This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation & Purification Reviews

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

Porous Layer Open Tubular Gas Chromatography Columns

J. G. Nikelly[a]
[a] Department of Chemistry, Philadelphia College of Pharmacy and Science, Philadelphia, Pennsylvania

To cite this Article Nikelly, J. G.(1974) 'Porous Layer Open Tubular Gas Chromatography Columns', Separation & Purification Reviews, 3: 2, 423 — 441
To link to this Article: DOI: 10.1080/03602547408066032
URL: http://dx.doi.org/10.1080/03602547408066032

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION AND PURIFICATION METHODS, 3(2), 423-441 (1974)

POROUS LAYER OPEN TUBULAR GAS CHROMATOGRAPHY COLUMNS

J. G. Nikelly
Department of Chemistry, Philadelphia
College of Pharmacy and Science
Philadelphia, Pennsylvania 19104

Introduction

Throughout the two decade history of gas chromatography, the design and modification of the column has been the subject of numerous studies resulting in many improvements and innovations. One of the more important innovations is the concept of open tubular columns, and their modification to porous layer open tubular (PLOT) columns.[1]

Unlike packed columns, open tubular columns permit a relative uniform distribution of liquid phase on the internal surface of the column and at the same time provide an unrestricted flow of carrier gas thereby reducing the pressure drop. These characteristics mean more theoretical plates per column length and allow the use of longer columns with the result that the total number of plates can be and often is 100 times that of typical packed columns.

On the other hand, while open tubular columns may have more theoretical plates, they also have less sample capacity and a lower partition ratio, both of these due to the lower surface area which in turn limits the quantity of liquid phase that can be used in the column. While their low sample capacity makes open tubular columns less practical than packed columns, this problem can be compensated by the use of a sample (stream) splitter: a relatively large sample is injected into a higher flow carrier gas, evaporated, split into two streams of highly unequal flow and the smaller of the two is introduced into the column. A typical split ratio is 100:1 and a typical sample volume introduced into the column is 0.01 μl.

The lower partition ratio, k', of open tubular columns results from the high phase ratio, β, which is the ratio of the volume of gas phase (high in open tubular columns) to the volume of liquid phase (low in open tubular columns). Phase ratios of open tubular columns are usually between 50 and 100 compared with 10 to 20 for packed columns; therefore, according to equation 1, the partition ratio k'

$$k' = K/\beta \qquad 1$$

for open tubular columns is about 5 times smaller than that of packed columns, the partition coefficient, K, being of constant value for a given solute and being dependent only on the choice of liquid phase and on the temperature.

That a low partition (capacity) ratio is undesirable can be shown through the resolution equation 2 or the column performance equation 3:

$$R = \left(\frac{\sqrt{N}}{4}\right)\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k'}{k' + 1}\right) \qquad 2$$

$$C.P. = \frac{N}{t_{sec}} \left(\frac{k'}{k' + 1}\right)^2 \qquad 3$$

where R is the resolution of two (adjacent) peaks, N is the number of theoretical plates, α is the relative retention time of the two peaks, C.P. is an index of column performance and t_{sec} is the retention time of the second peak, expressed in seconds.

One way to increase the low partition ratio of open tubular columns is to increase the volume of liquid phase. But this must be done without increasing the thickness of the liquid film; otherwise, the plate number and, consequently, resolution will decrease as k' is increased. Such improved open tubular columns were originally suggested in 1960 and were first tried by Halasz and Horvath.[1,2]

HOW PLOT COLUMNS ARE MADE

The increase in liquid phase volume, without an increase in liquid film thickness, is achieved by increasing the internal surface area without restricting the flow or openness of the column. The increased surface is provided by using a finely divided diatomaceous or other support that is mixed with the liquid phase and coated onto the column walls by a static[3] or dynamic coating process that results in support-coated or porous layer open tubular (SCOT or PLOT) columns. PLOT will be the term used in this chapter since it is more generic than SCOT.[4]

PLOT columns made by the static method are commercially available and have been widely described in the literature.[4-8] PLOT columns made by the dynamic method are not available commercially but can be easily made in the orginary analytical laboratory without requiring highly specialized elaborate apparatus and techniques.[9-12] Consequently, they are considerably less expensive and can be tailored to the analytical applications of a particular laboratory, i.e., column parameters can be optimized. This chapter pertains largely to PLOT columns made by the dynamic coating method.

Except for the tubing, virtually all the apparatus and materials required for the preparation of PLOT columns are readily available in most laboratories. The recommended tubing is stainless steel, 0.03 or 0.04-in. i.d. X 1/16-in. o.d., in lengths of 25 to 50-ft. available from several suppliers, including Handy and Harman Tube Co., which supplies the tubing cleaned and precut in 50-ft. lengths.

COLUMN DIAMETER

Successful PLOT columns have been made with i.d. ranging from 0.01 to 0.04-in. In principle, the smaller diameter gives better columns for three reasons: the phase ratio, β, is smaller (because of smaller void volume) resulting in a higher partition ratio, k'; the HETP value is smaller; and the optimum average gas velocity for a component is much larger than for a large diameter column. It is not without reason that the first reported PLOT columns were of 0.01-in. i.d.

In practice, the larger diameters are better, particularly for PLOT columns made by the dynamic coating method.[13] The larger diameter not only makes it easier to reclaim tubing (rinsing out and recoating) but it also permits, in the coating step, the use of thicker (more viscous) coating mixtures with less risk of clogging. Furthermore, the coating step can be carried out at higher linear velocity, which together with the increased viscosity of the coating mixtures, results in increased thickness of the porous layer and consequently in increased column efficiency.

Moreover, larger diameter columns have higher sample capacity and decreased extra-column effects. Both of these factors can often be critical in PLOT column performance.

COATING MIXTURE (SUSPENSION)

The material which is used as the finely divided support necessary to form the porous layer, can be finely ground Chromosorb-W, Silanox 101 or Chromosorb R-6470. Chromosorb is a flux-calcined diatomaceous earth while Silanox is a hydrophobic fumed silicon dioxide, both supports having a particle size of less than 10 micrometers.

PLOT columns have been made with several liquid phases including Carbowax 1540 and 20,000, Apiezon-L, SE-54, SE-30, Squalane and DEGS.

The nature of the dynamic coating procedure requires the coating mixture to have characteristics that result in a continuous thick porous layer with the proper ratio of liquid phase to solid support. This is generally achieved by using as coating mixture, a 2 to 6% solution of liquid phase in chloroform containing about 10% of solid support; and by coating the column at a rate of 10 to 50 cm/sec, a coating rate that sometimes requires up to 60 psig of nitrogen or air pressure. Since the all important requirement of thickness of the porous layer increases with the viscosity of the coating mixture, and since this viscosity should not be increased by adjusting the ratio of liquid phase to solid support, it follows that those liquid phases that are more or less solid (or less fluid) make better PLOT columns. Typical coating conditions, composition of coating mixtures, and column characteristics are given in Table I. (The Silanox columns were made by Max Blumer, Woods Hole Oceanographic Institution.)

A simple test can be used to determine whether the coating mixture is satisfactory. In the case of Silanox, a clean and polished metal spatula is immersed into the suspension, rapidly withdrawn and dried. A

TABLE I

Characteristics of Typical Columns

Support	Silanox 101	Silanox 101	Chromosorb R6470-1	Chromosorb R6470-1
Liquid Phase	Apiezon-L	Carbowax-20,000	OV-17	SE-30
Liquid Phase %	2.5	2.5	7	3
Length, ft.	33	12	50	50
i.d., in.	0.02	0.03	0.04	0.04
Liq. Load,mg/ft.	0.2	----	1.2	1.5
HETP, mm	1.0	1.3	1.1	1.0

thin, smooth, nongranular and relatively strong layer indicates a good suspension, while a heavy, cracked coat is unsatisfactory. In the case of R6470-1, a small amount of the suspension is drawn up by light suction into a capillary Pasteur pipet, dried with a gentle air flow and inspected with a magnifying glass against a light source; the coating should be smooth, continuous and sufficiently thick so that no light appears to pass through.

COATING RESERVOIR

A coating reservoir or filling tube which is required for the dynamic coating procedure, can be assembled from tubing and fittings. A simple version of the filling tube consists of a 4-in. length of ¼-in. o.d. metal tubing connected at one end to the column through a ¼- to 1/16-in. reducing union, and at the other end it is connected to the outlet of a nitrogen or air regulator, preferably but not necessarily by using a Quick-Connect fitting [10,14] (Figure 1). The reservoir is first connected to the column, then the suspension is deposited near the bottom of the reservoir with a long Pasteur pipet. The combined reservoir and

FIGURE 1
Apparatus For Coating PLOT Columns

column are then connected to the nitrogen tank and the pressure is increased until the appropriate flow rate is reached. The coating flow rate can be monitored by inserting the column exit into a beaker of water and observing the effluent rate or by determining the time required for the excess suspension to emerge from the column.

A recent report describes an all-metal coating reservoir of improved tee design with a ½-in. o.d. filling tube.[15] The main component of the assembly is a Swagelok heat exchanger tee with a bored-through reducer. The required parts are listed in Table II and the assembled reservoir is shown in Figure 2. The upper arm of the tee, "process tube" in heat exchanger terminology, is a 1/16-in. tube fitting while both the side arm and the lower arm (jacketing tube) are ¼-in. tube fittings. The column is inserted through the upper arm to within 2 mm of the reservoir bottom. The side arm is connected to the pressure source (air or nitrogen), a "Quick-Connect" Swagelok fitting being very suitable for this purpose. The lower arm is fitted with a 1¼-in. long X ¼-in. o.d. metal tube which is connected to a 2-in. long X ½-in. o.d. metal tube (reservoir) via a ½-in. to ¼-in. reducing union. The bottom of the reservoir is a ½-in. cap fitting. To coat a column, the reservoir is first disassembled at the reducing union, filled with a few milliliters of suspension, reassembled and connected to the pressure source.

TABLE II

Main Components of Reservoir Assembly

Description	Swagelok No.[14]
Heat Exchanger Tee	B-400-3-1BT-4
Reducing Union	B-810-6-4
Cap	B-810-C
Metal tubing, ½-in. o.d. X 2-in.	---
Metal tubing, ¼-in. o.d. X 1-1/8 in.	---

COATING PROCEDURE

The following procedure which describes in some detail the coating of a 50-ft. X 0.04-in. i.d. OV-

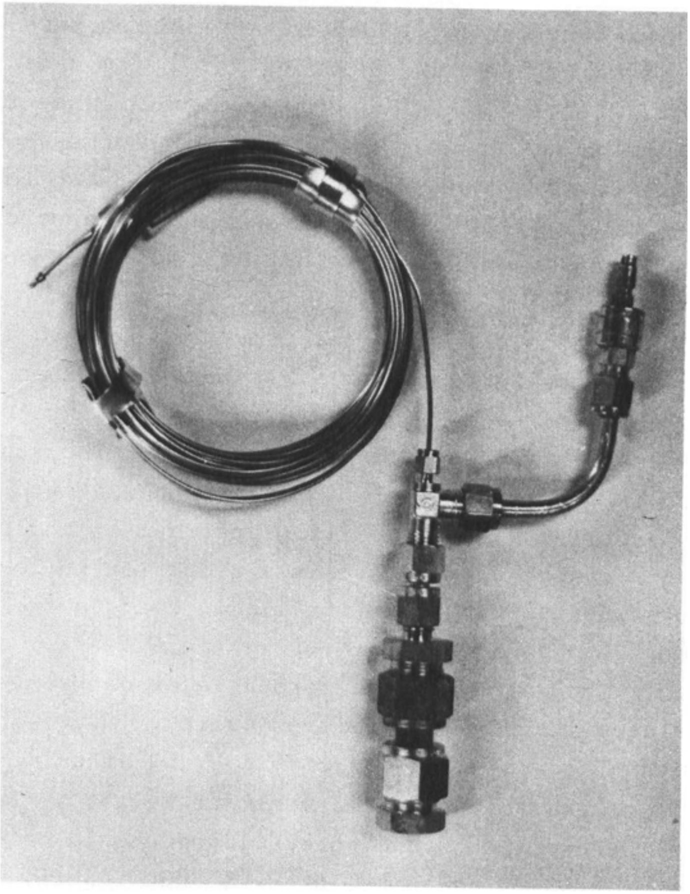

FIGURE 2
Improved Reservoir Assembly

17 column, can be used for other PLOT columns with suitable minor modifications.

New or used columns are rinsed with 10 to 20 ml. of chloroform and dried with nitrogen or air flow, a minimum of 3 or 4 minutes being required for this step. The column is then coated with solvent by adding 1.0 ml. of chloroform to the coating reservoir and applying 1 or 2 psig pressure for a few seconds. Four ml. of the coating mixture is then added to the coating reservoir, and pressure is applied, up to 60 (or in few cases 100) psig until the excess of coating mixture emerges from the column at which point the flow rate becomes considerably faster. The pressure is then reduced to 5 to 10 psig and the flow is thus maintained for another 10 to 15 minutes or until the weight of the coated column is constant.

A somewhat different procedure is used in the case of Silanox PLOT columns:[12] after the column is filled and drained of excess solvent, 5 to 10 volumes of suspension are added to the reservoir. The suspension is then flushed through the column at the desired flow rate; a valve or fitting upstream of the coating reservoir can be used to permit a reduction in gas pressure when the last coating liquid emerges from the column.

The weight of the porous layer can serve as preliminary indicator of column quality. By weighing the column before and after coating (and after driving off all of the solvent, i.e. constant weight), the minimum net weight of the porous layer should be 0.5 and 0.25 g. for 50-ft. columns, of 0.04 and 0.03-in. i.d., respectively. If the weight of the porous layer is lower than above, it is recommended that the column be rinsed with chloroform and recoated using a more viscous coating mixture, i.e., with higher concentration of liquid phase or solid support.

COLUMN CONNECTIONS

PLOT columns can be connected to each other or to the g.c. instrument inlet and outlet, using appropriate fittings of low volume. It is important that the fittings have essentially zero dead volume and sufficiently low total extra-column volume to prevent a significant loss of column efficiency.[16] For example, in a direct injection sample inlet (no sample splitting), the i.d. should be no more than 1.5 mm.; for the combining of two PLOT columns, an appropriate fitting is either a commercially available zero volume union or an ordinary 1/16-in. union modified by boring through with a 2/32-in. drill bit thereby enabling the two ends of the column to butt against each other.

For instruments that are not designed or equipped with 1/16-in. fittings, such fittings are usually obtainable from the gas chromatography instrument manufacturer. In those cases in which appropriate fittings are not available, the instrument may be converted by using reducing ferrules.[17] For example RF200/100 ferrules allow the connection of the 1/16-in. column into instruments of 1/8-in. fittings.

DUAL-LOAD PLOT COLUMNS

Since PLOT columns generally have a low liquid load, of the order of 1 or 2 mg. liquid phase per foot of column length, they can benefit from a gradient in k' (dual-load effect). Dual-load columns that contain about twice the liquid load in the front compared to the back of the column length, show up to 30% increase in column performance over that of equivalent single-load columns.[18] This is particularly effective in the case of large (0.05 ml.) injection volumes and for early or intermediate values of k'.

Dual-Load PLOT columns can be made by combining (with a low-volume union) two PLOT columns of appropriate liquid loads, e.g., 2 mg. per foot in the front and 1 mg. per foot in the back section.[19] Ordinary tubing unions (Swagelok) can be converted to low-volume by drilling through with a 2/32-in. bit in order to allow the ends of the columns to butt against each other.

Typical plate height and performance values for dual vs single-load columns are given in Table III.

TABLE III

Comparison of Dual and Single Load PLOT Columns

	HETP			Performance		
Load	$k' = 1$	$k_2' = 2$	$k' = 5$	$k' = 1$	$k' = 2$	$k' = 5$
Dual	1.7	1.6	2.1	9.7	2.0	11
Dual	1.9	1.6	2.0	24	19	17
Dual	2.3	1.5	2.4	6.5	21	10
Single	2.5	1.8	2.7	4.3	17	8.6
Single	2.2	1.9	2.7	6.9	16	8.1
Single	3.0	2.3	3.5	8.1	14	8.3
Average % change	-15	-22	-27	+27	+27	+28

The columns are 25 to 45 feet long, the liquid phase is Carbowax 1540 and the test sample is a four-component mixture of butanols and pentanol. The dual-load columns have lower plate heights and more effective plates per seond compared to equivalent single-load columns. As shown in the last row of Table III, this improvement (dual-load effect) is less for lower k' values, e.g., 15% decrease in plate height for k' = 1 vs 27% decrease for k' = 5. This is explainable by the increased overloading effect expected for early peaks. At high k' values, again the dual-load effect disappears because of peak-broadening that results as the peaks pass from the high to the low load, i.e., the front of a peak moves faster than the tail.

PLOT COLUMNS COMBINED WITH PACKED PRECOLUMNS

The dual-load effect can also be attained by using a packed precolumn.[20] As open tubular columns are limited to small injection volumes, packed precolumns are particularly useful in increasing the sample capacity. Furthermore, the use of 1/8-in. o.d. tubing for the precolumn is in itself a convenient method of adapting the popular 1/8-in. g.c. instrument fittings to the 1/16-in. fittings of PLOT columns. The only disadvantage of the combination columns is the peak-broadening that results from having to operate the precolumn at the relatively low carrier flow rates required by PLOT columns. It was found, however, that this was more than offset by the dual-load effect: as shown in Figure 3 the optimum flow rate (for minimum plate height) is not much different than that of plain PLOT columns, 5 to 7 cc per min. This is not unexpected since a typical precolumn length (1 ft.) is only 2% of the total length of the combination column. Even on a volume basis, the precolumn is less than 5% of the total combination, assuming that the total precolumn volume occupied by the carrier is approximately 60%. At 7 cc per min., the calculated average linear carrier velocity

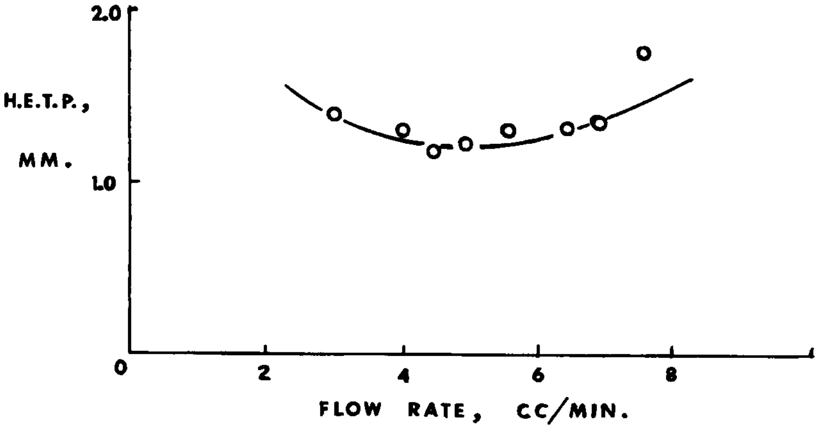

FIGURE 3
Column Efficiency As Function of Flow Rate

through the precolumn is considerably below optimum but nevertheless not low enough to make a significant contribution to the average plate height.

Variables such as precolumn length, inside diameter, % liquid phase, and carrier flow rate, can be empirically optimized for highest plate number, column performance index or sample capacity. A typical configuration is 24-cm. X 0.061-in. i.d. X 3% liquid phase combined with 50-ft. X 0.03-in. i.d. PLOT column of 1 to 2 mg. per ft. liquid phase. In favorable cases, e.g., for relatively large injection volumes, such as 0.1 microliters, the combination columns have double the plate number compared to plain PLOT columns. Such a comparison is shown in Table IV, which lists plate numbers for a combination and a plain PLOT column, with OV-17 as the liquid phase.

TABLE IV

Plate Numbers as a Function of Injection Volume and k'

Inj. Vol., μl.	PLOT		COMBINATION	
	k' ≅ 1	k' ≅ 6	k' ≅ 1	k' ≅ 6
0.01	7,500	11,000	13,000	10,500
0.04	6,800	9,100	9,000	10,400
0.10	4,300	4,600	9,000	8,900
0.15	-----	-----	7,900	6,900

The advantage of the combination columns is readily discernible in Figure 4 which compares the separation of an alcohol mixture on a PLOT and on a combination column.

APPLICATIONS OF PLOT COLUMNS

Examples of separation involving various compound types and PLOT columns are shown in Figures 5 to 8.

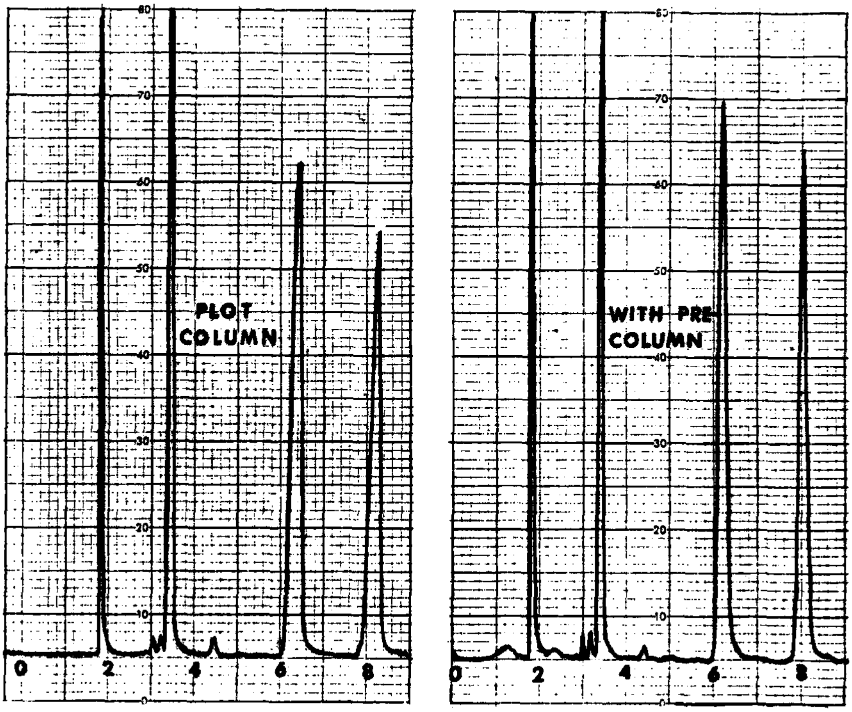

FIGURE 4
Separation of four alcohols on a PLOT column (50-ft. X 0.03-in. i.d., 1.0 mg. OV-17 per ft.) and on a combination column (24-cm X 0.06-in. i.d. X 3% OV-17 combined with above PLOT column). Injection Vol: 0.05 μl Retention time in minutes.

Figure 5 shows the separation on a DEGS column, of C_{16}-C_{18} methyl esters typical of linseed oil. The critical stearate-oleate separation is achieved in 8 min, even though the injected sample size is 0.05 μl, i.e., sufficiently large not to require sample splitting. This separation is comparable to that on a commercial 50-ft. PLOT column.[4,10]

Figure 6 shows the separation of lower primary alcohols on a Carbowax column. The resolution of MeOH-EtOH is more than complete. Owing to its low partition

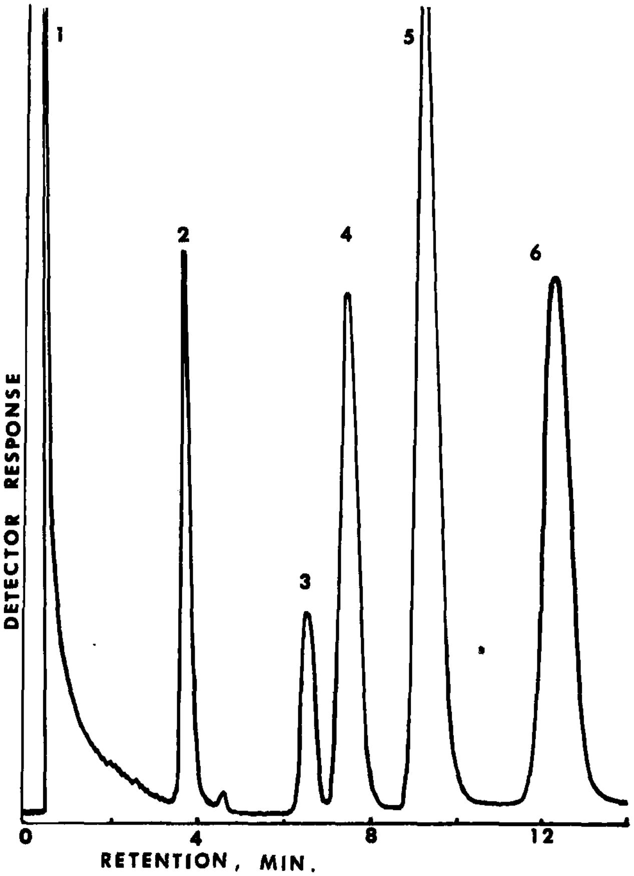

FIGURE 5
Separation of Methyl Esters. Column: DEGS, 25-ft. X 0.03-in. i.d. Temp: 180°C. Carrier: 7 cc per min. Sample Vol.: 0.05 µl. Peaks: 1-chloroform (solvent), 2-palmitate, 3-stearate, 4-oleate, 5-linoleate, 6-linoleate.

ratio, k'<2, this pair is normally considered a difficult separation for open tubular columns.

Figure 7 shows the separation of benzene homologs including the xylenes. Meta- and para-xylene are also considered a difficult pair, even on m-bis (m-phenoxyphenoxy) benzene, which is one of the very

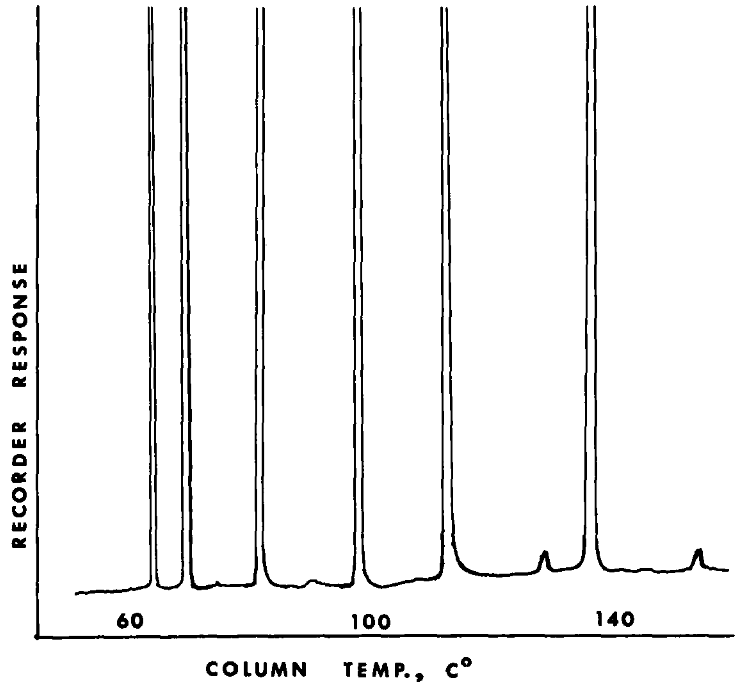

FIGURE 6
Separation of Lower Primary Alcohols. Column: 45-ft. X 0.040-in. i.d., Carbowax 20,000. Programmed Temp., 70 to 140°C. Sample: 0.06 µl normal alcohols, MeOH through hexanol

few liquid phases that can make this separation; the alpha value is barely 1.06 (ratio of retention times).

Figure 8 shows that a separation of #2 fuel oil hydrocarbons, which range up to C_{23}, can be completed in 20 min.

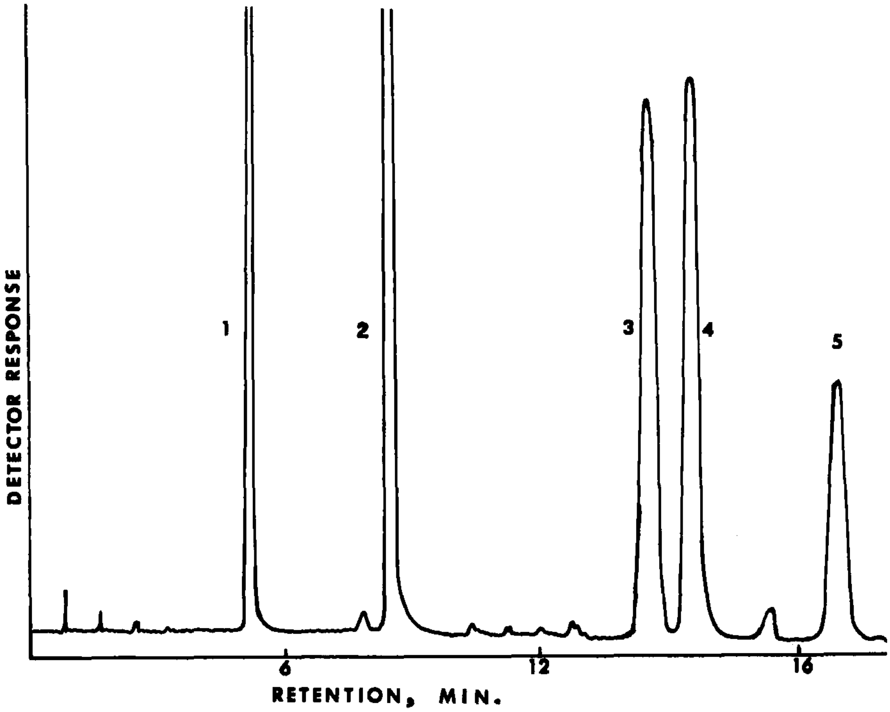

FIGURE 7
Separation of benzene homologs. Column: 50 ft. X 0.030-in. i.d. m-bis (m-phenoxyphenoxy) benzene with 5% Igepal Co-880. Temp.: 75°C. Sample Injection Vol.: 0.08 μl. Peaks: 1-benzene, 2-toluene, 3,4 and 5-xylenes.

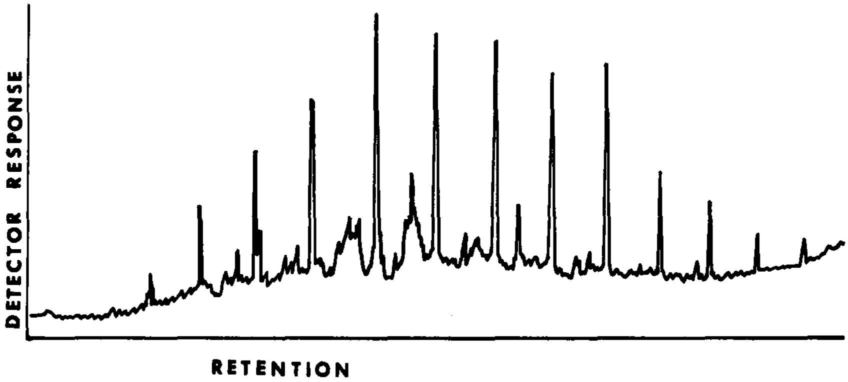

FIGURE 8
Separation of hydrocarbons in No. 2 Fuel Oil (up to C_{23}). Column: Silanox 101 with Apiezon-L (see Table I). From Max Blumer, Woods Hole Oceanographic Institution.[10]

REFERENCES

1. I. Halasz and C. Horvath, Anal. Chem., 35, 499(1963).
2. I. Halasz and C. Horvath, Nature, 197, 71(1963).
3. I. Halasz and C. Horvath, U. S. Patent 3,295,296 (1967).
4. L. S. Ettre, "Open Tubular Columns", Perkin-Elmer, Norwalk, Conn., 1973.
5. C. Horvath, L. S. Ettre and J. E. Purcell, Am. Lab., 6(8), 75(1974).
6. L. S. Ettre, J. E. Purcell and S. D. Norem, J. Gas Chromatog., 3, 181(1965).
7. L. S. Ettre, J. E. Purcell and K. Billeb, Separation Sci., 1, 777(1966).
8. L. S. Ettre, in "Gas Chromatography 1966", A. B. Littlewood, ed., The Institute of Petroleum, London, 1967, p.115.
9. J. G. Nikelly, Anal. Chem., 45, 2280(1973).
10. J. G. Nikelly and M. Blumer, Am. Lab., 6(1), (1974).
11. J. G. Nikelly, Anal. Chem., 44, 623(1972).
12. M. Blumer, Anal. Chem., 45, 980(1973).
13. J. G. Nikelly, Anal. Chem., 47, in press, (1975).
14. Crawford Fitting Company, Cleveland, Ohio 44139.
15. J. G. Nikelly, Anal. Chem., 46, in press (1974).
16. M. J. Hartigan and J. E. Purcell, Perkin-Elmer Chromatography Newsletter, 3, No. 1, 1(1974).
17. Alltech Associates, Inc., Arlington Heights, Illinois 60004.
18. J. G. Nikelly, Anal. Chem., 45, 1264(1973).
19. J. G. Nikelly, Anal. Chem., 46, 290(1974).
20. J. G. Nikelly, Anal. Chem., 47, in press (1975).