A SIMPLE APPARATUS FOR PREPARATIVE SCALE GAS–LIQUID CHROMATOGRAPHY

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Despite early interest in gas–liquid chromatography as a preparative tool surprisingly little use of it has been made in contrast with the vast utilization of analytical apparatus. Although preparative gas–liquid apparatus and techniques have been described in a number of papers, in many instances these have been complex and highly automated for cyclic operation, while in others the details of construction and operation have been inadequate. Commercial apparatus is now available and modifications of analytical apparatus may be employed, but the latter prevent the utilization of the apparatus for its normal function. In many cases the purification of gram-scale amounts of ordinary reagents is desirable to furnish pure standards or starting materials for small scale reactions. The apparatus described below (Fig. 1) is intended for such individual preparations and separations, and has been designed for flexible operation, low cost, and ease of construction in any laboratory with modest workshop facilities. The dimensions and materials may be varied to suit particular requirements.

OVEN

The oven was assembled from four basic pieces, the arrangement being shown in Figs. 2 and 3. The main part was a trough, inside dimensions 8 × 8 × 48 in., made of two pieces of 1/16-in. sheet aluminum (A, A_1) separated by two in. of Pittsburgh-Corning foamglass (B). The pieces of the latter were cemented together with Sairset cement. The exposed foamglass edges were recessed 5/16 in. and faced with 1/2-in. asbestos board (C). The edges of the two aluminum troughs were fastened to the asbestos board by 1-in. sheet metal screws. For greater rigidity the basic trough rested in a frame of aluminum angle raised above the bench top on short legs.

The top consisted of a 12 × 48-in. piece of 1/2-in. asbestos board equipped with handles and faced with 2-in. thick foamglass measuring 8 × 44 in., the latter fitting into the trough between the two end pieces. The foamglass was held in place by two aluminum strips bolted through the asbestos. A hole was drilled through the top to position a thermometer near the thermoregulator.

Two end pieces were made to cover the ends of the trough, consisting of 1/8-in. aluminum plate (D) faced on the outside with 1/2-in. asbestos board (E). On the inside a piece of 2-in. foamglass (F) 8 × 8 in. fitted into the trough end and was secured

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by a facing of 1/16-in. aluminum plate (G) bolted to the 1/8-in. plate. Four lugs on the edges of the latter fastened by bolts to corresponding lugs on the outside of the trough. The ends were designed for separate functions. One, Fig. 2, to carry the circulating fan and heater control connections, the other, Fig. 3, to carry the injection block, gas tubes and bridge circuit leads.

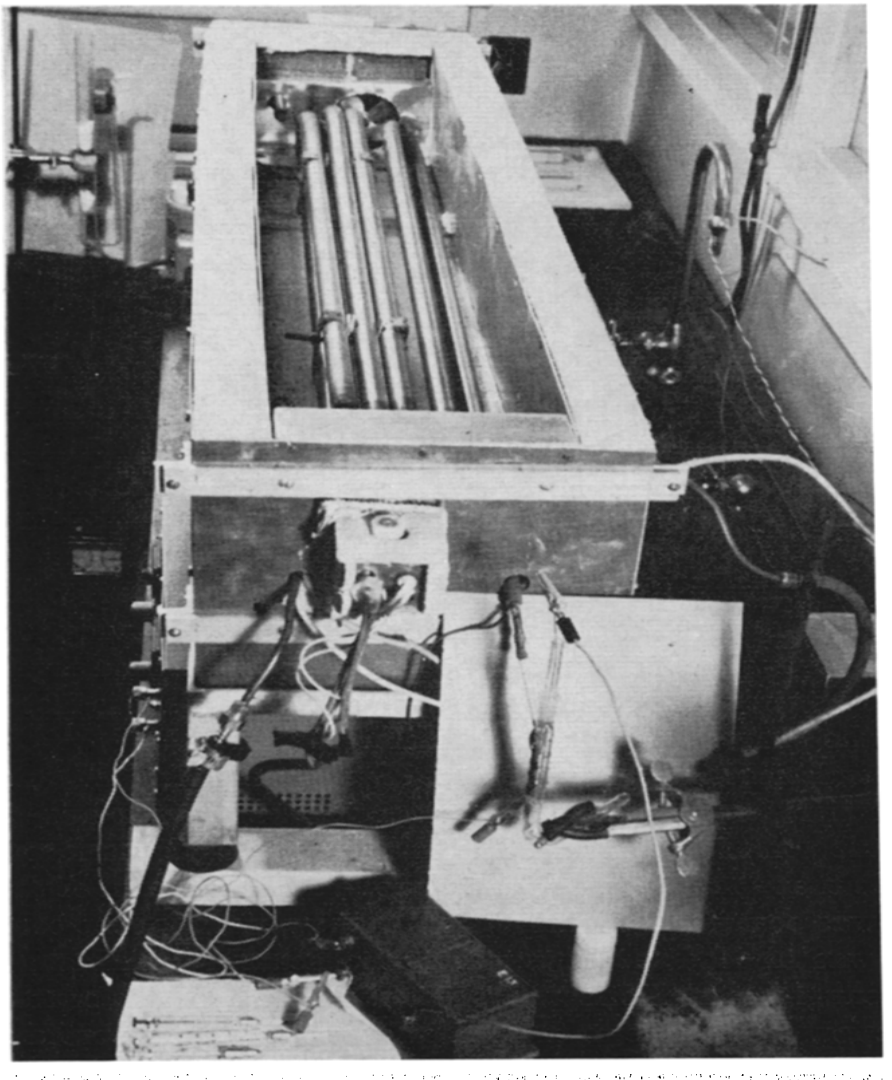

Fig. 1. Simple apparatus for preparative scale gas–liquid chromatography.

The heater control end piece was fitted with a sheet of masonite (not shown) bolted to the 1/8-in. aluminum plate and spaced 1/2 in. from the asbestos board insulation. The electrical lead wires passed through a 3/4-in. hole near the bottom (not shown). Initially asbestos-covered copper wire was used for the heater connections, but rapid oxidation at high temperatures limited the effective life. Asbestos-covered stranded stainless steel wire, No. 12, with crimp-on spade connectors was found very satisfactory. An Aminco bimetallic thermoregulator was mounted on the masonite and passed through a 3/4-in. hole (not shown) in the end piece and fan baffle into the column chamber. An Alliance shaded pole induction fan motor, 3,000

r.p.m., was also mounted on the masonite sheet and connected by a Renold Flexible Spider coupling to the fan shaft. The latter, of 1/4-in. steel drill rod, passed through

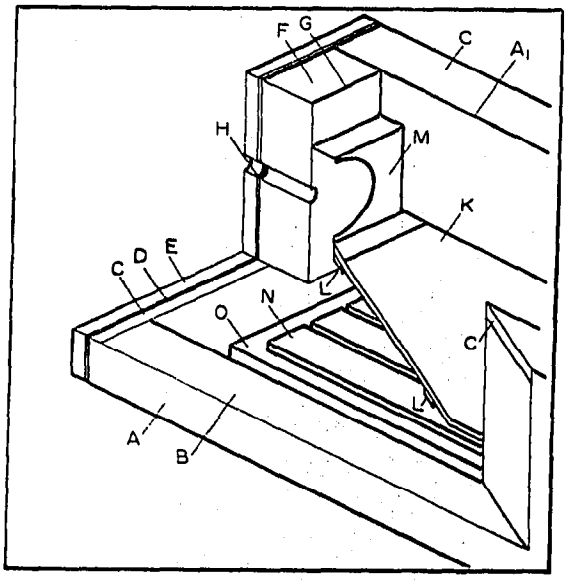

Fig. 2. Arrangement of heater end of apparatus.

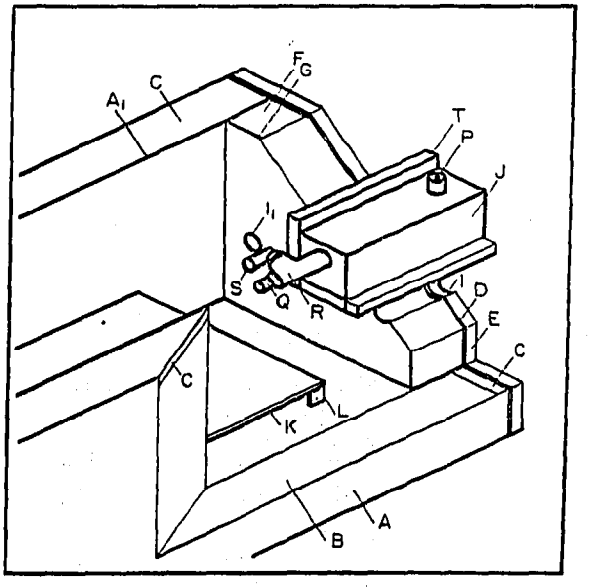

Fig. 3. Arrangement of injection and detector end of apparatus.

the end piece in a bearing drilled from teflon and press-fitted into a 2-in. length of 1/2-in. I.D. pipe (H) secured to the 1/8-in. aluminum plate. Owing to the high coefficient of thermal expansion of teflon this bearing has to be drilled slightly oversize for high-temperature operation. A Torrington 4-bladed 3-in. fan was fastened to the end of the shaft in the plane of the fan baffle plate.

The other end piece, Fig. 3, was pierced by 3/4-in. holes (I, I_1) near the bottom to admit the carrier gas tubing and bridge circuit leads on one side, and to pass the column outlet tube on the other side. The injector block (J) was so positioned in an appropriate hole that the exit was slightly above the upper arm of the columns. The detector block was positioned slightly below the lower arm of the columns.

The oven was divided into two parts, the heating chamber and the column chamber, by a snugly fitting horizontal sheet of 1/4-in. asbestos board (K) extending from below the fan baffle plate to the end of the columns, supported at intervals by steel cross braces (L) screwed to the inside of the trough. Aluminum was found unsatisfactory directly above the heaters. This sheet protected the columns from direct radiation and permitted efficient air circulation with the addition of a fan baffle plate (M). The column chamber space, approximately 8 × 6 in. in cross-section, would permit six columns of 2-in. pipe if desired. Half the length of the heater chamber, approximately 8 × 2 in. in cross-section, was required for heaters leaving the rest free to house a carrier gas preheater coil.

Heating was effected by General Electric strip heaters (N), mounted 1/2 in. above a sheet of 1/2-in. asbestos board (O) resting loosely on the bottom of the trough (Fig. 2). This arrangement permitted removal of the end piece and heaters for servicing without disturbing the rest of the apparatus. Flexible controlled heating up to 400° was achieved by having a 200 W heater operated by the thermoregulator

through a relay, one 500 W heater connected through a variable transformer, and two 500 W heaters on individual switches.

COLUMNS

The column employed was usually 24 ft. long and 0.72 in. in internal diameter, made up of four basic units connected in series. Each basic unit was made by bending a 6-ft. length of stainless steel tubing into a U shape. The radius of the bend was 1-1/2-in., but in order to make the apparatus more compact a 1-in. section was cut from the center of each bend and the pieces were welded together. Connecting fittings at the ends of the units were made by turning down the large end of a Swagelok reducing union, No. 810-6-4-316, to fit within the tubing and silver soldering it in place. The units could then be joined in series by short pieces of 1/4-in. stainless steel tubing. To retain the packing the exit end of each column unit was fitted with a stainless steel gauze disc pressed into the 1/4-in. tubing connector.

The column packing was prepared by coating 40–60 mesh Chromosorb with 30 % by weight prepared Dow-Corning High Vacuum silicone grease[1]. To fill the column an aspirator vacuum was applied at the exit end and a funnel attached at the other end by a short piece of tygon tubing fitted over the tubing connector. With the column vertical about 20 cc of packing was poured into the column which was then tipped over at a slight angle and tapped sharply to pack the exit arm. The procedure was repeated during filling of this arm and at intervals during the packing of the entrance arm. The four units prepared by this means required respectively 222, 219, 215, and 223 g of packing.

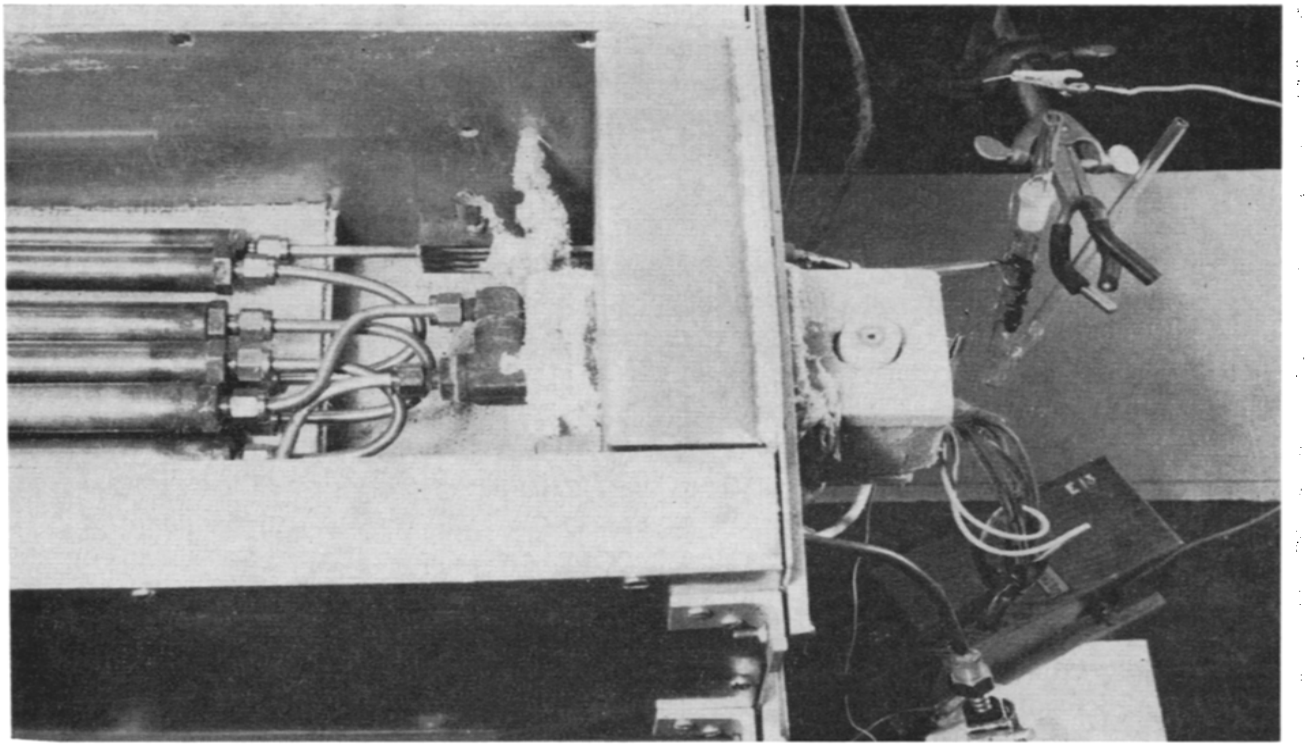

Fig. 4. Detail of injector block, column connections and glow plug detector block.

INJECTION SYSTEM

The injection system, Figs. 3 and 4, consisted basically of a stainless steel block (J), 2 × 2 × 5 1/4 in., fitted with two General Electric 6A77 cartridge heaters of 200 W each, and a Fenwal No. 17002-0 thermoswitch. Injection was made through a 1/4-in. thick silicone rubber septum held in place by a threaded teflon cap (P) as illustrated. A brass ring was press-fitted over the teflon to prevent it loosening by thermal expansion. The actual injection port was turned from stainless steel rod, bored through with a 3/16-in. hole, with a 1/2-in. diameter coarse thread at one end for the teflon cap. The other end was turned down to 5/16 in. and silver soldered through a hole leading into the vaporization chamber, protruding into this chamber 1/4 in.

The carrier gas, after passing through a preheater coil of 1/4-in. tubing, was led through a bored-out Swagelok reducer (Q), No. 400-R-10-316 connected onto a No. 1010-3-316 "T" piece (R), in turn silver soldered to the block, to the injection end of a 5/8-in. diameter vaporization chamber bored 5 in. into the block. This ensures rapid flushing out of vaporized materials, which are swept out through the side orifice of the "T" piece. The pipe thread end of a No. 400-8-2-316 female elbow (S) was turned down to fit into the "T" orifice and silver soldered in place, enabling easy connection of the column to the injector block by a short length of 1/4-in. stainless steel tubing (Fig. 4).

The entire block was sheathed in 1/2-in. sheet asbestos (T) and so mounted in one end of the oven that the injection port was just outside the oven wall.

DETECTION SYSTEM

Model airplane glow plugs, O.K. type G-2 long, or Testor No. 1, were employed as detecting elements. The former were more sensitive, but had a short operating life at oven temperatures above 200°. These were mounted in a block of stainless steel, 3/4 × 1 × 1 1/2-in. (Fig. 4).

The sides of this block were grooved by 1/8 × 1/8-in. channels to promote thermal equilibrium. The gas stream was passed in and out by 1/4-in. stainless steel tubing silver soldered in the inlet and exit holes. The interior arrangement of the block, and the bridge circuitry, as described by FELTON AND BUEHLER[2,3] were satisfactory at low gas flow rates, but for higher gas flow rates a by-pass design gave better base-line stability with only slight loss in sensitivity. In this design 1/4-in. holes were drilled from either end of the block, leaving a section 1/8-in. thick immediately below the glow plug position. Through this remaining section a 1/8-in. hole was bored, and the glow plug well was drilled down to within 1/8-in. of the top of the 1/4-in. bore holes. Holes 1/32-in. in diameter were then drilled from the bottom edges of the glow plug well into the respective 1/4-in. sections of the main gas flow section. The reference glow plug was not mounted in the inlet gas stream, but in a dummy steel block sitting on the floor of the oven. To allow for the thermal expansion of air, a 1/64-in. hole was drilled through the block at the bottom of the plug well.

The lead wires from the bridge control panel to the glow plugs were of No. 12 asbestos covered stranded stainless steel wire, silver soldered to spade ends. The latter were fastened by brass screws to the tops of small brass cylinders. The latter had holes drilled in the base of just sufficient diameter to fit down over the terminal post of the glow plugs and were held in place by 6–32 Allen set screws. The return circuits

were in the one case silver soldered directly to the dummy block, and in the other fastened by ordinary solder to the exit end of the stainless steel tubing from the detector block. In preliminary work the column itself was utilized as one side of the circuit but the Swagelok connections, although gas tight, vibrated sufficiently to cause a very unstable base-line at high gas flows. A tenfold increase in response was obtained when the glow plug filament was exposed by filing away half of one side of the base of the glow plug. An ammeter was preferred to a voltmeter in the bridge circuit, and operating currents were 1.4–1.6 A for the O.K. glow plugs and 3.2–3.6 for the Testor. Bridge power was furnished by a 6 V automobile battery and the output recorded on a Minneapolis-Honeywell Elecktronik recorder with a temperature scale of 0–200°, corresponding to 0–9.28 mV.

OPERATION AND SAMPLE COLLECTION

Nitrogen was the only carrier gas utilized, drawn directly from the cylinder through a two-stage regulator. Input pressures up to 40 p.s.i. were employed, giving a flow rate of over 2,000 ml/min, although such high flow rates diminished detector response. The flow rate at 300° was found to be only half that at 100°, for the same pressure. During the warm-up period of 1–3 h, depending on the temperature desired, a lower flow was maintained to economize on nitrogen and a lower bridge current to conserve battery and plug life. The base-line recovered within minutes from any change in either gas flow or bridge current.

Commercial hypodermic syringes of 1/4 to 5 cc capacity were used with needles of 26 to 22 gauge. Manual injection against pressures up to 40 p.s.i. was quite feasible, and greatly facilitated by the use of Becton-Dickinson Luer-Lok syringes where the needle is fastened to the syringe barrel. The silicone rubber septums withstood numerous injections when the temperature of the injection block was as high as 300°, although the life was shorter at higher temperatures or if solvent type materials such as ethyl acetate were being injected.

At low flow rates and temperatures simple cold trapping was moderately effective in recovering samples, but under more extreme conditions the formation of aerosols necessitated the use of a trap where the exit gas passed through petroleum ether and then through defatted cotton wool wetted by the agitated solvent (background of Fig. 1), or of an electrostatic precipitator[4] visible in the foreground of Fig. 1. Connection to any trap type was made by a very short piece of silicone rubber tubing, cleaned just prior to each sample collection by a short piece of pipe cleaner inserted into the exit tube from the detector block.

DISCUSSION

Simplicity of construction was a foremost consideration in the apparatus described, but the design was governed by a flexible approach to permit modifications to be incorporated as desired. Recently the theory of preparative scale gas–liquid chromatography columns has been studied[5–7], and it is probable that greater efficiency could be obtained if the U-bends were omitted. Packing technique has also been shown to be an important consideration[7,8].

The column employed is no doubt still grossly overloaded with samples of one or

more grams, but this can be tolerated to effect practical separations. This is illustrated in Fig. 5, where the number of theoretical plates declines rapidly with sample size, but complete separation is still attained.

The response of the glow plug detectors under these operating conditions is definitely non-linear, with lesser components giving an area response several times that of the proportionate larger component. The incomplete separation of some peaks on

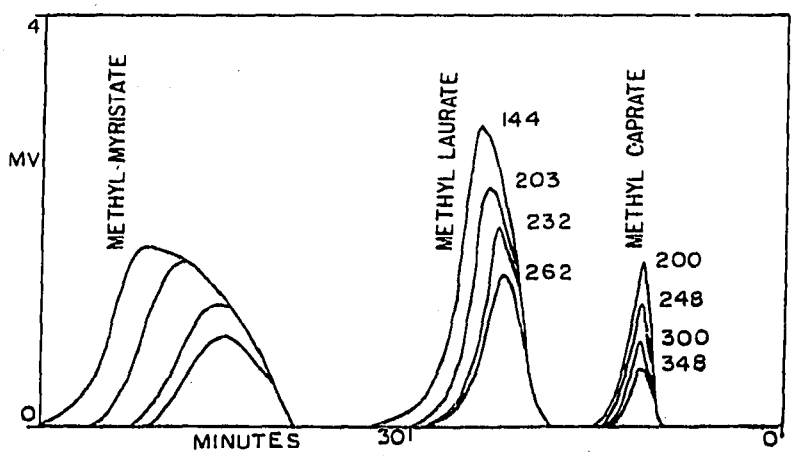

Fig. 5. Reduction in number of theoretical plates with sample size. Mixture of 5% methyl caprate, 45% methyl laurate and 50% methyl myristate; samples of 1/4, 1/2, 1 and 2 ml; 230°; nitrogen flow 1,200 ml/min; column length 24 ft.

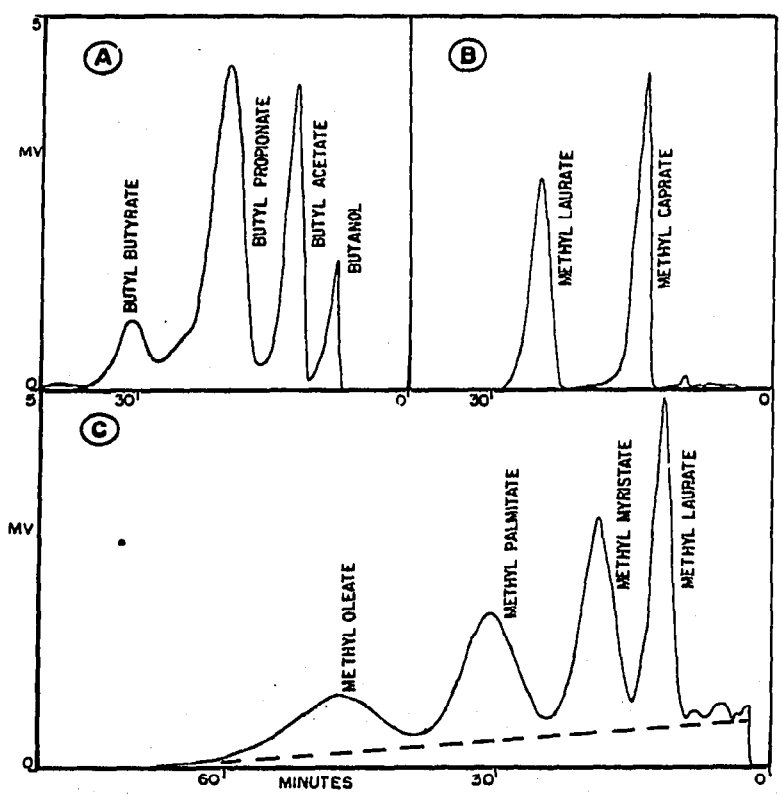

Fig. 6. (A) 2 ml technical butyl propionate; 100°; nitrogen flow 800 ml/min; column length 12 ft. (B) 1 ml equal parts methyl caprate and laurate; 200°; nitrogen flow 600 ml/min; column length 24 ft. (C) 1 ml equal parts methyl laurate, myristate, palmitate and oleate; 325°; nitrogen flow 1,200 ml/min; column length 24 ft.

the chromatograms may be due therefore to only traces of material tailing from the first major component. This tailing from preceding major components may give up to 1 % contamination of the next peak in a multicomponent mixture, but a second chromatographing usually reduces this to a figure of 0.01 % or less.

Some examples of separations are given in Fig. 6. In the case of the butyl propionate, (Fig. 6A), amounting to only 60 % of the starting materials, the recovered product was 99.2 % pure although only a 12-ft. column was employed. The disturbance in the base-line on injection of the sample in Fig. 6C may be ascribed to "plug flow" and the true base-line is believed to be that indicated by the dotted line. This last example is intended only to illustrate the separations possible with high boiling materials, as it is improbable that unsaturated fatty acids would be recovered unaltered under the operating conditions employed. Although this apparatus has been used primarily for preparations of esters of fatty acids at moderate temperatures, the flexibility of design should make it equally applicable with other materials at higher or lower temperatures.

SUMMARY

A simple low-cost preparative gas–liquid chromatography apparatus is described, employing model airplane glow plugs as the detecting elements. The design is suited to flexible operation at temperatures up to 400° with samples of 1 to 5 ml. Examples are given of the separation of esters of fatty acids under various conditions.

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