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CONSTRUCTION AND OPERATION OF A PILOT SCALE PRODUCTION GAS CHROMATOGRAPH FOR SEPARATING HEAT-SENSITIVE MATERIALS

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SUMMARY

A pilot scale production gas chromatograph, with a column diameter of 10 cm, has been constructed to separate two heat-sensitive essential oil mixtures, geraniol-nerol, and α -pinene- β -pinene. The principal features of the apparatus derive from previously published design principles and include recycling and deoxygenating the carrier gas, high gas velocities, a timed mode of injection, sectional design of the column with efficient distributors, and fraction collectors with provision for trapping aerosols. Comparison between the performance and operating parameters achieved and recently published design calculations shows that the design of the evaporator is the major item needing improvement. The equipment and its operation are costed.

INTRODUCTION

Production chromatography differs from preparative chromatography in that the economics of the continuous process govern the design. Most previous studies of equipment have either been largely empirical and aimed at large-scale laboratory preparative separation or have been particularly concerned with maintaining column efficiency in large diameter columns. Recently we have described a design study¹ for a production gas chromatograph to separate two heat-sensitive essential oil mixtures, geraniol-nerol, and α -pinene- β -pinene. Heat-sensitive materials were chosen because many of the separations where production chromatography offers the greatest advantages in separating power or high purity over other techniques also entail thermal lability. Here we describe the construction and operation of a pilot scale production chromatograph (based on a 10 cm diameter column) and compare it with the design specification previously devised. The equipment was designed to be flexible enough to accommodate different materials to be separated and was intended to operate under optimum conditions for each separation, though this last intention was not completely achieved. The principal features of the apparatus derive from the pro-

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duction scale of operation and the need to handle heat-sensitive essential oils without too much thermal degradation.

(1) Large volumes of gas are used at high flow-rates. To do so economically the carrier must be continuously recycled. The gas is cleaned up before recycling since fraction collectors suitable for bulk collection, *e.g.* cooler-condensers and mist collectors, are never 100% efficient. Clean-up is achieved by an adsorption technique.

(2) For long life of stationary phase and minimum degradation of the heat-sensitive feed being separated, it has been found² essential to both deoxygenate and dry the carrier gas.

(3) Batches of the material being separated are injected in a timed mode with a sharp cutoff to give rectangular feed band profiles. The feed introduction would be automated for repetitive batch injection³ in a unit producing continuously. Automation was not needed, however, in the present apparatus designed for development work and study.

(4) Provision is made for collection of a mixed fraction as well as pure components, since it has been shown that optimum performance is achieved by deliberately choosing conditions so that the peaks are only partly resolved at the column outlet and then recycling the mixed (overlapping) fraction³.

(5) The total column length is made up in short sections linked by short lengths of small diameter tubing. This is partly to permit reasonable oven dimensions. It also provides periodic remixing of the contents of the flow cross-section and so helps to keep down the plate height contribution from nonequivalent flow-paths through the packing. In addition, flow distributors are provided at both ends of each column section. These help maintain equivalent flow-paths and avoid regions of slow-moving gas in the packing, so minimising tailing and plate height contributions. The distributor design was based on porous discs of large pressure drop, rather than conical end pieces which are less satisfactory.

(6) The carrier is preheated to column temperature to prevent substantial cooling of the evaporator or column inlet which would otherwise occur with large diameter equipment. In continuous production this heat could be provided more economically by heat exchange between preheater and cooler-condenser of the fraction collector.

(7) Many heat-sensitive materials have a relatively high molecular weight (essential oils, pharmaceuticals, etc.) and therefore a low mass diffusivity in comparison with their thermal diffusivity. As Colburn and Edison have shown⁴ this makes them very prone to form aerosols when condensed from a mixture with an inert gas. An efficient fraction collector therefore needs to include provision either to prevent aerosol formation or to trap the aerosol once formed. We have begun a study of various types of collector^{5,6} but meanwhile have devised, as an interim measure, an improved form of a trap, originally patented by Carel and Perkins⁷, which uses porous metal discs to provide a large condensing surface.

APPARATUS

General arrangement of equipment

A flow diagram of the apparatus is shown in Fig. 1, and a photograph of the main part of the equipment in Fig. 2. The carrier gas, nitrogen, was supplied from

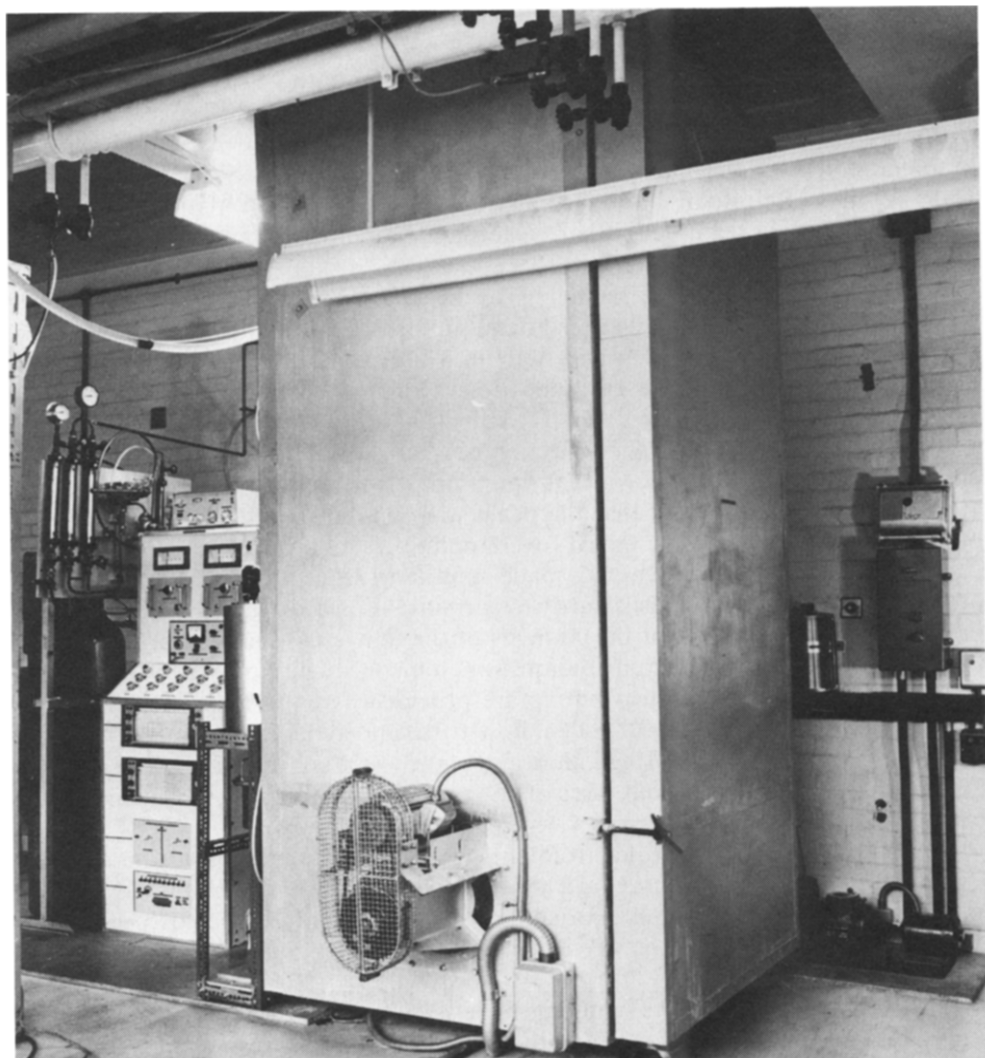


Fig. 2. Photograph showing (from left to right) gas flow and pressure control system, electrical instrumentation (temperature controllers and recorders for temperature and detector), part of fraction collection assembly, 3.10 m high oven with one of the two air circulating fans at the front, and feed pump (on the floor).

a flow and pressure control system via an oxygen removal column and drier. The gas was directed by a three-way valve either directly to the column through a preheater mounted in the oven, or through an external preheater to the evaporator and thence to the column. This arrangement permitted study of alternative modes of injection involving both on-line and off-line evaporation and, in the on-line mode, with or without a sharp cut-off of the vapour leaving the evaporator. When the evaporator was used in the on-line mode, a second three-way valve in the feed line allowed the carrier gas to be directed through the line between this valve and the evaporator

nozzle to sweep out liquid in the line and so obviate one source of tailing of the feed-band.

A small flow (1 cm³/sec) of the vapour-rich gas leaving the evaporator was diverted to a flame ionisation detector to obtain the feed inlet profile. After passing through the columns, a second small portion of the main gas stream was similarly split off to obtain the outlet profile. Three cooler-condensers, each followed by an aerosol trap held at -20°C, collected the two separated components and the mixed (overlapping peak) fraction. The three on-off valves controlling collector selection were placed downstream of the collectors to avoid causing unnecessary turbulence and remixing of the vapour components. One of two clean-up columns removed the remaining vapour not condensed by the fraction collectors. A compressor mounted between a pair of surge tanks then recycled the clean carrier gas.

The main parts of the apparatus are now described in more detail.

Gas supply, purification and preheating

The carrier gas was the oxygen-free ("white-spot") grade of nitrogen supplied from two cylinders. One cylinder was to make up for continuous small losses to the detector and small leaks. The other provided gas for initial purging, start-up and regeneration of the clean-up columns. The pressure in the whole assembly was maintained constant by a diaphragm pressure regulator on the make-up gas cylinder and pressure reducers and spring-loaded safety valves where necessary.

Removal of the 10⁻⁵ (vol. basis) parts of oxygen present in the "oxygen-free" grade of nitrogen has been found² to be very beneficial in raising the decomposition temperature and/or extending the life of polyethylene glycol 20 M, the stationary phase used in the columns. Accordingly, two oxygen removal columns were provided to purify the gas for the separation system and for regeneration of the clean-up columns, respectively. The columns contained activated manganous oxide supported on 5-20 mesh Phase-Sep W and were similar in design and operation to units described previously². The packing, 15 × 2.5 cm I.D., was sufficient to purify 132 m³ gas (1 atm, 0°C) before regeneration with hydrogen at 350°C, and produced a pressure drop of only 2.7 p.s.i. in normal operation.

The two preheaters permitted heating the gas from room temperature to either column or evaporator temperature, as desired. The preheater in the evaporator line had a capacity of 7 kW and consisted of a 4.88 m × 12 mm I.D. stainless-steel U-tube wrapped with 17 m of 18 gauge nichrome wire and insulation. The other preheater was 17 m × 12 mm I.D.; it was placed inside the oven from which it drew its heat and so required no separate power supply or insulation. The uniformity of temperature in the oven was not harmed by this arrangement.

Feed injection system

The evaporator was of stainless steel, 61 × 9.5 cm I.D. This fairly large aspect ratio was chosen to minimise problems of liquid distribution. To provide sufficient heat to evaporate each batch of feed without suffering a temperature drop of more than 20°C, the evaporator was packed with 18 kg of 3.175 mm diameter stainless-steel ball bearings which occupied a height of 50.8 cm. This provided a large heat transfer surface. The ball bearings were supported on a 9.5 cm diameter porous stainless-steel disc. The evaporator was wrapped with 29 m of 15 gauge nichrome

wire giving a heating capacity of 4 kW. The whole unit was covered with 7.5 cm of calcium silicate as insulation and located inside the column oven to minimise heat losses.

The liquid feed to be chromatographed was pumped at a constant flow-rate by a gear pump (Zenith metering pump) driven by a motor and a Graham transmission unit which permitted infinitely variable flow-rates from 0 to 292 ml/min. A nine-hole spray nozzle 4 in. above the packing in the evaporator was provided to distribute the feed evenly over the packing.

Column and oven

The required column length was made up of a combination of 2.44 m and 1.22 m sections of 9.5 cm I.D., connected together with short lengths of 12 mm tubing. Construction was in stainless steel and details are shown in Fig. 3. Each column contained a flow distributor at each end to distribute the gas uniformly over the cross-section of the packing. Each distributor consisted of a 3.175-mm deep "mixing chamber" enclosed between the flanged cover plate and a 6.35-mm deep porous stainless-steel disc. The ratio of the pressure drop across two porous discs to that (6–10 p.s.i.) across the packing in each column section was about 1, the minimum value needed to ensure that the gas velocity is uniform through the discs instead of peaking at the centre. This approach to flow distribution is fundamentally more sound than using conical distributors, which do not create completely equivalent flow-paths. The body of the column between the discs was completely filled with 30–40, 5–30 or 9–42 mesh packing, consisting of 22% of Carbowax 20M (Union Carbide) on Phase-Sep P.

The oven measured $1.37 \times 1.27 \times 3.10$ m high overall (Fig. 4). The walls and door contained 15.2-cm thickness of insulation to permit operation up to 250°C with minimal heat losses. The interior was divided by two vertical baffles into a central compartment containing the column sections, evaporator, katharometer and preheater, and two side compartments each containing electrical heaters and a centrifugal air-circulating fan of 28 m³/min capacity. Air circulated upwards in the heater compartments and downwards in the central compartment with a circulation time of 3 sec. The heater compartments contained booster heaters rated at 8 kW for heating up purposes and proportionally controlled heaters rated at 8 kW maximum for temperature control. Both were subject to a safety cut-out controller. With these arrangements temperature uniformity at 200°C was found to be better than $\pm 1^\circ\text{C}$ in both time and space. After switching on, set temperatures were achieved in 75 min by the oven, and 150–180 min by the column packing.

Detectors

Monitoring of feed inlet and outlet profiles (from bleed streams) was normally carried out with a flame ionisation detector (FID) mounted outside the oven, but a katharometer, mounted inside the oven and in series with the FID, was also available. The line to the FID was heated to prevent condensation of essential oils.

Fraction collection system

The condenser manifold, heated to prevent premature condensation of vapour, led to three fraction collectors for the two separated components and mixed (over-

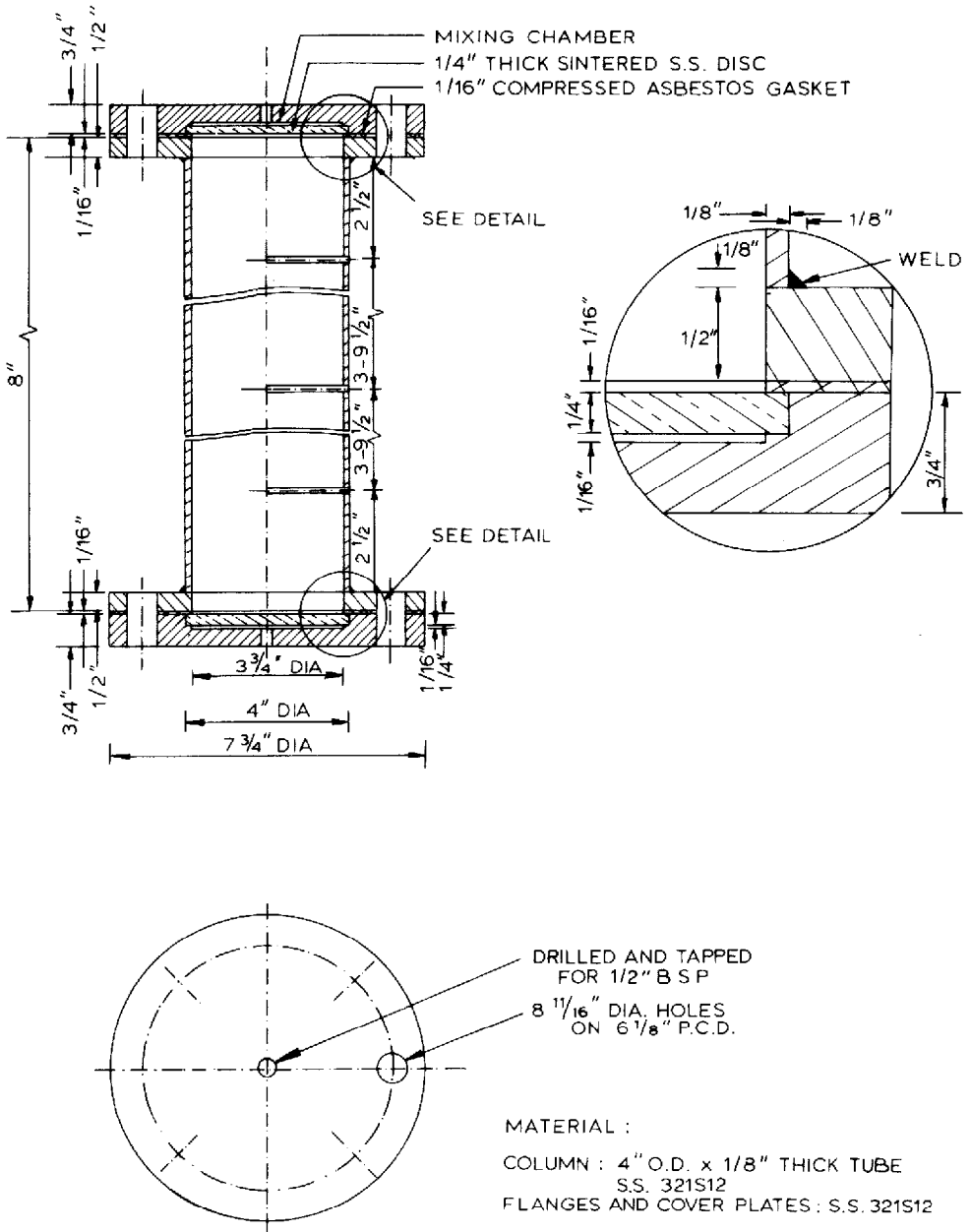


Fig. 3. Column construction. Three thermocouple pockets are shown.

lapping) fraction, respectively. A fourth collector was used when regenerating the carrier clean-up columns. Each collector consisted of a 3 m × 12 mm O.D. water-cooled stainless-steel coil, serving as a cooler-condenser, followed by a 2.5-l collection trap constructed entirely in stainless steel. The design of the trap is shown in Fig. 5.

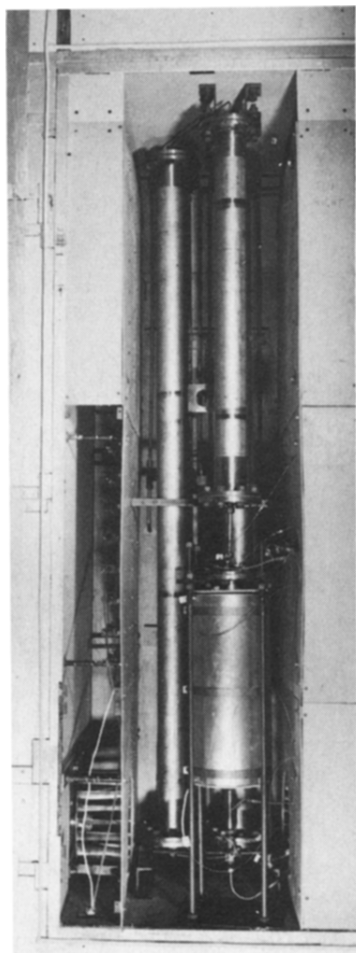


Fig. 4. Photograph of oven interior showing a 2.44-m column section, with the evaporator below a 1.22-m column section. Part of the left-hand compartment has been opened up to show the heaters and (at the bottom) air circulating fan.

The porous discs provide the final cooling effect and help to trap out aerosol. The efficiency of the trap is raised by 20–30% if the lower porous disc is covered with the liquid being condensed and the gas is allowed to bubble through the liquid. This fraction collector is an improvement on the one Carel and Perkins⁷ originally designed in two respects. First, a longer cooling coil permits a lower thermal gradient and hence less aerosol formation. Secondly, use of a second (lower) porous disc increases the aerosol collecting surface both in itself and at the bubble–liquid interface by giving smaller bubbles than created by having the funnel neck merely immersed in the liquid.

Vapour condensing in both the cooler-condenser coils and trap drained to the bottom of the trap, from where it was run off at intervals. Geraniol and nerol were collected with the traps cooled only by water jackets. α - And β -pinene, however, have

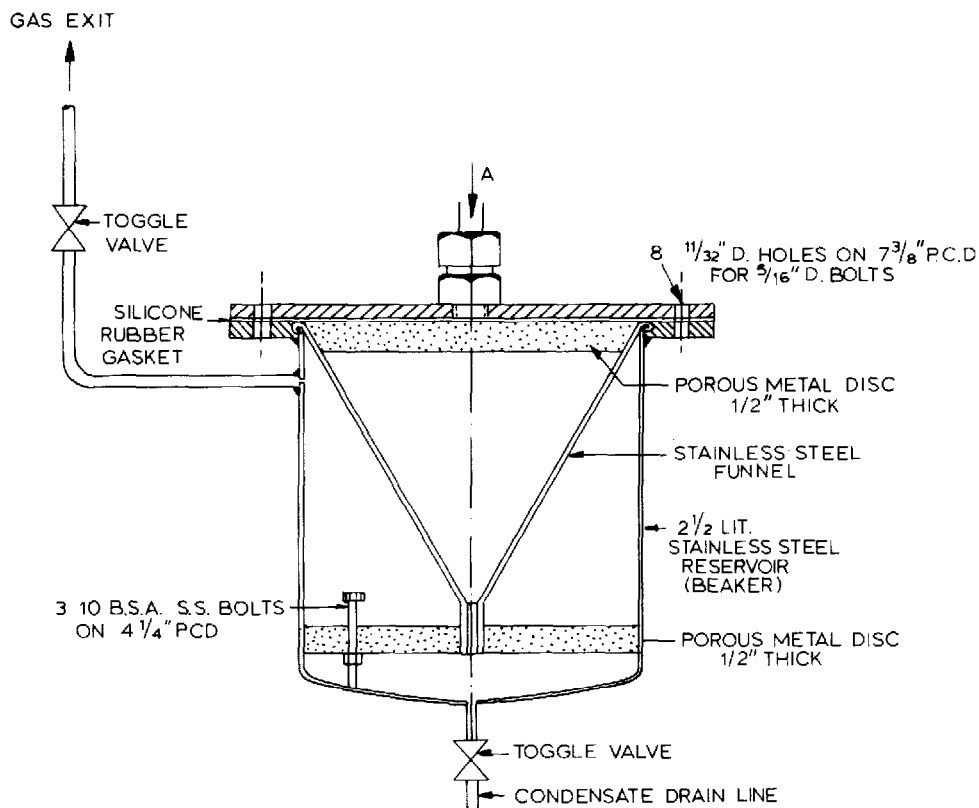


Fig. 5. Collection trap. A = gas inlet.

an appreciable vapour pressure (3 mmHg) at room temperature and were collected with the traps refrigerated at -20°C . The coolant in this case was ethylene glycol-water (50:50), cooled in turn in an intermediate heat exchanger by refrigerant circulated from a secondhand ice-cream making machine.

Carrier clean-up and recycle system

The carrier gas leaving the fraction collectors was cleaned up by passage through a 1.22 m \times 100 mm O.D. stainless-steel column packed with an adsorbent. Two columns were used, with flow paths arranged (Fig. 1) so that one column was on line at room temperature while the other was being regenerated at an elevated temperature in a stream of deoxygenated and dried "oxygen-free" nitrogen. Regeneration was needed when the column had passed a sufficient volume of gas for adsorbed essential oils to be about to break through. This retention volume was determined in small scale experiments. In early work the adsorbent was the same as used in the separation columns, *viz.* Carbowax 20M coated 22% loading on Phase-Sep P. This was unsatisfactory as one 100-mm diameter absorber could handle only 520 l gas when adsorbing the pinenes and the stationary phase tended to decompose² at high regeneration temperatures. It was therefore replaced by molecular sieve 5A with a retention volume of 5440 l for the pinenes. This packing was also less friable,

TABLE I
COMPARISON OF DESIGN PARAMETERS WITH TEST SEPARATIONS

	<i>Geraniol-nerol</i>		<i>Pinenes</i>	
	<i>Test separation</i>	<i>Design</i>	<i>Test separation</i>	<i>Design</i>
<i>Operating parameters</i>				
Column temperature (°C)	170	170	142	142
Evaporator temperature (°C)	225	225	190	190
Separation factor, α	1.186	1.186	1.425	1.425
Column length [cm (ft.)]	1097 (36.0)	1087 (35.7)	366 (12.0)	378 (12.4)
Feed injection time (min)	5.4	8.8	1.0	1.59
Feed sample size (ml)	97		21	
Weight fraction of solute, w	0.136	0.4	0.060	0.4
Gas velocity, \bar{u} (cm/sec)	15.4	15	9.8	15
Column inlet pressure, P_1 (p.s.i.g.)	62	59	62	59
Support mesh size	20 ft of 30-40 16 ft of 5-30	30-40	9-42	30-40
Recovery ratio, r , for slow cycling	0.71		0.57	
Recovery ratio, r , assumed for fast cycling	0.6	0.6	0.6	0.6
Cycle time, t_c , for fast cycling (min)	37		14	
<i>Performance parameters</i>				
Product purity* (%)	96	96	98	99
Throughput for fast cycling (g/h)	62	339	43	1200
Thermal degradation of products (%)	25	low	2.6	low

* 100% = two main components only; trace constituents and degradation products excluded.

required no processing before packing, and allowed a higher regeneration temperature, so minimising the volume of gas used. Regeneration was accomplished in 12.7 min at 260°C at a flow-rate of 60 l/min.

Clean gas was recompressed to provide 60 p.s.i. pressure at the column inlet by a Compton two-stage diaphragm compressor. A diaphragm compressor was chosen to prevent contamination of the gas by oil. Two 0.085-m³ surge tanks, constructed from galvanised cast iron pipe, served to smooth out transient pressure fluctuations. A diaphragm valve in a line by-passing the compressor provided control of the compression ratio and acted as a safety device for the compressor in the event of failure of the compressor or a blockage in the line on the high pressure side.

Start-up procedure

Before starting up, the whole system was first evacuated, then repeatedly purged and evacuated with "oxygen-free" nitrogen at 5 p.s.i. until analysis of gas samples on a molecular sieve 5A chromatographic column showed that the oxygen concentration was below 1 part in 10³ by volume. This was low enough for the manganous oxide columns to be able to remove the residual oxygen subsequently. The chromatograph was pressurised, using both start-up and make-up cylinders,

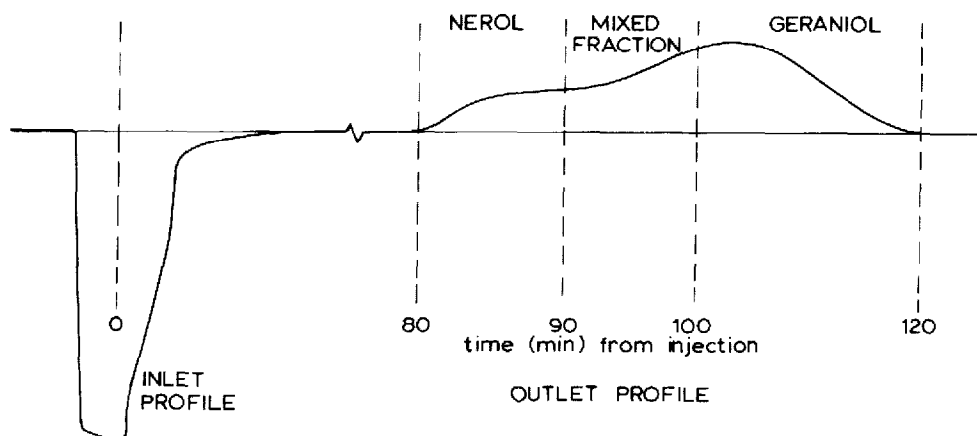


Fig. 6. Chromatogram for test separation of geraniol from nerol under experimental conditions in Table I.

until all relevant pressure gauges read 40 p.s.i., a pressure previously found to give the desired flow (50 l/min at mean column pressure) at the desired column inlet pressure (60 p.s.i.). Both cylinders were then shut off and the oven carrier gas pre-heaters and evaporator switched on. The clean-up columns were by-passed and the compressor switched on. The carrier gas flow and column inlet pressure were adjusted by means of the pressure controller located between the main rotameter and the two gas cylinder rotameters. Once steady pressures were achieved the pressure at the outlet of the make-up cylinder was matched with the pressure on the high-pressure surge tank to maintain steady pressure and flow in the system. After 3 h when the column had reached a steady operating temperature, the bleed line to the detector was set to a suitable flow-rate and a clean-up column was switched into the flow line. The chromatograph was then ready for use.

RESULTS AND DISCUSSION

Test separations

Test separations were made of geraniol from nerol, and α -pinene from β -pinene. Experimental conditions are given in Table I, and an example of the chromatogram obtained in Fig. 6. The fraction cut points shown were chosen to give the desired purity of the two key components (meeting typical current commercial requirements for purity of these materials), as determined by small-scale analysis of the product fractions. The use of incomplete resolution, with an optimum recovery ratio around 0.6, helps to maximise the throughput³. Analysis of the product fractions also gave the amount of thermal degradation caused by processing; the data (Table I) show that the column and evaporator temperatures were right for the pinenes, but somewhat too high for geraniol and nerol.

A comparison of the test and design parameters is given in Table I. The design parameters are as calculated previously¹ but modified to allow for a higher optimum solute concentration, as will be explained.

The design throughputs are calculated from eqns. 1 and 2 of ref. 9 for the

optimum operating parameters listed in Table I. The test throughputs are readily derived from the test data, despite the use of only single injections, by dividing the mass of product by a cycle time (interval that would be used between successive batches if repetitive injection were employed) chosen by examination of the chromatogram to approximate a condition of fast cycling³ by giving an overall recovery ratio of 0.6 at the same product purity as the test separation; *e.g.* for geraniol-nerol, whose chromatogram occupies a total time of 120 min (Fig. 6) the cycle time is 37 min.

Although many of the test parameters meet the design specification, several critical ones do not, because the equipment was constructed at an early stage in the development of the optimisation model. The performance figures achieved illustrate the large losses of throughput caused when the operating parameters are not all optimised. The principal changes needed to raise the throughput to the design optimum are to raise the feed injection time, solute concentration and (in the case of the pinenes) carrier gas velocity, and to improve the packing quality. Packing quality¹⁰ was inadequate only insofar as it prevented attainment of the optimum number of plates in the column; this could have been countered by increasing the column length in proportion to the plate height so as to maintain the throughput¹¹. By far the largest source of difference between the test and design throughputs, however, is in the concentration of feed at the column inlet. The throughput is directly proportional to the partial pressure of feed³. Previously⁹ we have calculated the partial pressure from the mole fraction, x , in solution and suggested that, on the limited evidence available, x_{opt} lies between 0.2 and 0.5. The chromatograms for both systems studied, however, show negligible peak asymmetry at the concentrations used and it appears that considerably larger concentrations are optimum. Moreover, the mole fraction is an unsuitable concentration parameter for polymer solutions, and the weight fraction of solute in solution, w , is more suitable for a wide range of molecular weights¹². On present evidence we believe that w_{opt} lies between 0.15 and 0.5 and the design data in Table I are calculated using $w_{\text{opt}} = 0.4$ in place of the earlier $x_{\text{opt}} = 0.4$. This leads to feed partial pressures some four times (for geraniol-nerol) and ten times (for the pinenes) greater than attainable with the evaporator used, and inadequate evaporator performance¹⁰ is the main cause of the relatively poor test throughputs achieved.

The design throughputs in Table I are sensitive to the column temperature. If the solutes were not heat-sensitive, the throughputs would be up to several times larger again, as can be calculated⁹. If thermal degradation of the pinenes, for example, were considered acceptable at a higher operating temperature of 160°C (instead of 142°C), the throughput would rise from 1.2 to 2.0 kg/h.

Product collection efficiency

The efficiency of the fraction collectors in trapping the column effluent was determined. For short periods of continuous trapping of the pinenes the efficiency was 59% at room temperature and 82% at -20°C. Geraniol and nerol gave a significantly higher efficiency than the pinenes at room temperature. These figures were obtained with the trap initially empty and dry; considerably higher efficiencies were attained when liquid had collected above and below the lower porous disc. Other authors^{5,13} have reported the same finding. This type of trap therefore needs to be

operated "wet" as it was designed to do, and even then is satisfactory only with adequate refrigeration in relation to the boiling points of the solutes. More efficient types of trap are under study.

Costing

The equipment and its operation were costed to provide a basis for estimating product costs. The capital cost breakdown is as follows (corrected for inflation to January 1983 and excluding labour of construction).

Gas recycle, purification and preheat	£ 3524
Columns	2884
Column packing	1809
Oven	3968
Feed injection system	4045
Fraction collectors	1829
Detection and readout	1960
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The utilities element in operating costs is assessed on a basis of 4 p/kW for electricity and 16 p/1000 gal for industrial cooling water, assuming that the cooler-condensers use water and no refrigeration:

Electricity	£8.79/24h-day
Water	0.18/24h-day
Carrier gas	1.70/24h-day
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	20.67/24h-day

Refrigeration to -20°C adds a further £0.97/24h-day. By far the largest item in the cost of utilities is electricity. Operating costs could be reduced by about 30% by further improving oven insulation and by providing heat exchange between the gas streams entering and leaving the column.

The costs given here exclude the substantial items of labour, maintenance, packing changes and profit. Assuming linear depreciation of capital costs over ten years and 300 days of operation per year, the contribution of depreciation and utilities together to product cost is £1.14/kg for a throughput of 1 kg/h, and £3.80/kg at 0.3 kg/h.

CONCLUSIONS

A production gas chromatograph needs careful design if it is to perform satisfactorily for heat-sensitive materials. The major requirements, and practical means of realising them, have been described. Our experience shows that the principal difficulties are three:

- (1) The design of an injection system to evaporate a heat-sensitive feed without

decomposition and to mix the large volume of vapour uniformly with the carrier gas and give a rectangular feed band. The present packed design operating discontinuously and evaporating to dryness produces excessive decomposition and deposition of carbon and is incapable of handling the large vapour volumes adequately. A sub-boiling falling film evaporator has recently been studied¹⁴ and promises to be more satisfactory. If continuous operation of the evaporator is necessary to avoid thermal decomposition, the best approach may be to have one continuous evaporator serving more than one column. The columns are in parallel and each is supplied with feed in turn. The number of columns equals the ratio of cycle time t_c to injection time t_f .

(2) The need for a packing that does not require frequent changing because of bleeding, etc.; and the need to devise a recoating and repacking procedure that allows the existing support to be reused without degrading it.

(3) The desirability of using a more efficient fraction collector than the present improved form of Carel and Perkins' design.

These problems and means of solving them are under study and will be reported separately.

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