

AN APPARATUS FOR PREPARATIVE-SCALE GAS-LIQUID CHROMATOGRAPHY

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A number of preparative-scale gas-liquid chromatography units have been described¹⁻⁸ which for the most part employ columns of 1 in. or less in diameter and 25 ft. or less in length. Although an increase in column capacity is generally achieved by increasing the diameter of the column, the existing literature is somewhat conflicting with regard to the effect of increased diameter on column efficiency. In some instances, for example, it has been stated^{2,9} that an increase in column diameter above 1 in. results in a rapid decline in efficiency. In at least one case³, however, it was reported that a 3-in. diameter column resulted in little loss in efficiency over that of a 1-in. column. DE WET AND PRETORIUS¹⁰ have studied various factors affecting gas-liquid chromatographic separation of large samples with a 1½-in. diameter column and found that HETP (height equivalent to a theoretical plate) values below 1 cm can be obtained for samples up to 10 ml in volume. A similar study has recently been reported by HUYTEN, VAN BEERSUM, AND RIJNDERS¹¹. We describe below a column 1½ in. in diameter with sufficient length so that very efficient separations may be made on reasonably large samples. The unit has been used successfully for a variety of applications, including the separation of catalytically cracked gasoline, kerosene, isobutane-olefin alkylate, and olefin concentrates.

APPARATUS

The column section of the unit is composed of eight vertically mounted 1½-in. × 9-ft. stainless steel tubes connected by 3/8-in. tubing returns at both ends. Column tubes, heaters, and carrier-gas preheater line are cast in aluminum. At the base of the column in separately heated sections are found the sample vaporizer, thermal conductivity cell, and trapping manifold. The thermal conductivity cell is operated on a slip stream from the main flow. Effluent may be trapped from any one of three valves on the manifold.

A view of the entire unit is shown in Fig. 1 and a flow diagram is given in Fig. 2.

Column

The eight tubes of the column are arranged in bundle fashion with the ends of the tubes protruding 1½ in. from the end flanges. The bundle of tubes and the connecting

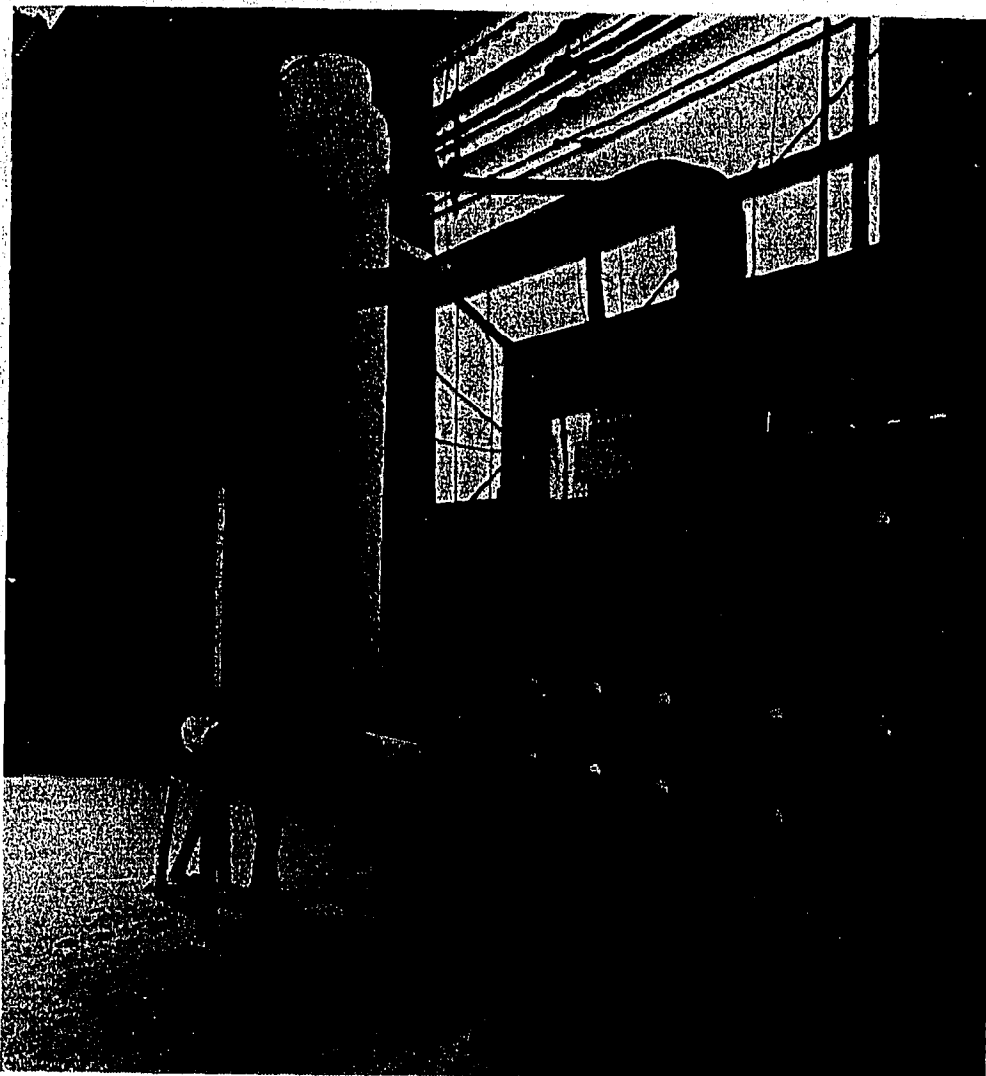


Fig. 1. Preparative-scale gas-liquid chromatograph.

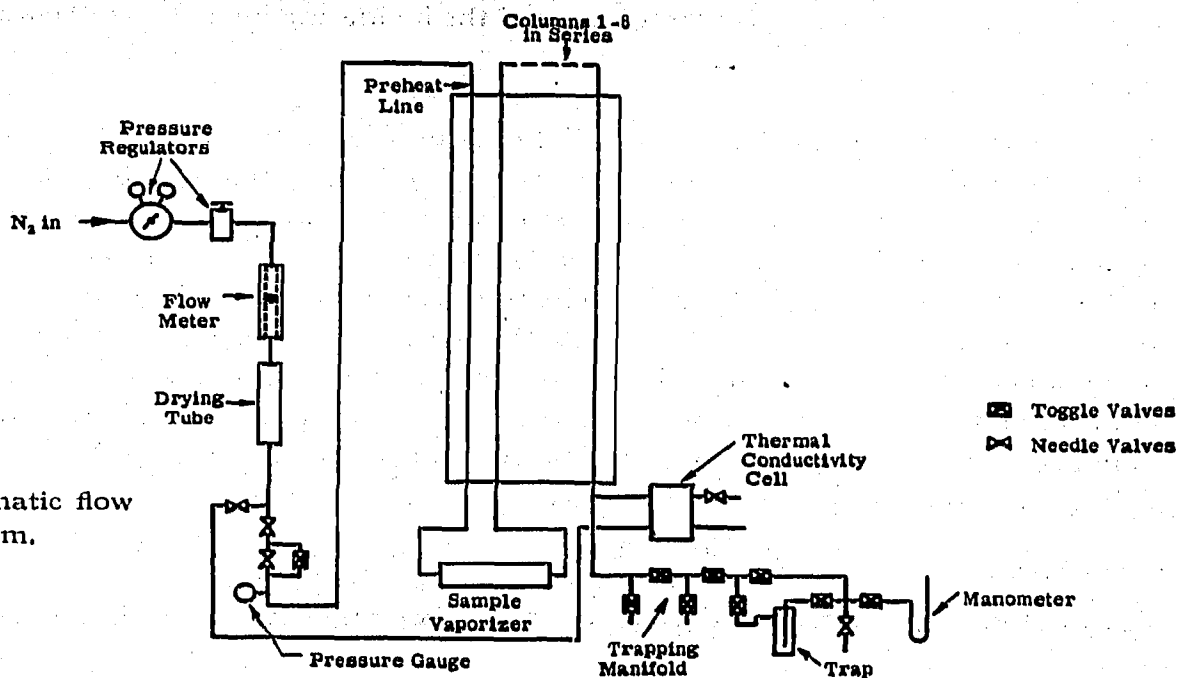


Fig. 2. Schematic flow diagram.

tubing returns are mounted so that the effective column length can be set at 18, 36, 54, or 72 ft., depending upon the number of pairs of individual tubes used. Six $\frac{1}{2}$ -in. Chromalox tubular heating elements (No. TS-13645) of about 1000 W each (110 V) are coiled around the eight tubes with $3\frac{1}{2}$ turns per heater and a coil height of $1\frac{1}{4}$ ft. These heaters are paired (series) so as to form three circuits. One tubular heater of 3800 W (220 V) passes through the center of the column tube bundle and is used to bring the column rapidly to the desired temperature. The $\frac{3}{8}$ -in. tubing returns at each end are heated by a Chromalox electric range element (MTC-926MN, 650 W, 110 V) which is located about 1 in. above (or below) the returns.

Four inches of 85% magnesia insulation covers the body of the column, and insulation caps of 12-in. diameter pipe insulation cover the tubing returns and hold the electric range elements in place.

Sample vaporizer

Carrier gas entering the sample vaporizer is preheated by passage through a $\frac{3}{8}$ -in. stainless steel tube which extends through the length of the column section. The vaporizer chamber is an $8 \times 1\frac{1}{4}$ -in. stainless steel bar with a $\frac{7}{16}$ -in. hole drilled through the center. Heating is provided by two 400-W strip heaters and the tubing making connection with the column is heated with a heating tape. Both the vaporizer and connecting tubing are insulated with asbestos pipe insulation. Samples are injected into the chamber through a serum bottle stopper near the inlet side.

Thermal conductivity cell

A Gow-Mac TE-III, Model No. 9234 thermal conductivity cell is used with a 6-V wet storage battery and a trickle charger. An automatic attenuator is included in the bridge circuit. The thermal conductivity cell is located in a container consisting of a small round can inside a larger round can with 3 in. of insulation between the two. Beaded Chromel A wire which is wound around the inside can heats the cell compartment.

Trapping system

Gas emerging from the last tube of the column is split into two flows; one small stream goes through the thermal conductivity cell, the remainder goes to the trapping manifold. The valves are Hoke 411-series all-metal cam-operated diaphragm valves which can be used up to 250° . Distance between valves was made as small as possible in order to reduce sample holdup and carryover. Final exit of gas from the manifold is through a needle valve used to adjust the outlet pressure. The inlet sides of the traps are connected to the manifold by ball-and-socket joints and the outlet sides are connected to the needle valve with tygon tubing. Heat for the trapping manifold is provided by 12 ft. of No. 25-gage Chromel A resistance wire (500 W), and the manifold is insulated with 1 in. of asbestos.

Instruments

Chromatograms are recorded with a 0-5 mV Brown strip-chart recorder. A six-point,

0–1200° F Weston Indicating Potentiometer controller (Celectray) is used to control the three main heating circuits of the column, as well as those of the sample vaporizer, thermal conductivity cell compartment, and trapping manifold. All other heated points are manually controlled.

High-temperature-limit system

A high-temperature-limit control system was designed to shut off the Celectray in case of failure of a relay. For each of the three main heating circuits of the column, a sensing thermocouple is provided. This high-limit control provides positive shut

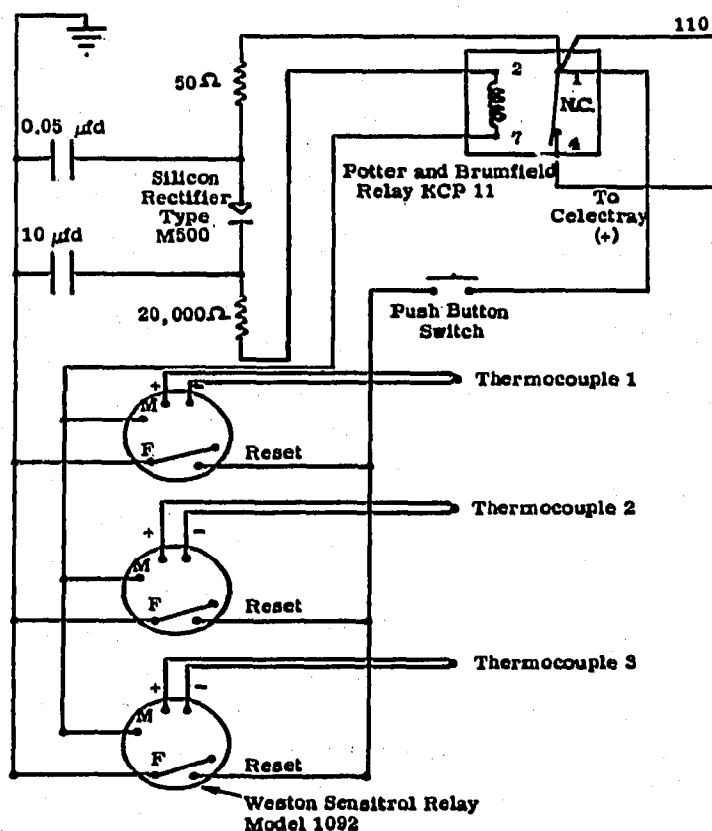


Fig. 3. Schematic wiring diagram for high-temperature-limit circuit

off until the condition has been corrected and the control reset. The system is simple, inexpensive, and can be made to monitor a number of points. A schematic wiring diagram is shown in Fig. 3.

PROCEDURE

Nitrogen carrier gas is dried by passage through a large tube filled with magnesium perchlorate and indicating drierite. A rotameter and a pressure gauge serve as rough indicators of flow rate. More precise flow adjustment is obtained by use of soap film meters of 50- and 350-ml capacity. Due to the large volume of the column, several minutes are required for a steady rate to be reached after each adjustment of the

regulating needle valve. The column is operated with an outlet pressure 10–20 mm above atmospheric pressure so as to assure a flow of 50–100 ml/min through the thermal conductivity cell.

The two silicone liquid phases used, GE-96 and DC-710, were deposited in the amount of 20 wt. % on 20–40 mesh Johns-Manville C-22 firebrick. Changing the column packing of the unit is a relatively simple matter. Removal of the two end insulation caps exposes the ends of the column tubes, and the diameter of the tubes is large enough to allow rapid removal or addition of packing material. It is our experience that uniform packing can be realized without agitation. However, if additional settling is required, a heavy-duty massage-type vibrator produces some vibration of the tubes.

Samples are introduced into the sample vaporizer chamber with hypodermic syringes. For samples larger than 1 ml, a 20-gage needle is used so that injection can be made rapidly. A 5-ml sample can be injected in about 2.5 seconds.

Temperature in the sample vaporization chamber is maintained 50–70° above the column temperature while the trapping manifold is held 20–50° above the column temperature. The thermal conductivity cell is usually operated at the same temperature as the column; however, for some higher-boiling samples the cell is held 10–20° above the column temperature. With its large mass, the body of the column heats up rather slowly; but, once the desired temperature is reached, it maintains a stable temperature to $\pm 1^\circ$. About 2 hours are required to bring the column to 100°, and 2 additional hours for each 50° increment up to 250°. The recorder baseline does not show appreciable fluctuation due to temperature cycling until 200° is reached.

The phenomenon of peak inversion^{12–14} was encountered under certain conditions with the Gow-Mac thermal conductivity cell and with nitrogen as a carrier gas. If gold-plated filaments are used in the cell, rather than tungsten, the temperature at which inversion takes place is raised. Pentane, for example, is inverted below 100° with tungsten filaments, whereas with gold-plated filaments it is not inverted until a temperature between 110° and 150° is reached.

One of the more important and difficult phases of preparative-scale gas-liquid chromatography is recovery of separated material from the carrier gas stream. When one attempts to condense relatively small amounts of vaporized material from a large amount of fast-moving heated carrier gas, the result is usually a fog which is difficult to precipitate. A sophisticated technique for overcoming this difficulty has been described by WEHRLI AND KOVÁTS¹⁵. We have investigated a number of simpler traps and techniques for collecting fractions.

Two of the most useful designs we have employed feature glass vessels tightly packed with glass wool in one case and with copper turnings in the other. The glass wool trap is 7.6 cm long and 2.5 cm in diameter. Gas enters through a side arm and exits through a central tube, around which the glass wool is wrapped. Gas enters the trap (15 × 1.7-cm Vigreux-type tube) containing copper turnings near the bottom and exits at the top. Recovery with the copper-packed trap is about 97 % and is

somewhat better than the recovery obtained with the glass wool packing. Small amounts of liquid held up by the glass wool can be recovered by centrifuging and withdrawal of the freed liquid with a hypodermic syringe.

For the most part, a dry ice-isopropyl alcohol cooling bath is used. As the carrier gas is nitrogen, the use of liquid nitrogen for cooling relatively small traps results in a freeze-up which restricts the flow of gas.

FACTORS AFFECTING COLUMN EFFICIENCY

Column length

The bundle-type column arrangement permits a simple study of the effect of column length on separating efficiency. A comparison of efficiency at three different column lengths and various sample sizes is shown in Fig. 4. The number of theoretical plates

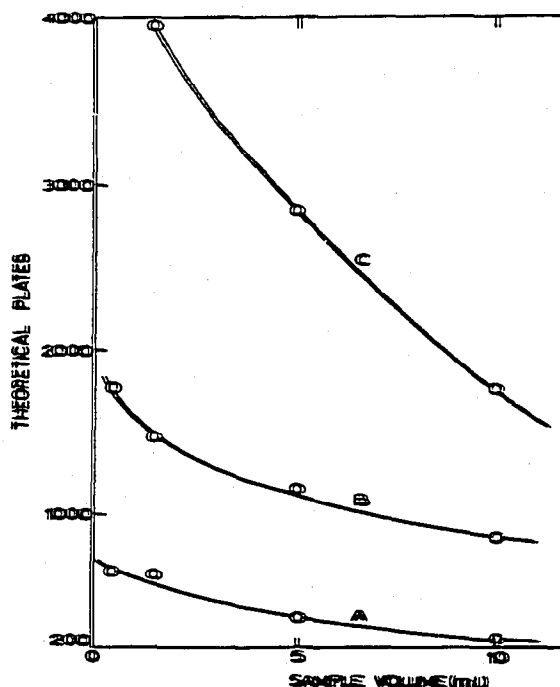


Fig. 4. Effect of sample volume and column length on number of theoretical plates. Sample: benzene, toluene, *m*- and *p*-xylene. Column packing: DC-710 silicone. Column temperature: 110°, Nitrogen flow rate: 1000 ml/min. Measured peak: *m*- and *p*-xylene. Column length: curve A, 18 ft.; curve B, 36 ft.; curve C, 72 ft.

was calculated according to JOHNSON AND STROSS¹⁶. Throughout the range of sample size indicated, doubling of the column length more than doubles the number of theoretical plates. Although the rate of decrease in efficiency with increasing sample volume is most rapid in the case of the full column length of 72 ft., the point of diminishing returns from an increase in column length has apparently not been reached.

Component concentration

To the extent that the concentration of a given component influences the number of calculated plates, Fig. 4 does not fully exemplify the performance of the apparatus.

In particular, components present in high concentration give rise to peak spreading (column flooding). As an example of the number of plates that can be realized for components present in low concentration, the peak for 2,4-dimethylpentane (2-3% of sample) in the chromatogram of an 8.7-ml charge of alkylate (cut 4 of Fig. 5 and Table I) shows an efficiency of over 9100 plates.

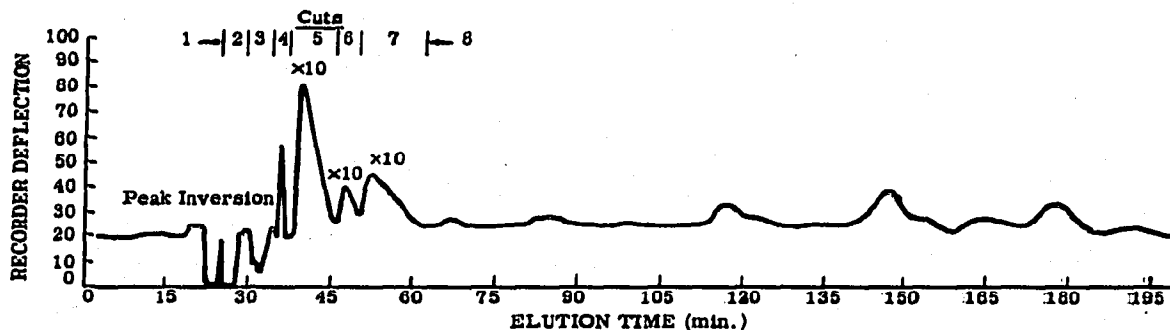


Fig. 5. Chromatogram of alkylate. Sample: 8.7 ml isobutane-butylene alkylate. Column packing: 36 ft. GE-96 silicone + 36 ft. DC-710 silicone. Column temperature: 150°. Nitrogen flow rate: 1000 ml/min.

Flow rate

The effect of carrier gas flow rate on separation efficiency is illustrated in Fig. 6 for 5-ml samples of a five-component mixture. As the flow rate increases, the number

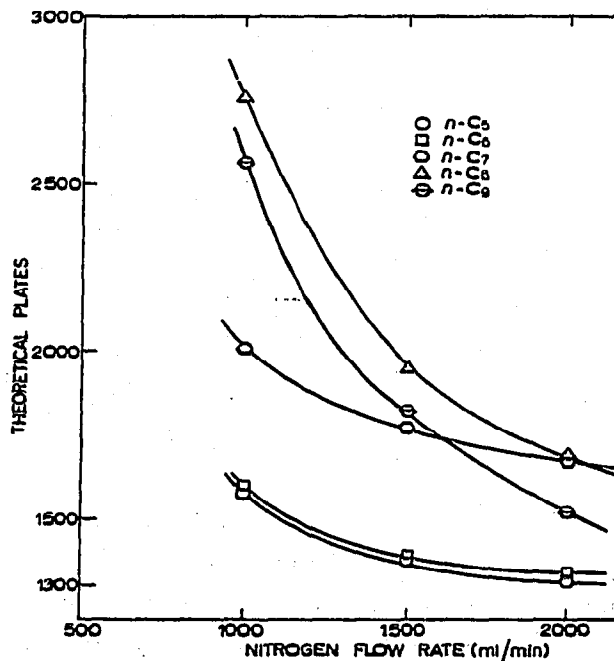


Fig. 6. Effect of flow rate on number of theoretical plates. Column packing: DC-710 silicone. Column temperature: 110°. Column length: 72 ft. Sample volume: 5 ml.

of plates for each component decreases; however, the rate of decrease is much greater for those components which have longer retention times.

Elution time

The relation between theoretical plates and elution time goes through a maximum which is illustrated in Fig. 7. This maximum moves toward shorter retention times with increasing flow rate. Examination of the chromatograms shows that the peaks near maximum efficiency are found to be very nearly symmetrical, while those with shorter retention time are tailed and those beyond the maximum show leading.

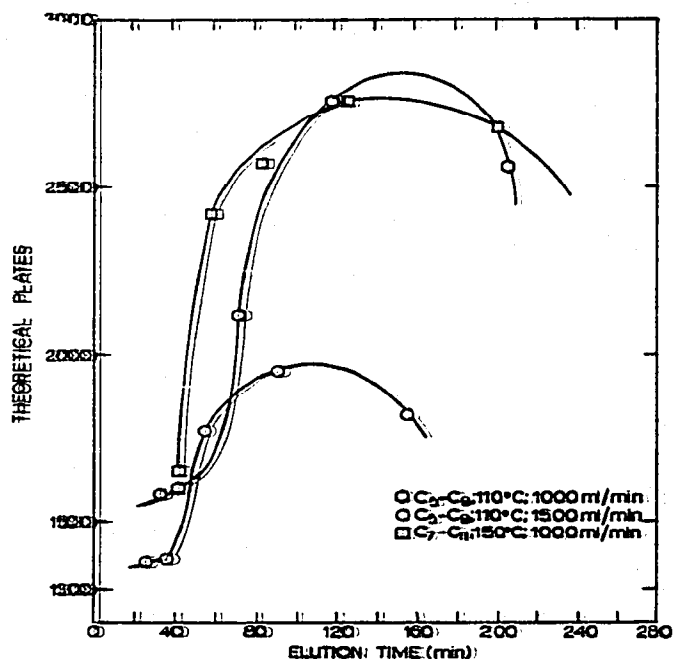


Fig. 7. Relationship between number of theoretical plates and elution time. Column packing: IDC-710 silicone. Column length: 72 ft. Sample volume: 5 ml.

This effect may be due to overloading of the column. Nonideal adsorption on the support causes tailing and nonideal solution effects produce leading¹⁷. Tailing can be avoided by using small samples which do not fall on the strongly curved region of the adsorption isotherm; however, as the samples used here are intentionally large, tailing cannot be avoided in this manner. Leading can also be improved by working at low concentration, where the activity coefficient varies only slightly, or by increasing the temperature in order to produce more nearly ideal solution conditions. It is seen in Fig. 7 that with an increase in temperature of 40°, the relative symmetries of the peaks are changed. Tailing probably occurs for all peaks, with the effect of leading becoming more pronounced as the retention volume increases. Symmetrical peaks occur when there is a balance between tailing and leading. Slow sample vaporization, a frequent difficulty in connection with large sample sizes, is a further factor influencing peak shape.

Stationary liquid

The IDC-710 silicone fluid used as one of the column liquid phases produces some separation by hydrocarbon type as may be demonstrated by the separation of 2,4-

dimethylpentane (b.p. 80.51°) and cyclohexane (b.p. 80.74°). On the basis of the formula $2\Delta y/(y_a + y_b)^{18}$, where Δy is the distance between the two peak maxima and y_a and y_b are the peak widths determined by the intercepts cut on the base line by the tangents to the two peaks, the column resolution for these two peaks with 18 ft. of DC-710 silicone was 0.995, and for 36 ft. of GE-96 silicone plus 36 ft. of DC-710 silicone was 1.99. If the column resolution value is ≥ 1 the peaks are completely separated. With the short 18-ft. column of DC-710 silicone, it was possible to prepare a 100% pure (by mass spectrometric analysis) sample of cyclohexane from the blend.

Sample volume

It has been reported^{18, 19} that with plug-flow sample introduction of sufficiently small samples, sample volume will not contribute to the peak width. With the apparatus described here, the peak width does depend on sample volume, probably because of several factors. The introduction of large samples by hypodermic syringe cannot be accomplished instantaneously and the charge time increases with increasing sample volume. Sample volumes for which this unit was designed (above 1 ml) are considerably above the limit for nonbroadening allowed by the equation of VAN DEEMTER *et al.*²⁰. For samples below about 0.2 ml, the sample volume has only a small effect on the base width, and the number of plates obtained is more uniform. If the plate numbers used here were corrected for the peak widening (due to the detector volume¹⁹), the values would be increased by about 10%.

APPLICATIONS

Light catalytically cracked gasoline

Samples of a $45-120^\circ$ catalytically cracked gasoline fraction were charged in volumes up to 20 ml with the column operated at 110° and at a nitrogen flow rate of 1000 ml per min. Seven distinct peaks were obtained from a 5-ml charge with 18 ft. of column, 12 peaks with 36 ft., and 16 peaks with 72 ft. (first 36 ft. packed with GE-96 silicone, second 36 ft. with DC-710 silicone). The first three peaks from the run with 18 ft. of column were trapped and rerun on a $\frac{1}{4}$ -in. \times 25-ft. GE-96 silicone column. The first peak contained C_6 saturates and olefins, the second contained mainly C_6 olefins plus a small amount of C_7 saturates and olefins (about 1.5 vol. %), and the third cut contained C_6 olefins and C_7 saturates and olefins with the amount of C_7 material increased. With a full column of 72 ft., very narrow concentrates could be obtained from such a sample.

Isobutane-butylene alkylate

A portion of the total liquid product from an experimental alkylation run was charged to the preparative-scale chromatography unit in 5-ml batches with eight cuts being taken (Fig. 5). Further identification was carried out on a $\frac{1}{4}$ -in. \times 4-ft. GE-96 silicone column with variable-temperature operation. Results are shown in Table II. In cases where there is a carry-over of a few tenths of a percent, and higher purity

TABLE I
SEPARATION OF ISOBUTANE-BUTYLENE ALKYLATE

Cut	Components	Basis cut, wt. %	Basis total liquid product, mole %
1	Isobutane	47.5	39.3
	<i>n</i> -Butane	51.6	11.4
	Isopentane	0.9	
2	Isopentane	72.4	4.40
	<i>n</i> -Pentane	27.6	1.08
3	<i>n</i> -Pentane	0.1	
	2,3-Dimethylpentane	87.7	3.80
	3-Methylpentane	12.2	0.30
4	2,4-Dimethylpentane	100.0	2.51
5	2,3-Dimethylpentane	3.9	0.94
	2,2,4-Trimethylpentane	95.5	14.4
6	2,2,4-Trimethylpentane	0.8	
	Dimethylhexane	99.2	3.66
7	Dimethylhexane	0.7	
	2,3,3- and 2,3,4-Trimethylpentane	83.2	12.6
	Trimethylhexane	15.6	1.88
8	Boiling range, °C *		
	125-140	8.2	0.47
	140-165	17.9	0.83
	165-180	18.5	0.65
	180-200	55.4	1.81

* From elution-time calibration data based on *n*-paraffins.

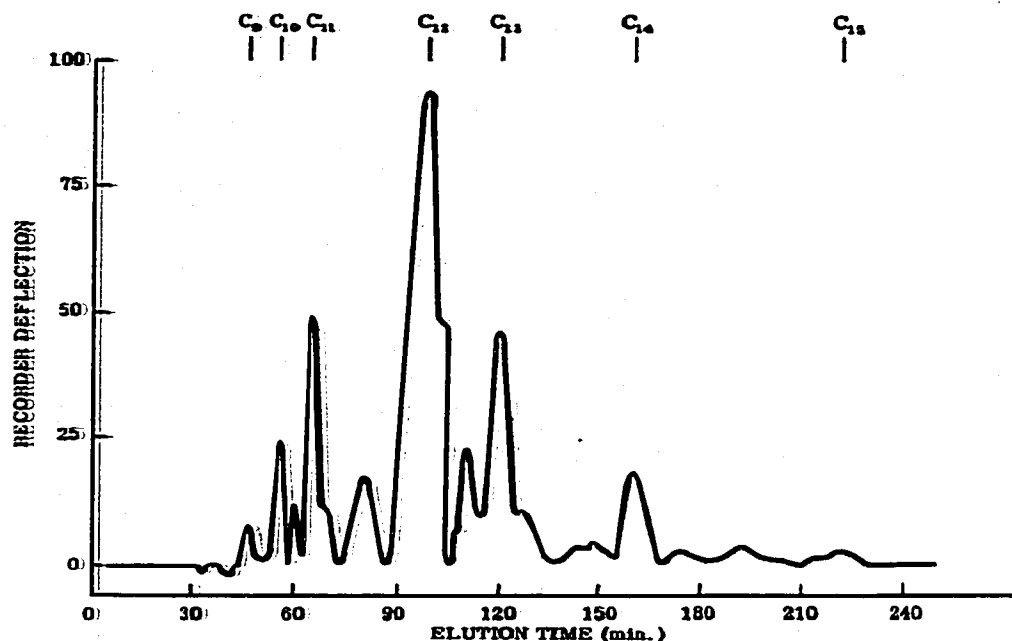


Fig. 8. Chromatogram of kerosene. Sample: 5 ml kerosene. Column packing: 36 ft. GE-96 silicone + 36 ft. DC-710 silicone. Column temperature: 200°C. Nitrogen flow rate: 1000 ml/min.

is desired, the cut points should be made so that the bottom of the valley between peaks is discarded.

Kerosene

Kerosene samples and a number of synthetic blends in the boiling range of 125–270° were run at a column temperature of 200°. A typical chromatogram of kerosene is shown in Fig. 8.

Olefin concentrates

A large number of olefin concentrates in the C_6 to C_{11} range which were prepared from a catalytically cracked gasoline sample by liquid chromatography and distillation were separated in 5-ml portions with 18 ft. of column (DC-710) at a flow rate of 1000 ml/min and column temperatures of 100–200°. The cuts taken from the unit showed that separation by z -number (in the empirical formula C_nH_{2n+2}) with about 90% selectivity was achieved even though complete resolution was not obtained in all cases.

Purification of 8-methylhexane

The preparative-scale unit was used to prepare a total of 175 ml of naphthene-free 3-methylhexane from Phillips technical-grade material for use in reaction studies. Previous attempts to remove the naphthenes by precision distillation were unsuccessful, but they were completely removed by the preparative-scale unit (5-ml sample, 36 ft. of DC-710-silicone, 110°, 1000 ml/min). Taking into account the sample lost through the thermal conductivity cell side stream, a recovery of 97.5% was obtained by using two traps in series, the first cooled with dry ice and acetone, and the second with liquid nitrogen. With a narrow-boiling-range sample such as this, it was possible to complete a run every 35 min.

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SUMMARY

An efficient preparative-scale gas-liquid chromatography unit has been developed which features a column composed of eight 1½-in. × 9-ft. tubes connected in series. The tubes are arranged so that the effective column length can be set at 18, 36, 54 or 72 ft. Operation at temperatures up to 250° and with sample sizes as large as 20 ml is practical. Performance studies indicate that separations equivalent to 9000 or more theoretical stages are possible. The unit has been applied to the preparation of narrow concentrates and compounds of high purity for analytical and reaction studies.

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