-percent ± S.D. (<i>n</i> = 10)
24	11.7	10.0 ± 0.479
32	22.2	21.25 ± 0.854
40	14.4	13.4 ± 0.665
50	24.4	26.7 ± 0.666
60	27.2	28.5 ± 2.56 ^a

^aPeak is on slightly rising background and shows some tailing.

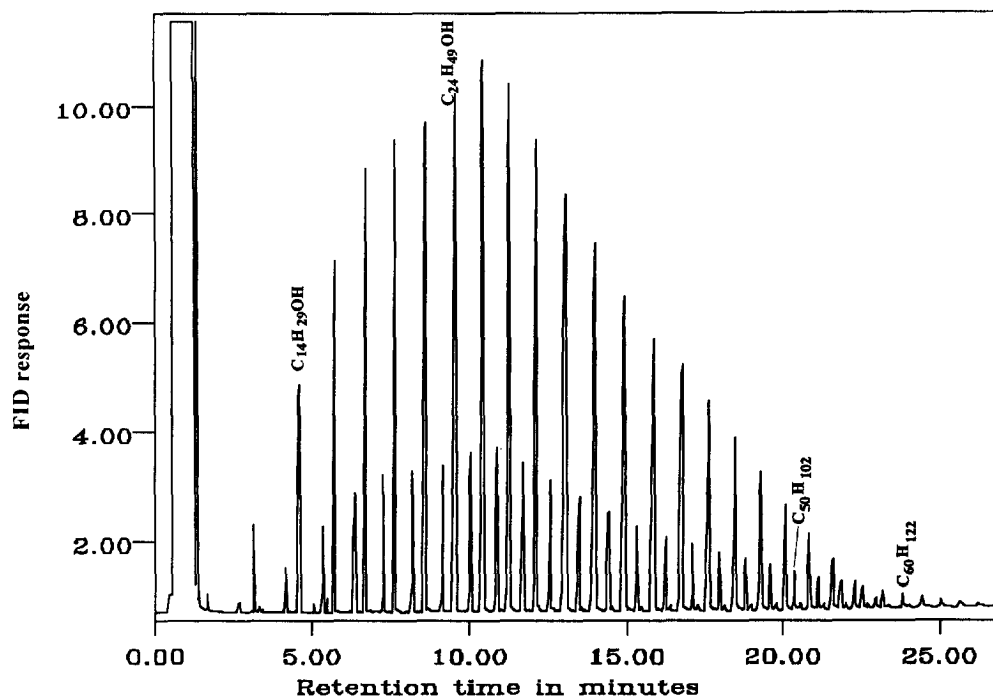


Fig. 7. Gas chromatogram of Unilin® 425 alcohol.

while the minor peaks are *n*-alkanes. After $C_{54}H_{109}OH$, the alcohols and alkanes co-elute. The sum of the area-percents of *n*-alkanols with carbon numbers 14 through 54 is 80.0 ± 0.163 (eight replicate runs). This value is consistent with the total *n*-alkanol content which is measured by the hydroxyl-number procedure. The mean values and standard deviations of the area-percents of selected *n*-alkanols in the carbon number range are presented in Table 4. These standard deviations show that the procedure is reproducible.

A known mixture of pure *n*-alkanols with 14, 16, 18, 20, 22, and 24 carbon atoms of weight-percents 19.7, 15.4, 20.5, 11.8, 16.2, and 16.4%, respectively, was prepared to determine retention times and to compare measured GC area-percents with these theoretical weight-percents. The weight-percents and area-percents of the *n*-alkanols in this mixture differed by less than 2%. $n-C_{24}H_{49}OH$ eluted without loss during injection or decomposition with PTV programs of either 50 to 285°C or 50 to 325°C. A source of

Table 4
Mean values and standard deviations of the area-percents of selected *n*-alkanols in Unilin® 425

Carbon number	Mean \pm S.D. ($n = 8$)
14	1.25 ± 0.0458
16	2.10 ± 0.0747
18	3.02 ± 0.0601
20	3.92 ± 0.0553
22	4.77 ± 0.0851
24	5.62 ± 0.0699
26	6.51 ± 0.0476
28	7.02 ± 0.0770
30	7.17 ± 0.100
32	7.02 ± 0.116
34	6.47 ± 0.114
36	5.57 ± 0.129
38	4.61 ± 0.0734
40	3.87 ± 0.129
42	3.15 ± 0.151
44	2.44 ± 0.142
46	1.85 ± 0.130
48	1.34 ± 0.118
50	0.920 ± 0.0952
52	0.590 ± 0.0746