PREPARATIVE SCALE SEPARATION OF ORGANIC MIXTURES BY SEMI-CONTINUOUS GAS-LIQUID CHROMATOGRAPHY

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TO MY PARENTS

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SUMMARY

A review is given of general chromatographic theory, the use of G.L.C. (gas-liquid chromatography) for the prediction of thermodynamic data, and the scale-up of the chromatographic process for preparative and production level separations. The application of G.L.C. for the separation of fatty acids is also reviewed and its industrial importance is discussed.

The design and construction of a sequential continuous chromatographic refiner (SCCR-2) for high temperature (up to 200°C) preparative-scale G.L.C. separations is described. In this equipment the counter-current movement between the gas and liquid phase is simulated by sequencing a system of inlet and outlet port functions around twelve fixed, 2.21 cm diameter and 61 cm long, columns.

The separating capabilities and other operating characteristics of the SCCR-2 unit have been investigated using mixtures of different separation difficulty and volatility. The feed mixtures selected had separation factors in the range of 1.1-5.8 and required equipment operation in the range of 55-200°C, while using F.F.A.P. (free fatty acid phase) on Chromosorb W or OV-275 (a cyanosilicone) on Chromosorb P, as chromatographic packing material.

Initially the separation of the equivolume halocarbon mixture of "Arklone" P/"Genklene" P was attempted and purities greater than 99.8% have been achieved for both products, at feedrates of 21 $cm^3 h^{-1}$ and operating at about 60°C. In addition the more difficult separation of a 50/50 V/V mixture of methyl chloroacetate/ethyl lactate (SF 1.5) was studied and the ability of the SCCR-2 unit to separate the mixture into two products with purities in excess of 99.8% has been demonstrated

at feedrates up to 80 cm^3h^{-1} and operating temperature within the range of 110-130°C. With lower separation factor systems (SF 1.2) such as "fungal oil" the equipment was found to have inadequate column length for successful separations.

A knowledge of the vapour-liquid equilibrium data for the systems used was necessary for the determination of the operating characteristics of the SCCR-2 equipment. Therefore, part of the present work was initiated with the aim of providing vapour-liquid equilibrium data.

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CHAPTER 1

Introduction

The earliest report on chromatography is that of Tswett (1) in 1906, who separated the components of plant pigments by passing their solutions through columns of solids adsorbents. This Russian biologist noticed the formation of coloured horizontal bands of the different pigments as the solution of the plant pigments was washed down the column with a light petroleum; and the term chromatography, which literally means "colour writing", was coined by the author to describe this phenomenon.

Following on Tswett's discovery, nothing important in the chromatography field was achieved until, after a lapse of 35 years, Martin and Synge (2) reported one of the most astonishing works in the history of analysis. These researchers reasoned that partition isotherms were more commonly linear for the distribution of a solute between two liquids than for its distribution between a liquid and a solid, and had shown how it was possible to construct and operate a liquid-liquid chromatographic system. In addition their finding that paper strips could be employed in place of columns was quite significant to the development of paper chromatography. The importance of their work was recognised in 1954 by the award of the Nobel prize.

In their original paper Martin and Synge pointed out that the flowing liquid could with advantage be replaced by gas. Another ten years elapsed before this proposition was experimentally performed by Martin, this time in collaboration with James (3). About one decade later, gas-liquid chromatography (G.L.C.) became one of the most successful analytical techniques for the qualitative and quantitative determination and resolution of complex chemical mixtures. At the present time, when the literature on chromatography contains at least five thousand papers,

G.L.C. is generally accepted as a standard rapid analytical technique with unique separating power and has widespread use in most laboratories.

Another aspect of G.L.C., apart from being able to analyse complex chemical mixtures, is that of the determination of thermodynamic data. This possibility has been appreciated since the early days of G.L.C. (3,4). Since then more than two hundred papers dealing with thermodynamic measurements by G.L.C. have established G.L.C. as an accurate and fast method for the determination of thermodynamic data.

The third important application of G.L.C. lies in the possibility of extending this successful analytical technique to preparative separations. This possibility was quickly realised, in the 1950's, with the growth of G.L.C. and the increasing demand for pure chemicals. However, nowadays only few examples of the use of G.L.C. on an industrial scale are available in the literature (see Section 2.3.3). This is because the scale-up of analytical systems by increasing the column diameter or the injected sample size, usually results in a significant deterioration of the quality of separation, leading to impure fractions and negating many of the advantages of G.L.C. over the other separation methods.

Overcoming the inherent restrictions on scale-up has provided a challenge to many research workers in the last twenty years. The attempts to improve large-scale column efficiency have been successful to some extent, and preparative-scale columns with efficiencies approaching those of analytical columns have been recently described in the literature (5).

Various schemes have been proposed to increase the column utilisation and therefore the feed-throughput of a G.L.C. system. Among them the "repetitive injection" batch operated systems and the

continuous counter-current systems have found the most success. Since the latter seems to give a greater column packing utilisation, considerable effort has been directed towards the development of G.L.C. systems based on the counter-current mode. With this technique, the gas and liquid phase flows are moved counter-currently, while the binary mixture to be separated is fed continuously into the middle of the column. The relative flow rates of the two phases are adjusted so that the less soluble component of the feed mixture travels in the direction of the gas flow and the other is carried with the liquid phase. The more soluble component is then stripped off the liquid phase in a different section of the column assisted by heat or a high gas flow rate.

Over a period of about 15 years Barker and co-workers (6-20) have actively developed various counter-current chromatographic systems. These may be classified into three main groups; 1. moving-bed, 2. moving-column and 3. SCCR (sequential continuous chromatographic refiner) systems.

The latter is a pseudo-moving bed system, based on simulating the relative stationary phase movement by sequencing a system of inlet and outlet port functions around a closed loop of chromatographic columns. Thus, the problems of solid handling encountered in moving-bed systems are avoided as well as the mechanical movement of columns involved in the moving-column systems, which are quite restrictive in scaling-up these processes to industrial levels. In general, the sequential chromatographic systems seem a very promising approach towards continuous chromatography, since they do not involve moving beds or any moving seal, are expected to be more mechanically reliable; also they are adaptable to any column dimensions to facilitate their scale-up.

The first SCCR unit (SCCR-1), designed and constructed by Barker and Deeble (17-20), consisted of 12 chromatographic columns, each 7.6 cm in diameter and 61 cm long. This G.L.C. unit has also been successfully used by Barker, Deeble and Bell (18-21) to separate binary halocarbon mixtures at feed rates of up to 1500 cm^3h^{-1}, with typical purities in excess of 99.7% for both products. However, the construction of the SCCR-1 unit was limited by economic considerations as its material of construction was brass and copper, with air as carrier gas and lacked any heating facilities.

Although the majority of separation studies by Barker and co-workers have been attempted at temperatures near ambient, Barker and Al-Madfai (12-14) have demonstrated the possibility of continuous separation of essential oils at temperatures of up to 120°C using a moving-column G.L.C. system.

One of the objectives of the present study was to develop a preparative scale G.L.C. system capable of working to 200°C and operating on the principle of the sequential continuous chromatographic refiner (SCCR). Having established a sequential G.L.C unit to operate at high temperatures, the separation of various fatty acid ester mixtures such as that of methyl chloroacetate/ethyl lactate was proposed, leading to an attempt to recover γ-linolenic acid from "fungal oil". This is a purification problem with high industrial interest to pharmaceutical companies.

Additionally, the operating and general performance characteristics of the equipment were to be determined. As part of this work the vapour-liquid equilibrium data for the mixtures to be used would have to be determined using a commercial analytical-scale G.L.C. This was thought to be necessary since no data was available in the literature.

CHAPTER 2

Literature Survey

2.1 BASIC THEORETICAL ASPECTS IN G.L.C.

Separation is achieved in chromatography as a consequence of the different affinities of individual solutes within a mixture for a common solvent. In gas-liquid elution chromatography (G.L.C.) an inert carrier gas is passed through a column packed with a solid support on which the liquid solvent (stationary phase) is impregnated. When the mixture of solutes to be separated is introduced into the column, the difference in their selective retardation by the stationary phase causes the solute bands to travel at different rates. Consequently they will be separated and are eluted in the order of least retarded first.

Fig. 2.1 shows a typical chromatogram (elution curve) of a mixture of compounds I and II that has been completely separated. The ordinate represents detector response and the abscissa represents time. The first sharp peak is obtained for unabsorbed gas, while the second and third peaks have undergone the chromatographic process. Also,

t_m = "elution" or "retention time" for an unabsorbed component, which is a measure of the gas hold-up in the column (dead volume of column).

t_R = "elution" or "retention time" for a component

t'_R = $t_R - t_m$, "adjusted retention time", which measures the effect of the chromatographic process on a component.

The "distribution" or "partition coefficient", K, is defined as the equilibrium ratio of the solute concentration in the liquid solvent to the concentration in the gas phase and is a measure of the affinity of a solute for a solvent (Section 4).

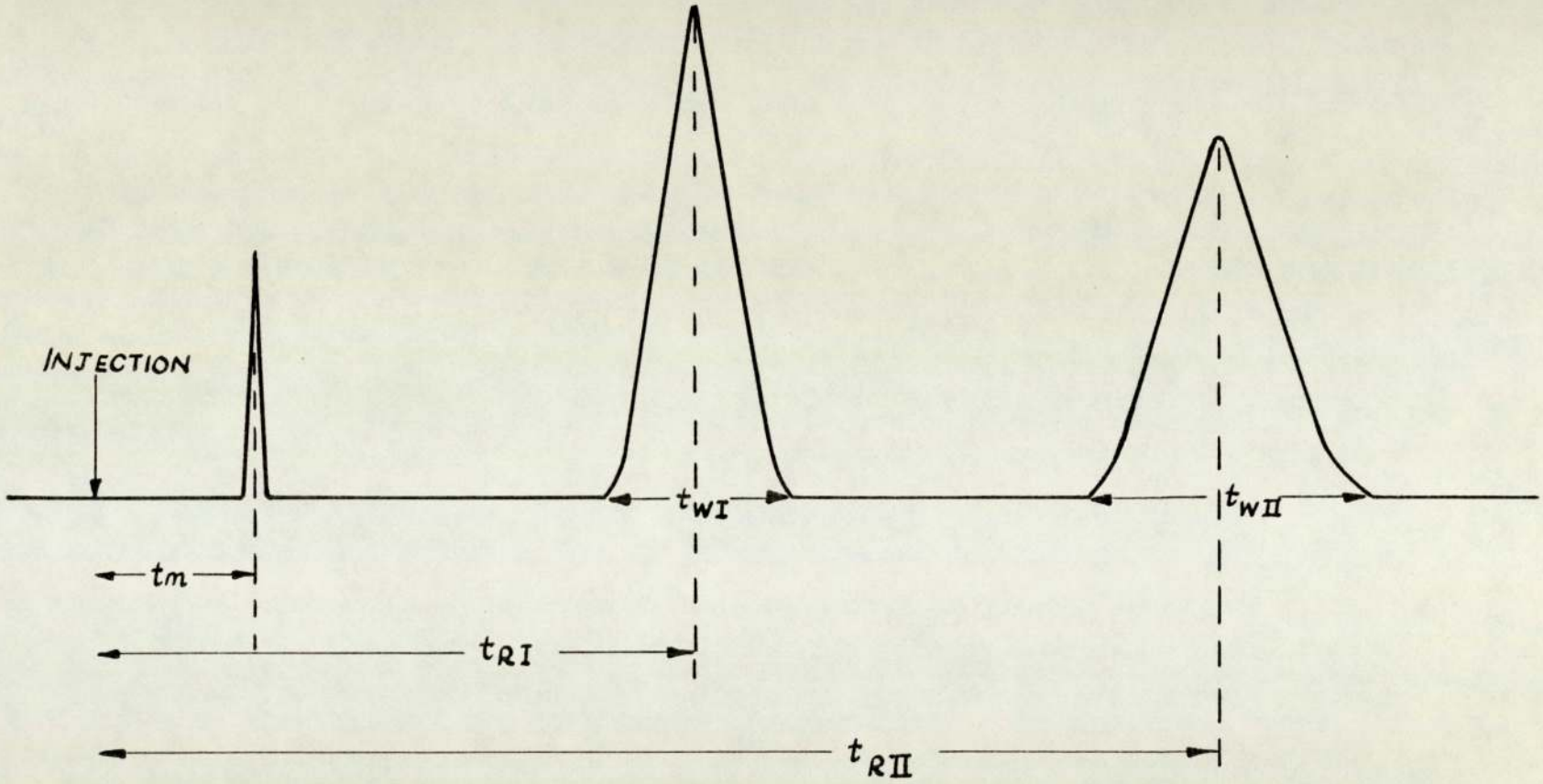


FIGURE 2.1 ELUTION DIAGRAM

The ratio of "partition coefficient" of component II, to that of component I defines the "separation factor", SF, of solutes I and II.

Thus, $$SF = \frac{K_{II}}{K_I} \qquad (2.1)$$

and since the larger value of K is placed in the numerator, as the "separation factor" approaches unity, the separation becomes more difficult.

Further definitions, relationships and theoretical aspects of the basic elution G.L.C. chromatographic theory, discussed here, as well as for the other types of chromatography can be found in general texts (22,23,24).

In general, separation in elution chromatography is achieved through differences in migration rates of solutes, governed by thermodynamic equilibrium. However, the effectiveness of a separation is also dependent on the degree of overlap of the solute zones, which is governed by column dynamics. It is obviously desirable to keep narrow the solute zones to reduce or eliminate overlap.

The solute zone broadening theories are dealing with the factors that contribute to zone dispersion and therefore are briefly reviewed in the following sections.

2.1.1 PLATE THEORY

Considering a mass transfer process as a series of theoretical plates or equilibrium stages is a well known procedure, particularly in the field of distillation processes. This model was first extended to chromatography by Martin and co-workers (2,3), based on a gas-liquid chromatographic system.

With the plate theory for chromatography, a number of simplifying assumptions are made. These are as follows.

(1) The chromatographic column is divided into a number of theoretical plates, N, such that the solution leaving a plate is in equilibrium with the mean solute concentration in the stationary phase throughout that plate.

(2) Mobile phase flow is regarded as discontinuous, consisting of a stepwise addition of volumes of mobile phase, each equal to the free volume per plate.

(3) The partition coefficient is constant throughout the column and independent of concentration, i.e. "linear" chromatography.

(4) The solute exchange process is thermodynamically reversible. This implies that the equilibrium between solute and solvent is instantaneous (mass transfer coefficient is infinitely high and the diffusion neglected).

However, some of the assumptions made are either over-simplified or physically tenuous. Thus, in the case of gas chromatography, axial diffusion of the solute molecules cannot be neglected since it contributes significantly to the broadening of the solute zone. Also, the partition coefficient is concentration dependent. The most severe assumption is that of a discontinuous flow. This is obviously wrong in most chromatographic methods where the mobile phase is continuously flowing. Glueckauf (25) attempted to improve the model by describing a continuous flow plate model.

In spite of these simplifications, the plate theory succeeds in several aspects. It is able to approximate in some cases the shape of the eluted solute peak, and it gives a measure of the column

efficiency, namely the height equivalent to a theoretical plate, H or H.E.T.P., which has a considerable value for comparing chromatographic columns.

By definition, H is given as

$$H = \frac{d\sigma^2}{dL_M} \tag{2.2}$$

where σ^2 is the variance or second moment of the elution curve, which is approximated by a Gaussian type distribution, and dL_M is the distance migrated.

The name "height equivalent to a theoretical plate" is a misnomer which is a result of the plate model itself. Instead, H should be regarded as a measure of column efficiency or better as a measure of peak's spreading relative to the distance migrated.
For a uniform column, H is given as

$$H = \frac{\sigma^2}{L_M} = \frac{l}{N} \tag{2.3}$$

where l is the column length and N is the number of theoretical plates.

An important property of σ^2 is that independent contributions to H are additive,

$$H = \frac{\Sigma\, \sigma_i^2}{L_M} \tag{2.4}$$

Thus, contributions to plate height such as finite mass transfer rates, longitudinal molecular diffusion and eddy diffusion may be determined independently (Section 2.1.2) and summed to give an overall H value.

In practice, H may be related (24) to the chromatogram shown in Fig. 2.1 by the following equation:

$$H = \frac{1}{16} \left(\frac{t_w}{t_R}\right)^2 \qquad (2.5)$$

where t_w is the peak width.

The determined H values, describe the summation of all the contributions to peak dispersion (σ^2), without any consideration of the mechanisms within the chromatographic column which determine them, such as partition phenomena, molecular diffusion and flow patterns through packed beds.

2.1.2 RATE THEORIES

The idealised reversible process considered in the plate model is unattainable in practice. Van Deemter, Zuiderweg and Klinkenberg (26) developed a theory and included contributions to non-ideality caused by axial molecular diffusion, eddy diffusion and mass transfer rates. A mass balance approach led them to the well known "Van Deemter equation", which in its simplest form is

$$H = A + B/u + C_s u \qquad (2.6)$$

Where, u is the interstitial mobile phase velocity, A is the term for eddy diffusion, B/u is the longitudinal molecular diffusion term, and $C_s u$ is the mass transfer in the stationary phase term.

This equation has been further extended and/or modified by many workers, deriving thus several other similar forms of rate equation. Van Deemter (27) added another term to his original equation to allow for the contribution to the plate height made by resistance to mass

transfer in the mobile phase. Golay (28) had developed a theory for capillary columns, while more recently Grushka (29) derived another rate equation.

The individual terms of the basic "Van Deemter" equation are given in expanded form in Table 2.1 along with several other rate equations.

An extensive theoretical study of the mechanisms causing zone broadening has been carried out by Giddings, details of which are given in his well known text (24). His "random walk" approach gives an insight into individual molecular processes occurring in a chromatographic column. According to this model, as a single solute moves through a chromatographic column, the individual molecules undergo a large number of sorption-desorption steps. When they are in the mobile phase, they move at the velocity of the mobile phase. When they are sorbed, they are immobile relative to the mobile phase. The probability that a given molecule will be mobile or sorbed is entirely random, and the molecular movements of the solute have an equal chance of being forward or backward. For simplicity, steps in the forward or backward direction are assumed to have constant length, equal to the average (root mean square) step length (l'). This random molecular movement results in a statistical spread of molecules in the form of a Gaussian curve. The variance, σ^2, is equal to $l'^2 n'$, where n' is the number of steps taken. Each process occurring in the column has its own value of l' and n', and the individual variances, σ_i^2, may be summed to give the total variance.

Thus,

$$\sigma^2_{TOTAL} = \Sigma\sigma_i^2 = \Sigma(l_i'^2 . n_i') = H.L \qquad (2.7)$$

TABLE 2.1 COMPARISON OF SOME RATE EQUATIONS

AUTHOR	EDDY DIFFUSION TERM	LONGITUDINAL MOLECULAR DIFFUSION TERM	RESISTANCE TO MASS TRANSFER IN STATIONARY PHASE TERM	RESISTANCE TO MASS TRANSFER IN MOBILE PHASE TERM	OTHER TERMS	SYMBOLS
Van Deemter	$2\lambda dp$	$2\gamma' \frac{D_m}{u}$	$\frac{8}{\pi^2} \frac{K F_m' u d^2}{(1+K \frac{F_m'}{F_s'})^2 D_s F_s'}$	-	-	λ = packing characterization factor for eddy diffusivity dp = mean packing particle diameter γ' = labyrinth factor to allow for tortuous flow path D_m, D_s = molecular diffusivities in mobile and stationary phases F_m', F_s' = fractional volumes of mobile and stationary phases V_m, V_s = volumes of mobile and stationary phases K = partition coefficient d = stationary phase liquid film thickness u = interstitial mobile phase velocity $k' = K \frac{F_s'}{F_m'}$ = capacity ratio k_f = rate of exchange of solute between the two phases R = relative solute zone migration rate f(k') = function of capacity ratio w = constant taking into account the geometrical effects of the packing structure.
Golay	-	$2 \frac{D_m}{u}$	$2R(1-R) \frac{d^2 u}{D_s}$	$\frac{1+6k'+11k'^2}{24(1+k')^2} \frac{dp^2 u}{D_m}$	-	
Grushka	-	$2 \frac{D_m}{u}$	$\frac{2 k' d^2 u}{3(1+k)^2 D_s}$	$\frac{k' V_s u}{(1+k)^2 V_m k_f}$	-	
Giddings (random walk model)	$2\lambda dp$	$2\gamma' \frac{D_m}{u}$	$2R(1-R) \frac{d^2 u}{D_s}$	$\frac{f(k') w d_p^2 u}{D_m}$		
Giddings (coupling theory)	-	$2\gamma' \frac{D_m}{u}$	$2R(1-R) \frac{d^2 u}{D_s}$	-	$(\frac{1}{2\lambda d_p} + \frac{D_m}{f(k') w d_p^2 u})^{-1}$	

Giddings (24) based on his theory and considering the four most important causes of zone broadening (longitudinal molecular diffusion, eddy diffusion, mass transfer resistance in the mobile and stationary phase) derived an equation of similar form to the "Van Deemter" equation. It differs only in the additional term for the resistance to mass transfer in the mobile phase, C_m u (see Table 2.1).

However, in a more realistic manner, Giddings (24) maintains that the eddy diffusion and the resistance to mass transfer in the mobile phase are not independent, and consequently their variances not additive. He introduces a "coupling theory" for which the following equation, in its simplified form, can be written.

$$H = B/u + C_s u + \frac{1}{1/A + 1/C_m u} \qquad (2.8)$$

The validity of the "coupled equation" was proven by many workers and it is now generally accepted as theoretically more sound than the classical "Van Deemter" expression.

Giddings (24) further developed the more powerful "generalized non-equilibrium theory" of zone broadening, which unlike the microscopic "randon walk theory" considers bulk properties of the chromatographic system. Non-equilibrium arises from the fact that the mobile phase is constantly moving, carrying the solute molecules with it. The solute molecules partition themselves between the moving and the stationary phases. Due to the thermodynamic nature of the partitioning process, the solute molecules aspire to be in state of equilibrium. However, the flow of the mobile phase prevents that state of equilibrium from occurring. The mobile phase in the front of zone continuously brings solute molecules into the stationary phase. On the back half of the

zone, the carrier is the concentration poor phase and sweeps the solute molecules as they desorb from the stationary phase. Thus, during passage of a solute zone through a column, true equilibrium is only achieved at the centre point of the zone.

In the non-equilibrium model, it is the magnitude of the departure from equilibrium that determines the solute zone broadening. The front of the zone in the mobile phase is richer in concentration while the rear of the zone is poorer than it would have been in the case of equilibrium. The "generalized non-equilibrium theory" is more powerful than the "random walk theory" since it allows calculations of H for much more complicated systems, where the latter model fails. In fact this theory is only used to calculate the mass transfer resistance terms ($C_s u$, $C_m u$), which for practical chromatography, using high mobile phase velocities, are the most significant contributions to H. The difficulty in the model lies in the complexity of the mathematics involved. However, the advantage of the "non-equilibrium model" is its ability to include the geometrical effects of the support structure, and a balance has to be made between the assumptions made and complexity of mathematics thereby involved. Giddings in his text (24) gives a list of various expressions for C_m, C_s derived by using the "non-equilibrium model".

The models outlined here provided a firm theoretical background for the mechanisms occurring in chromatographic columns. However, it is noticeable that as knowledge increased, the models became more complex. The plate height expressions allow the worker to relate the experimental conditions to the efficiency and hence to improve it. H depends explicitly on the mobile phase velocity, on the nature and amount of the stationary phase, on the support particle size, on geometry of the

packing and on the diffusion of the solute in both phases. Implicitly, H is also a function of the temperature and pressure (30).

2.2 THE USE OF G.L.C. FOR THE DETERMINATION OF THERMODYNAMIC DATA

2.2.1 INTRODUCTION

Martin (4) one of the inventors of G.L.C., was the first to recognize the potential value of G.L.C. for thermodynamic determinations. In 1956 he pointed out "the method provides perhaps the easiest of all means of studying the interaction of a volatile solute with a non-volatile solvent, and its potential value for providing this type of data should be very great". Since then more than two hundred papers dealing with thermodynamic measurements by G.L.C. have established G.L.C. as a good method for the determination of thermodynamic data.

The best way of checking G.L.C. thermodynamic data is to compare them with the same quantities measured by an independent technique, i.e. static methods. Some papers (31-33) deal with such comparisons and the good agreement indicates the suitability of G.L.C. for thermodynamic measurements.

The thermodynamic quantities which may be determined by G.L.C. are:

1) partition coefficients of solutes at infinite or finite dilution in the stationary phase (K).

2) activity coefficients of solutes at infinite or finite dilution in the stationary phase (γ)

3) second, cross virial coefficients of solutes - carrier gas mixtures (B_{12})

4) excess partial molar enthalpy of mixing ($\bar{h}^E$)

5) excess partial molar entropy of mixing ($\bar{s}^E$).

Other non-thermodynamic quantities which can be obtained by chromatographic methods, are:

(1) liquid and gaseous diffusion coefficients

(2) solid support surface areas.

In G.L.C. the instrumental requirements for making thermodynamic measurements are fairly straightforward, except for special systems involving very high pressures or finite concentration studies. An ordinary commercial analysis chromatograph normally provides the apparatus requirements needed for accurate thermodynamic measurements. These are as follows.

(1) Accurate control and measurement of the gas flow rate.

(2) Accurate control and measurement of temperature.

(3) A means of injecting a liquid as gas phase sample into the system immediately upstream of the column.

(4) A means of detecting a very small sample as it leaves the column and recording its change of concentration in the gas stream with time.

(5) A means of measuring accurately the retention time of the sample in the column.

(6) To know accurately the weight of stationary phase present in the column.

In general G.L.C. methods are more rapid than conventional techniques and require only very small quantities of sample for thermodynamic studies, thus allowing the use of rare, expensive chemicals. But the applicability of G.L.C. is restricted to symmetrical elution peaks. Tailed peaks indicate that a problem exists such as adsorption of solute on the solid support, large sample size used, or poor sample introduction; all these lead to inaccurate thermodynamic determinations.

2.2.2 REVIEW OF THERMODYNAMIC DETERMINATIONS BY G.L.C. METHODS

The development of the thermodynamic treatment of G.L.C. is summarised in Table 2.2. As is shown, the latest theories are far more complex than the originals but certainly and the most realistic ones, providing more accurate thermodynamic data.

Table 2.3 shows some of the most important works appearing on the subject and a brief discussion of the observations is given.

2.2.3 THEORETICAL AND PRACTICAL IMPORTANCE OF THERMODYNAMIC DATA

A systematic study of the thermodynamics of a volatile solute in a non-volatile solvent in the presence of a carrier gas stream is of interest from two aspects. Firstly it facilitates the design (e.g. the selection of a suitable stationary phase or the selection of carrier gas) and operation of preparative-scale G.L.C. equipment. Secondly such a study is of great value in comparing experimental thermodynamic properties with theories of solution and theories of gas phase interactions. The systems best suited for the first purpose are not generally the same as the systems best suited for the second purpose. In this work we are mainly concerned with the thermodynamics of G.L.C. to predict data for the design and operation of the SCCR-2 (sequential-continuous-chromatographic-refiner-two) equipment (Section 4).

2.2.3.1 IMPORTANCE OF B_{12}

The gas phase interactions between solute and carrier gas have the effect of lowering the retention time of solute in the chromatographic column. This can be seen from the equations in Table 2.2, where the more negative B_{12} the more the net retention volume will decrease with increasing pressure.

Desty et al. (35) have observed that the degree of separation of close-boiling pairs of hydrocarbons in the gasoline fraction of a crude petroleum could be significantly altered by the use of hydrogen instead of nitrogen as carrier gas. These workers have also examined the effects of carrier gas on various separations. They pointed out that although the change in the separation factor may be small, the number of theoretical plates, required to achieve a given separation, may be considerably altered. Thus, the number of theoretical plates required to separate benzene and 2,4-dimethylpentane in helium and argon at 292 KN m^{-2} is 429,000 and 99,700 respectively.

Finally, the prediction of B_{12} values and hence PVT data is very important in a variety of chemical engineering problems.

2.2.3.2 IMPORTANCE OF K^{∞} AND γ^{∞}

In unit operations such as distillation, absorption, extraction and G.L.C., the separation is based on the differential change in concentration developed in two phases. The maximum attainable separation occurs when the two phases are finally in equilibrium. Separation factors are calculated from vapour-liquid equilibrium data. Therefore, a knowledge of vapour-liquid equilibrium data is essential in the design and operation of the equipment handling these operations.

Binary and ternary vapour-liquid equilibrium data at finite concentrations can be predicted by using solution theories such as Van Laar's and Margule's equations. These equations relate activity coefficients to composition with constants equal to the logarithms of activity coefficients at infinite dilution. The activity coefficient at infinite dilution is the limiting value of the solute activity

coefficient when the solute concentration approaches zero and its logarithm is called "the end value". "End values" are independent of the type of predicting equation chosen and practically independent of pressure, making them very useful quantities in the prediction of vapour-liquid equilibria. Having obtained the two "end-values" in the case of a binary system and the six "end-values" in the case of a ternary system, one can evaluate the vapour-liquid equilibrium data for the whole concentration range without any experimental measurements, by using the appropriate predicting equation.

2.2.3.3 IMPORTANCE OF K AND γ

The importance of K and γ is in the provision of vapour-liquid equilibrium data for preparative-scale chromatographs and other units operations, when high solute concentrations are involved, as well as for testing the applicability of the solution theories.

TABLE 2.2 PROGRESS IN THERMODYNAMIC MEASUREMENTS BY G.L.C.

AUTHORS	REFER.	ADDITIONAL FACTORS CONSIDERED	BASIC EQUATIONS FOR THERMODYNAMIC DETERMINATIONS
James and Martin	(3)	Basic G.L.C. equation	$V_N^\circ = J_3^2 . V_N = J_3^2 (V_R - V_m) = K . V_L$ $V_N^\circ = \frac{n_L . R_g . T}{\gamma_1 . P_1^\circ}$
Everett and Stoddart Desty, Goldup Luckhurst and Swanton	(34) (35)	Fugacity of solute in carrier gas	$\ln V_N^\circ = \ln(Ko . V_L) + \beta . Po . J_2^3$ $\ln Ko = \ln(\frac{n_L . R_g . T}{V_L . \gamma_1 . P_1^\circ}) - \frac{(B_{11} - V_1^\circ)}{R.T} P_1^\circ$ $\beta = \frac{2 B_{12} - \bar{V}_1^\infty}{Rg.T}$
Everett	(31)	Pressure dependence of K (a linear relationship approximation)	$V_N^\circ = Ko . V_L (1 + \beta . Po . J_3^4)$ $\beta = \frac{2B_{12} - \bar{V}_1^\infty}{Rg.T}$
Cruickshank, Windsor and Young	(36)	Pressure dependence of K (thermodynamic relationship), non-ideality of carrier gas and pressure dependene of carrier gas viscosity	$\ln V_N^\circ = \ln(Ko . V_L) + \beta . Po . J_3^4$ $\beta = \frac{2B_{12} - \bar{V}_1^\infty}{Rg.T}$
Cruickshank, Gainey and Young	(37)	Carrier gas solubility in the stationary phase	For up to 203 kN m^{-2} pressure drop across the column, $\ln V_N^\circ = \ln(Ko . V_L) + \beta' . Po . J_4^3 + J' (Po . J_4^3)^2$
Conder and Purnell	(38)	Finite solute concentrations	$V_N^\circ = V_L (1 - a . J . Yo) (\frac{\partial q}{\partial c})_{\bar{P}}$

SYMBOLS

- V_N : net retention volume
- V_N° : corrected net retention volume
- J_m^m : correction factor for gas phase compressibility
- V_R : retention volume
- V_m : column gas hold-up
- V_L : volume of liquid phase in the column
- K : partition coefficient (q/c)
- Ko : partition coefficient at zero pressure
- n_L : number of moles of stationary phase
- Rg : gas constant
- T : column temperature (°K)
- γ_1 : activity coefficient
- P_1° : vapour pressure of solute at temperature T
- Po : column outlet pressure
- B_{11} : second virial coefficient of solute
- B_{12} : cross virial coefficient of solute-carrier gas mixture
- β',J' : expressions related to the solubility of the carrier gas in the stationary phase, virial coefficients, and activity coefficient of solute.
- $\bar{P}$: mean column pressure
- Yo : the mole fraction of solute in the gas phase at the column outlet
- a,J : expressions which may be approximated by 1 and J_2^3 respectively, at low column pressures and solute concentrations

TABLE 2.3 REVIEW OF THERMODYNAMIC DETERMINATIONS BY G.L.C. METHODS

THERMODYNAMIC QUANTITY MEASURED	REFERENCES	COMMENTS
General reviews	C.L. Young (32)	The theoretical development for the determination of thermodyamic data by G.L.C. is reviewed. Also the factors effecting the applicability of G.L.C. methods and the problems arising are discussed. The published experimental papers, referred mainly for the determination of γ^{∞} and B_{12} by G.L.C. methods, are briefly reviewed and critically commented.
	D.C. Locke (39)	The advantages and limitations of chromatographic methods for making thermodynamic measurements are discussed. An introduction to the application of G.L.C. and L.L.C. (liquid-liquid chromatography) for the determination of most thermodynamic and non-thermodynamic quantities is given.
Partition and activity coefficient at infinite dilution (K^{∞},γ^{∞})	Porter, Deal and Stross (40) Pierotty, Deal, Derr and Porter (41)	They have investigated the extent to which partition coefficients may be assumed to be independent of operating variables. The partition coefficients found constant to within 5-10% over a wide range of variables such as column length and gas flowrate. They have calculated average partition coefficients and activity coefficients for about 40 solutes on 3 different stationary phases. A semi-empirical method was developed to correlate the activity coefficients with the structure of homologous series of non-polar solutes and solvents. But their work was not sufficiently accurate to give activity coefficient data for use in any solution theory (42).
Activity coefficient at infinite dilution	Barker and Hilmi (43) Hilmi (44)	Measurements of activity coefficients of several solutes at infinite dilution using the G.L.C. method with volatile stationary phases. Good agreement with static data was obtained.

TABLE 2.3 continued

THERMODYNAMIC QUANTITY MEASURED	REFERENCES	COMMENTS
Partition and activity coefficient at infinite and finite dilution	Barker and Lloyd (45)	They have determined partition and activity coefficients of some non-polar solutes over a wide range of temperatures at finite and infinite dilution, using a specially designed G.L.C. apparatus. Their results at least at finite concentrations are rather qualitative than quantitative.
Partition and activity coefficients at finite dilution (K, γ)	Sunal and Barker (46) Sunal (47)	They successfully modified a commercial chromatograph to measure the partition and activity coefficients of various solutes at finite concentration in polymer stationary phases, by the technique of "Elution on a Plateau". The experimentally determined activity coefficients were correlated well by the Florry-Huggins equation.
Activity coefficient at infinite dilution and second, cross virial coefficient (γ^{∞}, B_{12})	Everett and Stoddart (34) Everett (31) Desty, Goldup, Luckhurst and Swanton (35)	Everett et al. and Desty et al. have developed independently a method for the determination of activity coefficients at infinite dilution and second, cross virial coefficients from the net retention volume measurements over a range of pressures. Everett has shown by comparison with static methods that activity coefficients may be obtained by this G.L.C. procedure with an accuracy better than ± 1%.
Activity coefficient at infinite dilution (γ^{∞}) and second, cross virial coefficient (B_{12})	Cruickshank, Windsor and Young (36) Windsor and Young (48) Young (32,42)	Based on the previous method Cruickshank et al. have developed a more accurate equation for the determination of B_{12} and γ^{∞} by G.L.C. A specially designed G.L.C. apparatus was used for measuring specific retention volumes in packed columns under carrier gas pressures up to 2533 kN m^{-2} (25 atm). From the variation of net retention volume of a solute with the pressure of carrier gas, γ^{∞} and B_{12} could be obtained. Their experimental results found in very good agreement with those obtained by other conventional methods.

TABLE 2.3 continued

THERMODYNAMIC QUANTITY MEASURED	REFERENCES	COMMENTS
	Wičar and Novák (49)	The specific retention volumes of various solutes were measured in the Apiezon K-hydrogen, nitrogen and carbon dioxide systems at pressures of 1013-10133 kN m^{-2} (10-100 atm). The effect of carrier gas solubility in the stationary phase, for the determination of thermodynamic data, was evaluated.
	Laub and Pecsok (33)	The determination of second, cross virial coefficients by G.L.C. is reviewed. The precision apparatus and experimental procedures required to measure B_{12} values are considered, and the importance of virial coefficients is also discussed.

2.3 LARGE-SCALE CHROMATOGRAPHY

The remarkable ability of gas-liquid chromatography (G.L.C.) to physically separate chemical compounds efficiently and rapidly has made G.L.C. very successful as an analytical technique. The success of analytical chromatography has encouraged considerable effort in extending this technique to preparative and production scale separations. As the most direct approach to scale-up is to increase the diameter and/or length of the analytical column, effort and interest in developing large-scale batch G.L. chromatographs have not been lacking. Unfortunately the scale-up problem has been restricted by various factors, discussed later, affecting the performance of large-scale chromatographs.

The interrelation between the chromatographic column efficiency, the speed of separation and the feed capacity of a chromatographic equipment was recognized quite early as the most severe restriction. Thus, a compromise between the above factors seems always to dictate the design of the large-scale chromatographs.

It is interesting to note that all the subject matter in this section is based on the elution type of chromatography, although many of the conclusions are equally applicable to frontal analysis. The following survey is also restricted to batch-wise operating chromatographic systems with particular reference to G.L.C.

2.3.1 FACTORS AFFECTING THE PERFORMANCE OF LARGE-SCALE CHROMATOGRAPHIC COLUMNS

2.3.1.1 FINITE SOLUTE CONCENTRATION EFFECTS

Comparing analytical with large-scale elution chromatography one fundamental difference arises because of the large difference in

the sample sizes employed. Thus, in analytical chromatography the sample size is so small that the chromatographic process is conducted essentially at infinite dilution. In contrast, the large sample sizes used in preparative or production-scale chromatography creates finite solute concentrations in the column which in turn changes the peak propagation and separation process, requiring a major revision of the basic chromatographic theory discussed in Section 2.1 (50).

Basically at finite solute concentration, chromatographic behaviour is affected by three major effects: the absorption isotherm, the sorption and enthalpic overloading effects.

Absorption isotherm effect

This effect causes a change in the partition coefficient with the concentration of solute in the mobile phase and results in non-linear absorption isotherms. Thus, the equation $V_N^\circ = K.V_L$ derived from the basic James and Martin theory (see Table 2.2) which holds true for a linear absorption isotherm must be modified to

$$V_N^\circ = V_L \left(\frac{\partial q}{\partial c}\right)_c \qquad (2.9)$$

at finite concentrations as the absorption isotherm is non-linear (51). In fact at infinite dilution equation (2.9) becomes identical to the James and Martin equation as $\left(\frac{\partial q}{\partial c}\right)_{c \to o} = \frac{q}{c} = K.$

Concluding, at finite dilution the point value of the partition coefficient, $K = q/c$, changes with solute concentration. For a Langmuir type of isotherm, K decreases with increasing concentration, resulting in elution peaks with sharpened leading edges and diffuse trailing edges. In contrast for an anti-Langmuir type of isotherm, K increases with increasing concentration and the trailing edge of the

elution peak is therefore sharpened, while the leading edge becomes diffuse.

At infinite dilution, the linear absorption isotherm produces a Gaussian type elution peak as discussed previously (Section 2.1).

Sorption effect

Basic chromatographic theories are based on the assumption that mobile phase flow remainsconstant throughout the column. Several workers (38,52) have shown that it is not the case at finite solute concentrations since as the solute concentration increases the mobile phase flow increases (i.e. in a G.L.C. column and in the region where the solute band passes, the gas flowrate is higher because of the additional presence of the vapour of the solute in the carrier gas). This effect tends to give a sharp forward front and diffuse tail to the elution peak as the solute zones of high concentration move faster than those at a lower level. Conder and Purnell (38,52) modified equation (2.9) to include the sorption effect as follows:

$$V_N^{\circ} = V_L (1-y) \left(\frac{\partial q}{\partial c}\right)_c \qquad (2.10)$$

where, y is the mole fraction of the solute in the mobile phase at the concentration c.

Enthalpic overloading effect

At finite solute concentrations, the heats of absorption and desorption of the solute in the stationary phase become significant and generate local temperature variations throughout the column due to the inability of the column to rapidly attain thermal equilibrium. These local temperature variations are particularly pronounced in large diameter columns because of the inherent low thermal conductivity

of most packing materials and result in different absorption isotherm characteristics between the column wall and interior regions (53,54). The total effect is a distorted and broadened elution peak. This effect which was named by Higgins and Smith (55) as the enthalpic overloading effect has been recently experimentally studied by M. Bell (21) in a sequential type of chromatograph.

In conclusion, increasing the sample size and therefore the solute concentration results in broader elution peaks which leads to reduced column efficiency in terms of the number of theoretical plates. Thus, in preparative-scale chromatography a balance between column efficiency loss and gain in throughput must be made in order for the maximum equipment performance to be obtained (56). However, in production-scale chromatographs, where the throughput is the main concern, it seems advantageous to operate at the maximum possible solute concentration level, as concentration is directly proportional to throughput (57).

2.3.1.2 EFFICIENCY LOSS IN LARGE DIAMETER COLUMNS

The most direct means for increasing the throughput capacity of a chromatograph is to increase the column diameter. Large diameter chromatographic columns represent the only way of truly increasing feed throughputs to any appreciable level and therefore it is not surprising that this scheme has been most extensively investigated. The principal drawback of this approach is the characteristic decrease in column efficiency.

Variations in the mobile phase flow across the column cross-section was widely recognized as the main cause of the efficiency loss

in large diameter columns. The main source of this flow variation is the non-uniformity of the packed density, since the conventional packing techniques cause size segregation of the particles with the larger particles congregating near the column walls resulting in lower mobile phase flow packing resistance (58). In addition the "wall effects" have been considered by some workers (59) to have a significant contributive factor for mobile phase flow variations.

Attempts by several workers (58,59) to describe the precise shape of the mobile phase profile in large diameter columns have resulted in many disagreements. However, the variation in the mobile phase flow is generally acknowledged and is dependent on the column diameter, the ratio of packing particle to column diameter and the packed density.

This flow variation results in solute band broadening which is further complicated by radial diffusion and leads to significant column efficiency losses. Quantitative treatment for evaluating the efficiency loss in large diameter columns has been considered by many workers and is reviewed in several reports (56,57,60,61).

2.3.1.3 METHODS OF IMPROVING THE EFFICIENCY OF LARGE DIAMETER CHROMATOGRAPHIC COLUMNS

The low efficiencies found with large diameter columns provided a challenge to many research workers to experimentally study and develop large chromatographic column technology, providing means for improving column efficiency to standards approaching those met in analytical columns. Despite the work already completed, large-scale chromatography is not a highly developed technique and many problems remain to be solved. However, this first step was quite significant and encouraged further work for the establishment of chromatography to preparative and production-scale separations.

A. Advanced column packing techniques in G.L.C.

The simplest method of packing large-scale columns is equivalent to that of packing an analytical column, i.e. pouring small amounts of packing into the column, while the column wall is tapped or vibrated. Huyten et al. (62) have shown that this method is not reproducible and leads to a non-uniform packed density when applied to large diameter columns.

Higgins and Smith (55) described several methods of packing such as "bulk", "snow", and "mountain" packing. In the first method the entire column packing is poured in at once, followed by vibration and tapping. In the second, the packing is allowed to trickle in slowly while the column is being vibrated. Finally in the "mountain" technique, the packing is added via a funnel which is maintained at all times above the packed portion of the column. Surprisingly the best efficiencies were obtained with the latter method and HE.T.P. values as low as 1.0 mm were reported for 2.54 cm diameter columns.

Guillemin (63-65) has proposed a new method, which involves fluidization of the column packing after filling the column. Reproducible column efficiencies and H.E.T.P. values of 1.6 mm for 15.2 cm diameter columns were reported. The drawback of this method is that the packed bed is not very stable and tends to collapse after some period of time.

More recently Hupe et al. (54) among others used a conical shaped plunger to obtain high column efficiencies (H.E.T.P. = 2.7 mm) with 10 cm diameter columns.

An improved packing technique has been described by Albrecht and Verzele (66), known as "S.T.P." method. This method combines

mechanical rotation of the column along its axis, shaking, and application of pressure, while the column is being packed. Very high efficiencies (H.E.T.P. = 1.2 mm for 7.6 cm diameter columns) were obtained by this method, which seems one of the best for packing large-scale G.L.C. columns.

More recently Reese and Grushka (5) have developed a new method of packing preparative-scale G.L.C. columns. The method consists of pulling the packing upward into the column by the application of a vacuum, homogenizing the bed, turning the column over, and tapping it. This process is repeated until the column is filled. High column efficiencies (H.E.T.P. = 0.5-0.7 mm) equivalent to those of analytical columns have been achieved by this procedure for 3.3 cm diameter columns.

Finally more comprehensive reviews about packing methods may be found in the literature (20,56).

Unfortunately, the packing uniformity, which is an important factor influencing the efficiency in preparative and production columns, cannot easily be achieved by the present packing techniques. In addition the reproducibility of the packing techniques is in general quite poor, except in a few instances. Consequently other methods, apart from using controlled packing techniques, have been developed to maintain column efficiency with large diameter columns.

B. The use of flow distributors

Various designs of flow distributors have been proposed by several workers in order to improve the non-uniform flow profile encountered with large diameter columns. With this approach columns could be scaled-up without large efficiency losses, facilitating thus the development of production-scale chromatography.

The most common means for achieving this flow uniformity is to incorporate mixing devices at intervals along the column. These may be either insertions such as washers and baffles (67-69) or thin mixing chambers (70-73) provided by constructing the column in a number of short lengths, each supplied with a porous disc at each end of the packing and connected by narrow diameter tubing.

In general, the introduction of flow distributors in production-scale columns has resulted to improved column efficiencies and has been a significant factor in improving the viability of chromatography as a production-scale process.

A comprehensive review about flow distributors may be found in Pecsar's report (56).

C. Entrance and exit cones

It is generally accepted that the efficiency of a large diameter column may be greatly increased by using inlet/outlet cones. These entrance/exit cones operate as flow distributor devices resulting in a more uniform flow velocity distribution over the column cross-section.

Several designs of inlet/outlet cones have been proposed in the literature (56,74) varying in the cone angle, material filling the cone, i.e. inert spheres or packing, and the degree of filling the cone. Despite this, general conclusions are difficult to make since the ideal cone design seems to depend on the column diameter and operating conditions. Such devices however, undoubtedly improve column efficiency and therefore have a viable place in the production-scale chromatography.

D. The use of columns of non-circular cross-section

Several column designs, other than those of standard circular cross-section, have been proposed to eliminate the packing particle segregation and to improve the heat transfer properties of the column. Thus oval, annular, finned columns and others have been studied and significant column efficiency improvements were reported (56,75,76).

The major drawback of this approach is due to the difficulty and expense of constructing such columns for production-scale application.

In conclusion, it should be emphasized the need for improving large column efficiencies, which in addition to being essential for good separations, is also of crucial theoretical importance. Since the modelling of the solute zone broadening mechanisms in large diameter columns is at present largely empirical, it is expected that as more efficient columns are prepared, more information about column characteristics may be obtained, and this would greatly facilitate the scale-up of chromatography.

2.3.2 SCALE-UP TECHNIQUES

2.3.2.1 INCREASE OF COLUMN LENGTH

The throughput capacity of a chromatograph may be increased by increasing the column length, without significant efficiency loss. In fact it has been shown that the H.E.T.P. for preparative columns remains essentially constant with increasing the column length above a certain minimum length (56). However, this length increase cannot be extended too much, as the pressure drop associated with the length increase becomes limiting. Larger packing particle sizes would not overcome this restriction as it would result in mass transfer efficiency losses.

Another drawback with this approach is due to the high retention times associated with the long columns which set throughput rate limitations.

In general, a minimum number of plates and hence column length is required for a given separation which increases with the difficulty of separation (56). Thus, for very difficult separations, i.e. separation factors less than 1.15, a long column length is needed if a high degree of resolution between the feed components is to be achieved. In addition long narrow columns have the advantage of being more amenable to temperature programming.

Concluding, it should be noted that in practice the above mentioned drawbacks limit the utilization of this method to mixtures that are very difficult to separate and cannot be handled in any other way.

2.3.2.2 USE OF MULTIPLE PARALLEL COLUMNS

Utilizing several columns in parallel has the obvious advantage of allowing each individual column to have a reasonable diameter and length, while the total throughput capacity of the chromatograph is increased. With this approach the previously discussed large diameter column effects are avoided without reduction in throughput capacity.

However, the method of multiple columns has not gained wide acceptance because of the difficult and tedious effort involved in balancing the array of parallel columns. In fact the need to maintain geometric packing similarity and equal stationary phase loading in each individual column is obvious. The first is necessary to ensure identical flow resistance and the second identical solute velocities in each column. In addition an even distribution of feed and mobile phase flow in the

columns is required which is usually achieved by an inlet manifold.

This balancing operation must be very precise otherwise the individual solutes from each column elute at slightly different times resulting in additional solute zone broadening and therefore to efficiency losses. However, in practice the difficulties encountered in achieving these balancing requirements seriously limit the application of the multiple parallel columns method (56).

2.3.2.3 INCREASE OF COLUMN DIAMETER

The most interesting way to increase the throughput capacity of a chromatograph is to increase the column diameter. It is expected that the capacity throughput increases in proportion to the square of the column diameter, so that a tenfold increase in radius results in a hundredfold increase in feed capacity (60).

This approach, however, involves some drawbacks. The efficiency loss encountered with large diameter columns, which has been more extensively discussed in Section 2.3.1.2, is the main problem. Despite this, a number of techniques have been developed (see Section 2.3.1.3) to reduce the efficiency loss by increasing the column diameter. However, in practice a compromise between efficiency loss and gain in throughput must be made which limits the above method.

It is expected that more knowledge about column flow dynamics and a better understanding of the solute zone broadening mechanisms in large diameter columns will give the answer to this problem.

2.3.2.4 REPETITIVE INJECTION

In analytical chromatography, normally a single solute sample is injected at one end of the column and the resolved components are collected at the other end. This process is rather undesirable in large-scale chromatography because as the solute zone migrates through the column it only occupies part of the available column length at any one time.

In order to increase the column utilization and therefore the capacity throughput the "repeated injection" technique was introduced. With this method subsequent sample injections are made before the previous injection has emerged from the column, and consequently several samples are being separated by the column packing at the same time. However, the rate of injection and sample injected size is limited to avoid excessive overlapping between successive samples.

Two different approaches have been developed based on the "repetitive injection" technique.

The first requires the time interval between sample injections to be set, so that the leading edge of one sample just catches up with the trailing edge of the previous one as they reach the column outlet. Thus, two fraction cuts per binary sample is involved, one between the component peaks and one after the second peak and before the next sample. This scheme has been extensively studied by Pretorious and de Clerk (59) who derived a mathematical expression to evaluate the performance of a preparative chromatograph operating under these conditions.

In the second scheme the successive sample solutes are allowed to partially overlap at the column outlet, consequently a three fraction technique per binary sample is employed with the central impure portion removed and recycled.

Gordon et al. (77,78) indicated that significant gain in throughput may be obtained by the latest "three fraction" method when high purity products are required. This throughput gain, however, is decreased when lower product purities are permissible.

Conder in his review (57) emphasizes that in production chromatography it is the throughput capacity that matters and not the column efficiency or peak resolution. He concludes that the "three fraction repetitive injection" procedure is the preferable procedure for production-scale applications. In addition he has shown that the optimum recovery of product per injected sample is 60%, the impure 40% being recycled, and generally that columns should be operated at maximum carrier gas velocity and feed-band width (79).

2.3.2.5 CONTINUOUS CHROMATOGRAPHY

An alternative way to increase throughput is achieved by operating the chromatograph in a continuous manner. Various schemes have been proposed in order to achieve this continuity, which are reviewed in Section 2.4.

In general the continuous chromatographic systems are mechanically complex, requiring a high degree of precision engineering but in addition have the advantage of allowing the whole of the chromatographic column to be utilized for separation (see Section 2.4.1). Therefore, significant gain in throughput is expected, and as most of the continuous mass transfer separation processes are more economical over the equivalent batch processes, cheaper products may be obtained.

2.3.3 PRACTICAL IMPORTANCE OF LARGE-SCALE CHROMATOGRAPHY

2.3.3.1 G.L.C. IN COMPARISON WITH OTHER COMMON MEANS OF SEPARATION

It is extremely difficult to find conclusive experimental data allowing a fair comparison between G.L.C. and other common separation processes. There are, however, some important differences between chromatographic and other separation techniques which may facilitate in selecting or discarding chromatography for a particular separation problem (57,60,80).

By far the most commonly physical separation process used in industry at present, is fractional distillation at atmospheric pressure. This is due to the simplicity of equipment, low investment and operating cost compared with many other separation processes.

In contrast, chromatography seems less attractive for industrial applications. It involves expensive carrier gas recycling procedures, expensive chromatographic packing materials which need replacement after some period of time, requires efficient product collection systems and very good column temperature control.

Despite these drawbacks large-scale G.L.C. becomes competitive in the following cases:

1) the separation of close boiling point and azeotropic mixtures
2) the separation of thermally unstable compounds
3) where high purity products are required.

Such separations are encountered in most parts of the chemical industries but in particular in the pharmaceutical, perfume and food industries where separations of essential oils or fatty acids are involved.

The high column efficiencies experienced in chromatography largely results from the small packing sizes used combined with the even distribution of the liquid phase on the support surface. In

addition the use of a liquid phase means that a difficult separation may be simplified by "tailoring" the liquid phase to the separation problem.

Therefore, separations too difficult for distillation can be more easily carried out by chromatography.

One of the features of G.L.C. is the ability to separate azeotropic or close boiling point mixtures which is also a property of azeotropic or extractive distillation. These distillation processes, however, have higher capital cost than ordinary distillation, as well as higher running cost requirements, making G.L.C. very competitive.

High equipment costs are involved in the processing of thermally unstable materials by vacuum distillation, while low vapour pressures lead to reduced throughput capabilities. G.L.C. has in its favour no permanent "hold-up" of solutes in the column, and shorter residence times making it to appear more suitable for such separations.

Liquid-liquid extraction shares with G.L.C. the advantage that ease of separation is a variable that is under the designer's control because of the presence of a solvent. However, the choice of the extracting solvents is much more limited than that of G.L.C. stationary phases, because the two phases must be mutually immiscible, and this requirement is most difficult to meet at high solute concentrations. In addition after extraction, a further separation process, usually distillation, is required.

Another common separation process is fractional crystallization which involves the handling of a solid phase and therefore has a disadvantage in continuous operation relative to processes in which all phases are fluid. In addition the drawbacks due to the need to allow for drainage and separation of occluded mother liquor, the large

heat load, and the time required for mass and heat transfer make crystallization a more cumbersome and costly process than fluid-fluid contacting processes (57,81).

Concluding, G.L.C. may be considered as a very useful alternative for many separation problems and having in mind the technological development of large-scale G.L.C. in the last ten years, the future of G.L.C. for industrial-scale separations seems very promising.

2.3.3.2 THE APPLICATIONS AND THE FUTURE OF LARGE-SCALE CHROMATOGRAPHY

A number of applications making use of laboratory-scale G.L.C. units have been developed and reported in the literature (82-85). Among them, the most interesting application, is the removal of 1 to 2 per cent quantities of impurities to the p.p.m. level from valuable compounds that are too labile to be so highly purified by other methods (82,83).

Moving to production-scale units Timmins et al. (69) have reported the use of a co-current type of L.L.C. system in a pharmaceutical plant, having capacity of 0.9 million Kg/year. The same workers reported the design and total operating cost of a G.L.C. unit used for the separation of m-xylene and p-xylene at a production rate of 45 million Kg/year.

Design and costing details are also available for a G.L.C. unit used for the separation of α- and β-pinenes at a production rate of 0.84 million Kg/year (68).

Some comparative separation costs have been published by Ryan (86) for G.L.C. and the corresponding conventional separation methods which show considerable cost reduction for the G.L.C. separations.

The Abcor Corporation of Massachusetts (68,69,73,86), a company marketing production-scale chromatographs, favour the use of mixing devices along the column in order to increase the chromatograph efficiency. They manufacture columns with diameters ranging from 10.2 cm to 30.5 cm and have projected the use of columns with diameters up to 6.1 m. Recently a French company (87) has produced columns of comparable size, with commercial developments in view.

The Universal Oil Products Company (88,89) currently applies chromatography for the separation of paraffins from other hydrocarbons (Molex process), for the separation of olefines from paraffins (Olex process) and for the recovery of p-xylene from other C_8 hydrocarbons (Parex process). These processes use molecular sieve adsorbents and operate in the liquid phase. The "Parex" process is currently at a production level of 1.1 billion Kg/year (90).

Recently Conder (91) has reported an extensive study on the optimisation of production-scale G.L.C. systems, from which important conclusions, very useful for the design and operation of such chromatographs were drawn.

Concluding, small laboratory-scale chromatographic units are at present widely used to prepare standard substances, i.e. for spectroscopic purposes and radiochemically or isotopically labelled compounds.

For industrial-scale separations it is stated that whenever fractional distillation can do the necessary separation or purification, it is the process to choose, for it is likely to be cheaper (81). However, chromatography has a number of points in its favour, i.e. flexibility, high selectivity power, making it attractive in the whole spectrum of separation methods, particularly when the separation involves high purity requirements, heat-sensitive materials, azeotropes or close boiling point

mixtures. Unfortunately, at the present time, very few chromatographic processes are in regular use at the production levels. Although significant contribution by several workers in the field have been made in the last ten years, some fundamental problems still remain to be solved. A much better knowledge, for instance, of the flow of fluids through large diameter chromatographic columns and methods of characterizing a bed are badly needed. Also the technological development of chromatography as a continuous process may well improve the throughput capacity of the method. Finally improved methods are required for optimising the chromatograph performance, which at present are empirical.

2.4 CONTINUOUS CHROMATOGRAPHY

2.4.1 INTRODUCTION

Chromatography is known for its superior separating capabilities and near universal applicability, although scale-up problems have still to be overcome before becoming a well established production-scale separating technique.

Various attempts have been made over the past thirty years to increase the throughput capabilities of chromatographs using either batch or continuous operation. The batch or co-current systems were reviewed in the previous section, while the continuous systems, which may be classified in the categories shown in Fig. 2.2, are described in the present section. It should be noted that the word "continuous" as used here refers to the introduction of the feed and withdrawal of the products.

As shown in Fig. 2.3, by comparing the solute concentration profiles obtained for a binary mixture being separated by counter-current chromatography (the most comprehensively evaluated scheme in continuous chromatography) with "repetitive injection" batch chromatography (the most favoured scheme in batch chromatography) it is indicated:

1. the continuous operation has the advantage of allowing the whole of the chromatographic column to be used for separation for all of the time.
2. the solutes need only be partially resolved within the continuously operated chromatographic column to permit nearly pure product collection at the column exits. In contrast complete resolution of components or recycling procedures are required in batch chromatographic systems, if high purity products are to be collected.

FIGURE 2.2 CONTINUOUS MODES IN CHROMATOGRAPHY

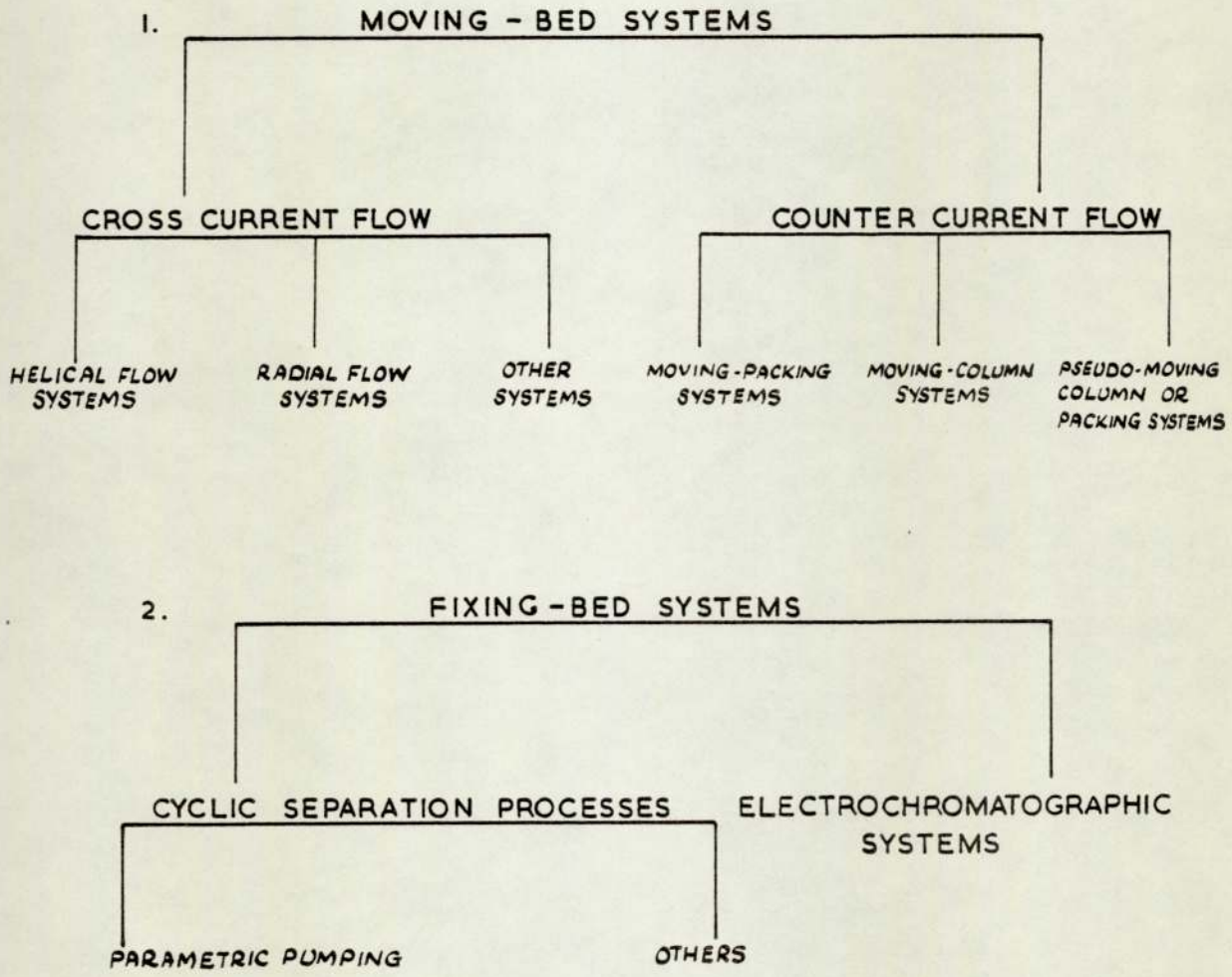
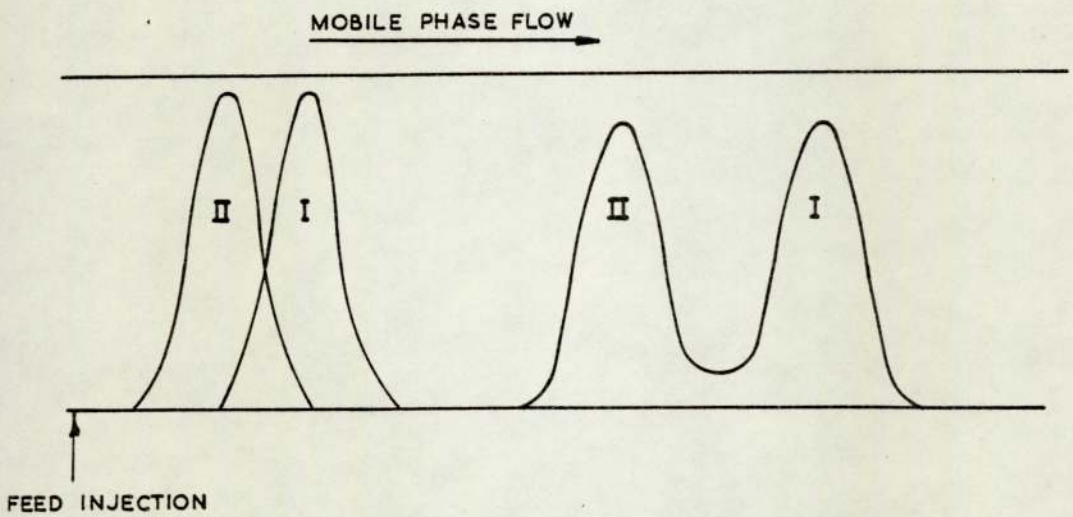
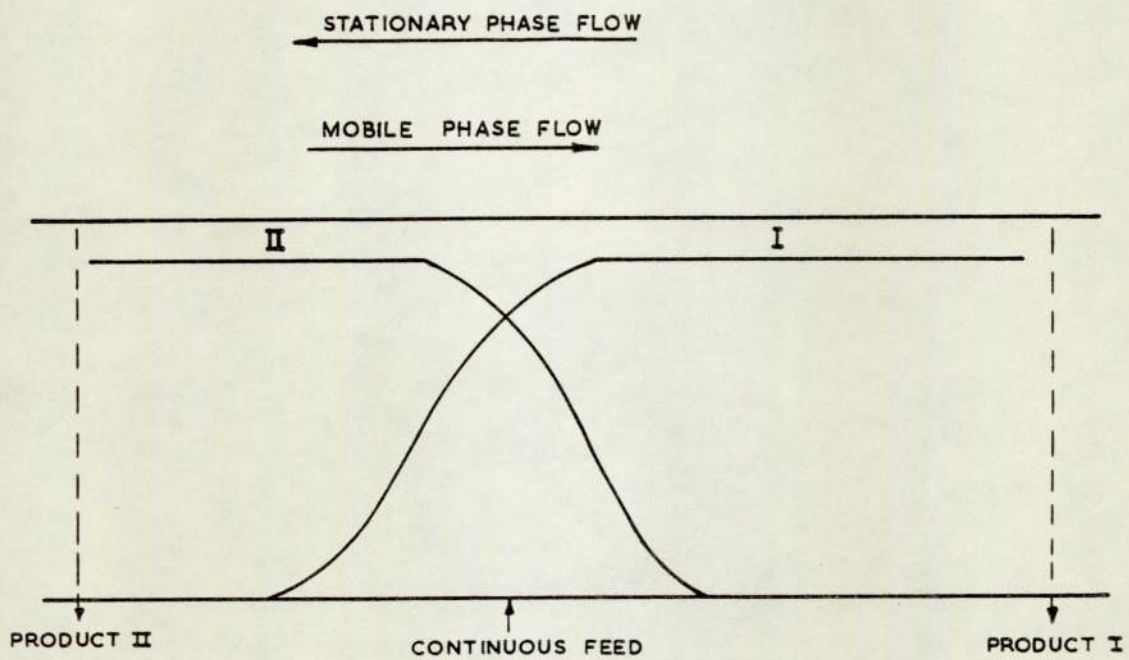


FIGURE 2.3 SOLUTE CONCENTRATION PROFILES OBTAINED FOR A BINARY MIXTURE BEING SEPARATED BY

(a) "REPEATED INJECTION" BATCH CO-CURRENT OPERATION



(b) CONTINUOUS COUNTER-CURRENT OPERATION



The above suggest that, in principle, a significant gain in throughput should be achieved by the continuous operation.

In fact a true comparison between production-scale batch and continuous chromatographs will require experimental and economic data from chromatographic units processing identical chemical systems, which at the time of writing are very limited in the literature.

Experimental work is currently being carried out in the Chemical Engineering Department of Aston University by K. England (92) which will facilitate a realistic comparison between the sequential type of counter-current chromatography and "repetitive injection" batch chromatography for the G.P.C. (gel-permeation chromatograph) fractionation of Dextrans.

2.4.2 MOVING-BED SYSTEMS

The basis of the moving-bed continuous chromatographic operation relies on the relative motion between the stationary phase and the point where the feed is introduced into that phase. This can transform the retention time differences of the components of the feed mixture into physical displacements, which in turn allows each component to be withdrawn continuously at fixed and characteristic distances away from the feed point.

Moving-bed systems may be classified into two classes: counter-current flow systems and cross-current flow systems. In counter-current flow systems the stationary phase and mobile phase move in opposite directions. In cross-current flow systems the movement of the mobile phase and stationary phase is at right angles.

2.4.2.1 CROSS-CURRENT FLOW

The cross-current flow systems may be classified into the following groups.

A. Helical flow systems

The principle of operation of this type of continuous chromatographic operation is illustrated in Fig. 2.4a. The feed mixture and mobile phase enter the system from the top of the chromatographic bed, which may be arranged as a circular array of parallel tubes or as a single annular cylinder. As the chromatographic bed rotates, the components of the feed mixture follow helical flow paths and finally are collected at fixed points in the circumference at the base of the annulus.

Martin (93) as early as 1949 had suggested this type of system and provided a theoretical analysis for its operation. Dinelli et al. (94) converted this concept to a working unit.

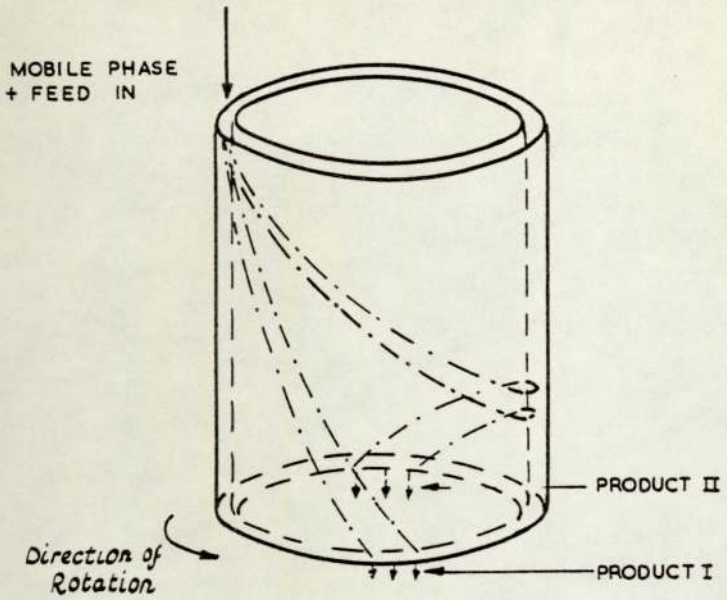
Since then many chromatographic units have appeared in the literature based on the above principle, such as that by Fox (95) used for the gel-permeation chromatographic separation of proteins at feedrates up to 22 cm^3h^{-1} with typical achieved purities of 97%.

Also significant was the contribution of Taramasso and his co-workers (96,97) in the development of this type of equipment, with particular reference to gas-liquid chromatographic applications on volatile organic compounds (i.e. hydrocarbons), and feed throughputs up to 200 cm^3h^{-1} and purities as high as 99.9% have been reported.

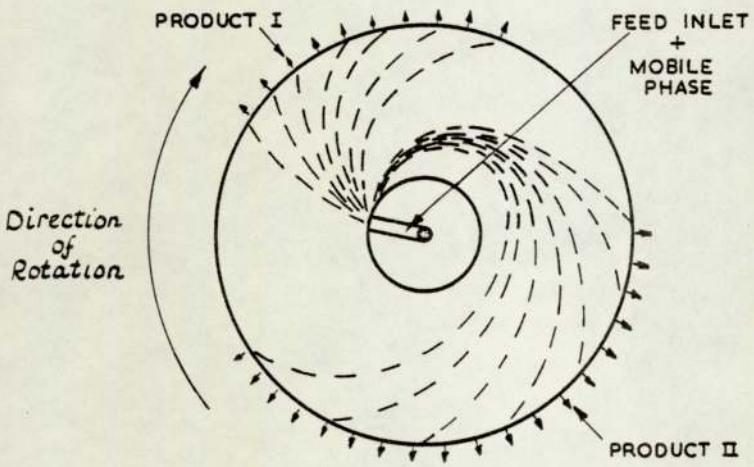
B. Radial flow systems

In the radial flow systems the feed enters at the centre of the chromatographic-bed, and as the annular cylinder is rotated the components of the feed mixture move in a horizontal rather than the

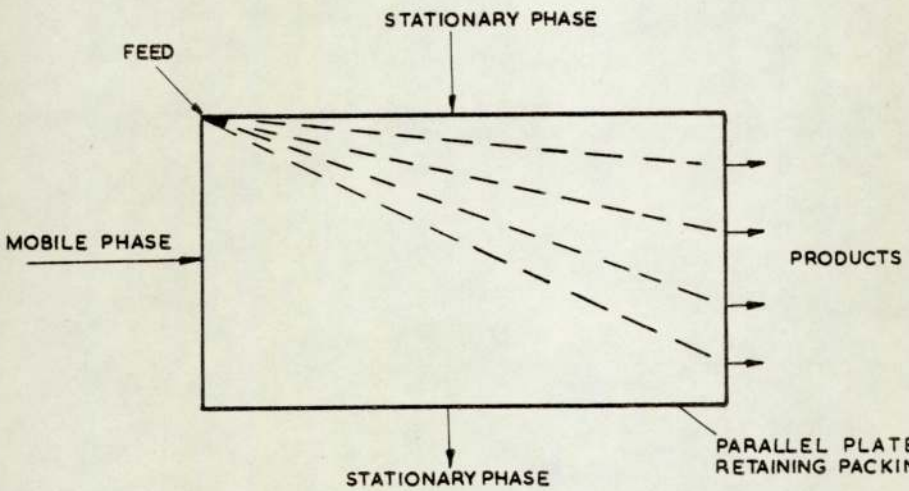
FIGURE 2.4 CROSS - CURRENT FLOW SCHEMES



(a) PRINCIPLE OF HELICAL FLOW SYSTEMS



(b) PRINCIPLE OF RADIAL FLOW SYSTEMS



(c) PRINCIPLE OF TURINA ETAL. (101) PROPOSED SCHEME

vertical plane such as in the helical flow systems, travelling from the centre to the circumference of the annular cylinder (see Fig. 2.4b).

This scheme was initially proposed by Moiser (98) and was later modified by Sussman and his co-workers (99,100),who reduced the packed annulus to an annular channel between two flat discs, the stationary phase being coated to the adjacent faces of the discs. The latest equipment has been successfully used for G.L.C. separations of binary and ternary hydrocarbon mixtures at throughputs up to 18.9 $cm^3\ m^{-1}$ (99,100).

C. Other systems

A cross-current system not quite similar to the previous ones has been described by Turina et al. (101) for G.L.C. applications (see Fig. 2.4c).

This apparatus consisted of two parallel glass plates 0.1 cm apart containing the inert support. The carrier gas enters one vertical edge, flows horizontally through the inert support, and emerges at the opposite edge. Meanwhile, the liquid stationary phase flows through the inert support vertically and leaves at the base. As the feed mixture is introduced continuously into the system at the corner situated between the entrance of both carrier gas and liquid phase, the individual components travel at different angles through the chromatographic bed emerging from different positions with the carrier gas.

In conclusion it should be noted the major advantage of the cross-flow systems for the continuous separation of multicomponent mixtures in a one stage operation, [illegible] at the present has been very poorly exploited. This is probably due to inadequate information on scale-up effects and the mechanical problems expected with large moving seals.

2.4.2.2 COUNTER-CURRENT FLOW

The technological development of moving-bed systems operating under counter-current flow conditions has undergone three main stages:

A) moving-packing systems

B) moving-column systems

C) pseudo-moving column or packing systems.

A. Moving-packing systems

This scheme usually involves a vertical column in which the mobile phase flows upwards, the packing moves downwards under its own gravity and the feed mixture is introduced continuously somewhere near the middle of the column. The relative flowrates of the two phases are adjusted so that the least soluble component of the mixture travels in the direction of the mobile phase flow, while the most soluble component is carried with the packing and is finally stripped off it by a combination of heat and an increased gas flowrate (see Fig. 2.5a).

Barker and co-workers (6-8,16) have extensively studied the above method on G.L.C. systems, and high separated product purities were reported for volatile organic mixtures separations (i.e. cyclohexane and methylcyclohexane) at feed throughputs of about 30 cm^3h^{-1} when using column diameter of 2.5 cm.

Other reports on similarly operated G.L.C. equipments are those given by Scott (102), Fitch et al. (103) and Schultz (104).

Bradley and Tiley (105) describe a system with a minor variant from the basic moving-packing principle, where the liquid phase flows downwards in a packed column.

Industrially the technique has been developed by the Union Oil Company, California (106), and a unit having a capacity of 0.45 million cubic metres per day was built by the Dow Chemical Company at Midland, Michigan (107) which is no longer in operation as it proved to be uneconomical compared to distillation. Also a production-scale chromatograph operated under moving-packing conditions has been used by the Phillips Petroleum Company to separate up to 225 cm^3 min^{-1} of 30% cyclohexane/70% benzene mixture (108).

In general, moving-packing systems suffer from the drawbacks of solids handling problems (solids flow control and recycling procedures), the resulting attrition necessitates re-sieving and replenishing of expensive packing, and finally the chromatographic efficiency loss due to the low, uneven packed densities.

B. Moving-column systems

In order to avoid the packing attrition experienced in the moving-packing chromatographs, the moving-column systems have been developed.

In the latest scheme, the packing is held stationary in a circular column which is rotated in the opposite direction to the mobile phase flow, passing fixed inlet and outlet ports. The principle of operation is illustrated in Fig. 2.5b. Thus, by adjusting the mobile phase flow and speed of rotation, the component of the feed mixture with the least affinity for the packing moves with the mobile phase, while the component with the most affinity for the packing moves with the column and is later stripped off the packing assisted by heat and a greater than theoretical quantity of inert mobile phase.

Although various designs, very similar in form, of moving-column chromatographs have been described in the literature, the most sophisticated seems to be the one illustrated in Fig. 2.5b, proposed by Barker (16).

Based on the above principle Barker and Huntington (9,10,16) constructed a G.L.C. unit, 1.5 m in diameter with a 3.8 cm^2 cross-section column, which was shown to be capable of separating to a high degree of purity azeotropic or close boiling volatile mixtures (i.e. dimethoxymethane/dichloromethane) at feedrates up to 450 cm^3h^{-1}.

Scaling-up the above unit was not thought practical, since an even larger diameter circular column would be required. The difficulty of compactness was overcome by Barker (11) who proposed using a circular array of parallel tubes linked alternatively at top and bottom to give a closed loop.

This compact circular chromatographic machine has been extensively studied over a period of about 10 years by Barker and co-workers (11-16,47,109,110) and a wide range of successful separations were demonstrated in the literature for both G.L.C. and L.L.C. systems.

The machine in general is mechanically complex, requiring seals between moving parts, which appears to impose limitations on the scaling-up of this type of unit to industrial size. However, in view of the high cost of chromatographic media the importance of a reliable laboratory-scale equipment is particularly relevant, since such equipment enables the assessment of both packings and suitable chemical systems for study to be economically undertaken. Consequently, further experimental work is currently being carried out by Barker, Hatt and Knoechelmann (111) on a mechanically improved circular chromatographic unit.

C. Pseudo-moving column or packing systems

The packing attrition encountered in the moving-packing systems and the mechanical difficulties in rotating large tube bundles experienced in the moving-column systems have led to the development

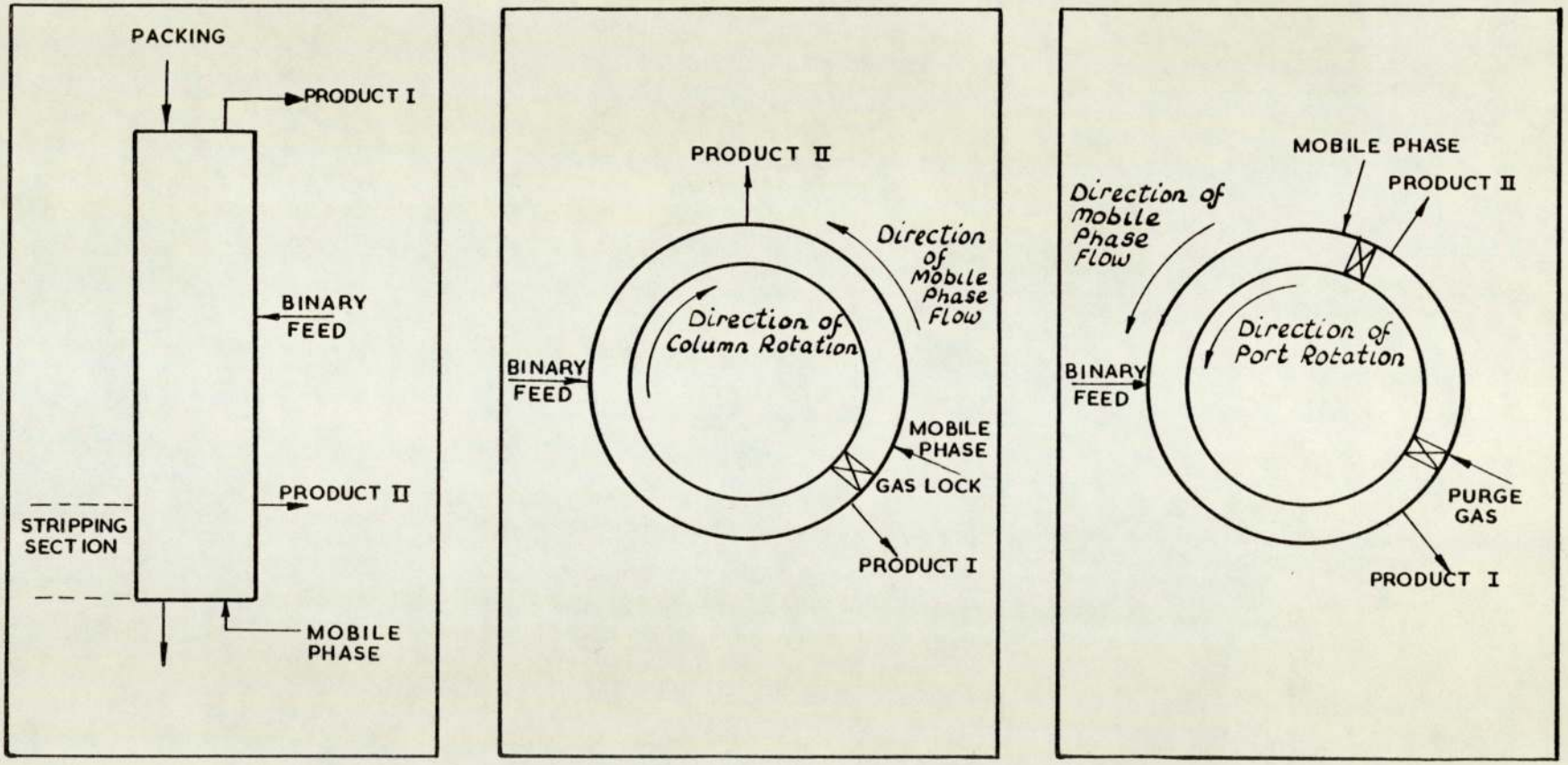
of the pseudo-moving column or packing systems. In the latest systems the chromatographic bed is held stationary and the counter-current flow conditions are simulated by simply changing the inlet ports (i.e. feed inlet, mobile phase inlet) and outlet ports (i.e. product outlets) locations along the fixed-bed (Fig. 2.5c).

The sequential type of chromatographs (17,18), including the SCCR-2 equipment used in this work, are based on the above principle and are described in more detail in Section 5.1. It is interesting to note that the sequential type of chromatography has been extensively applied at the University of Aston for G.L.C. applications (see Section 5.1.2), G.P.C. (gel-permeation chromatographic) fractionations of polymeric materials (61,112), and G.S.C. (gas-solid chromatographic) fractionations of carbohydrates (113).

Based on the same principle Szepesy et al. (114) developed an equipment which involves a mechanically rotating P.T.F.E. disc to move the inlet and outlet ports relative to a series of stationary columns. The equipment has been successfully applied for L.L.C. separations of fatty acid esters at feedrates up to 5 cm^3h^{-1}.

Industrially the "Parex", "Olex" and "Molex" processes (88,89), which are pseudo-moving packing processes developed by the Universal Oil Products Company, find current application for the recovery of p-xylene, olefin and n-paraffin separations. These processes involve a single-column and a rotary valve which simulate the movement of the column packing by indexing the column inlet and outlet ports so that counter-current flow conditions are achieved.

FIGURE 2.5 COUNTER-CURRENT FLOW SCHEMES



(a) PRINCIPLE OF MOVING-PACKING SYSTEMS

(b) PRINCIPLE OF MOVING-COLUMN SYSTEMS

(c) PRINCIPLE OF THE BARKER AND DEEBLE PROPOSED PSEUDO-MOVING COLUMN SYSTEM (18)

2.4.3 FIXED BED SYSTEMS

A. Cyclic separation processes

The continuous operation in a cyclic fashion involves cyclic pressure changes, cyclic concentration changes, cyclic temperature changes within the chromatographic bed, which cause variations in the partition coefficients of the components of the feed mixture thus affecting the separation achieved.

Wilhelm et al. (115-117) demonstrated the possibility of achieving a high degree of separation by cycling the mobile phase flow and temperature within a solid adsorption bed. Mobile phase flow alternated between the upward and downward direction, the packing being heated during the downward flow. The coupling of the concentration changes caused by the flow and temperature changes produced the separation of the feed components. This process has been called parametric pumping. Based on the same principle Tuthill (118) described an interesting design for a continuous chromatographic unit.

There are several reports in the literature referred to as cycling-operated continuous systems, which have been recently reviewed by Wankat (119), but none of the described systems is known to have achieved significant application or commercial success.

In general, cycling-operated systems seem a very promising approach towards continuous chromatography because they do not involve moving beds and may well be applied to all forms of chromatography, G.L.C., L.L.C. or L.S.C.

B. Electrochromatographic systems

Electrochromatography (120,121) combines chromatography and electrophoresis in such a way as to generate a continuous separation process.

The method relies on an electric field traversing the mobile phase flow path and causes different components of the feed mixture to be deflected by various degrees giving a series of curved flow paths. The result is the feed components appear in the column effluent at different locations. This method has been successfully applied in laboratory-scale equipments for the separation of enzymes or other biochemical materials.

2.5 SEPARATION OF FATTY ACIDS BY G.L.C. METHODS

2.5.1 ANALYTICAL-SCALE SEPARATIONS OF FATTY ACIDS BY G.L.C.

2.5.1.1 INTRODUCTION AND HISTORICAL

A close association of G.L.C. and fatty acids may seem peculiar, but is in fact, most logical. Historically, James and Martin introduced G.L.C. in 1952 through this particular analysis of fatty acids (3).

In biochemistry (122) the fatty acids are the basic constituents of biolipids which have vital importance in transport and in interfacing between the protein and water phases in our bodies. The structure and composition of many of those lipids are just beginning to be understood and most of the details relating fatty acids and their functions in the body's metabolic process have been worked out in the last ten years through the G.L.C. analysis of fatty acids.

In industry (123) fatty acids find a wide range of applications. The food, pharmaceutical, rubber, soaps and detergents, resins and plastics, greases and paint are some of the industries using large amounts of fatty acids every year. The above industrial processes require analysis of fatty acids or their derivatives in order to maintain quality control of their products. Therefore, it is not surprising that many analytical methods have been developed in some industrial laboratories for the analysis of fatty acids. However, most of the proposed analytical techniques were slow and tedious. With the development of G.L.C. a powerful new analytical tool became available, which is now generally used in the fatty acid industry.

The fatty acids may be analysed chromatographically either as free acids or after being converted into their esters. In general, free fatty acids are difficult compounds to analyse by G.L.C. The

main problems arise from the relatively high boiling points of fatty acids, their excessively long elution times, their molecular association in the stationary phase and the adsorption of acids in the column. Although direct G.L.C. analysis of free fatty acids has been performed with considerable success by many workers, analysis of their esters appears to give more consistent results with fewer difficulties.

2.5.1.2 G.L.C. OF FREE FATTY ACIDS AND PROBLEMS ARISING

The first gas chromatographic analysis of fatty acids has been achieved by James and Martin (3), who studied the separation of the C_1-C_{12} free fatty acids using DC-550 silicone fluid as a stationary phase. However, serious "tailing" of the elution peaks was encountered on their silicone columns and they found it essential to add either stearic or phosphoric acid to the liquid phase in order to remove the "tailing" effects.

Beerthuis et al. (124) have shown that the "tailing" problem can be eliminated by increasing the operating temperature and keeping the concentration of acids in the mobile phase very low. They analysed long chain free fatty acids on Apiezon-L at 276°C. However, the elution peaks were markedly asymmetric. This was reduced but not eliminated by increasing the column temperature to 300°C.

The most significant advance in the G.L.C. analysis of long chain free fatty acids has been achieved by Metcalfe (125) by introducing a polyester treated with phosphoric acid as the liquid phase. It is interesting to note that the addition of phosphoric acid into the polyester was found to eliminate the "tailing" of elution peaks and to increase the thermal stability of the liquid phase. Success of this type of column packing led several workers to try numerous other polyesters (126,127).

Supina in his review (126) classified polyesters into two groups, the high polar polyesters such as E.G.S. (ethylene glycol succinate) and D.E.G.S. (diethylene glycol succinate); and medium polar polyesters such as E.G.A. (ethylene glycol adipate), B.D.S. (butanediol succinate) and E.G.P. (ethylene glycol phthalate). He has also shown that the degree of separation between saturated and unsaturated fatty acids increases as the polarity of the stationary phase increases, and that the more polar columns give faster separations. As was mentioned in Section 3.4.2, the polarity of a liquid phase may be evaluated on the basis of the McReynolds constants in relation to the value of the X-factor (128).

A new, more polar polyester, the SP-216-PS, has been recently introduced by Ottenstein and Supina and successfully used for the separation of free fatty acids in the C_{14}-C_{20} range (129). The same authors comparing SP-216-PS with other currently used liquid phases, for the analysis of C_{14}-C_{20} free fatty acids, have reported that the fastest separation was obtained with SP-216-PS, while the most complete separation was achieved by using D.E.G.S.-P S. The "PS" designation denotes the incorporation of phosphoric acid into the stationary phase.

F.F.A.P. (free fatty acid phase), a product of the reaction between Carbowax W 20M and 2-nitroterephthalic acid developed by Varian Aerograph, has been reported to be a very effective liquid phase for the G.L.C. of the shorter chain free fatty acids (130,131).

Ottenstein and Bartley (132), studying the separation of the shorter chain free fatty acids (C_2-C_5), made a very comprehensive practical survey covering 27 columns, using polyesters, polyglycols and porous polymers packed into glass, stainless steel and aluminium columns. They conclude that their own specially developed packing of SP-1200 and

phosphoric acid, gives the quickest and most complete separation for the same solution of short chain fatty acids (C_2-C_5). The chemistry of SP-1200 has not been reported but is known to be a low polarity ester (133).

Table 2.4 summarizes some of the most preferred liquid phases used in the G.L.C. of free fatty acids, their specifications and some typical applications are also given.

In general it appears ironic that James and Martin first applied G.L.C. to the separation of free fatty acids, because of the problems associated with their separations. The main problems arising are the following:

1. Adsorption of the acids in the chromatographic column

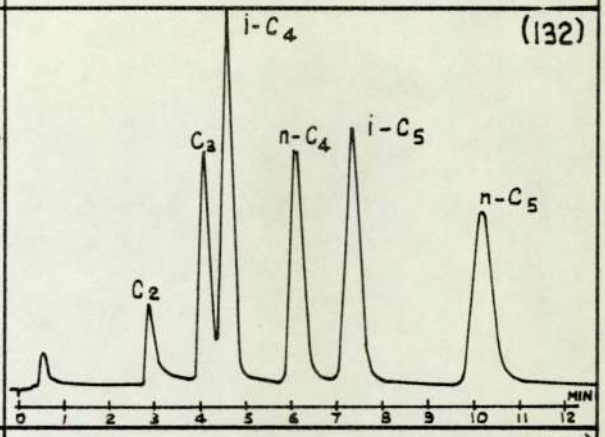
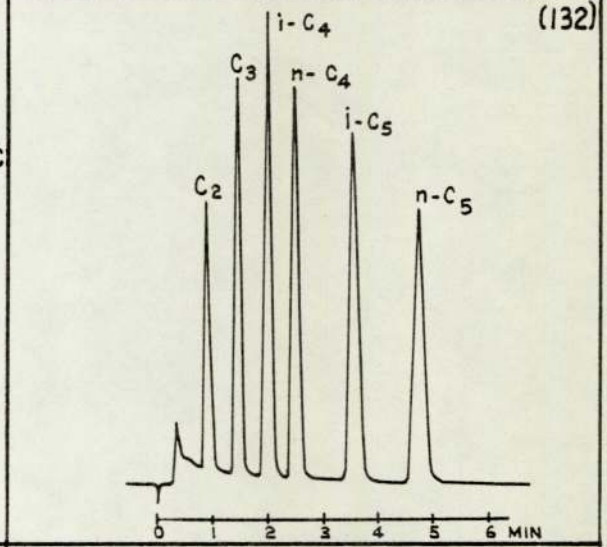
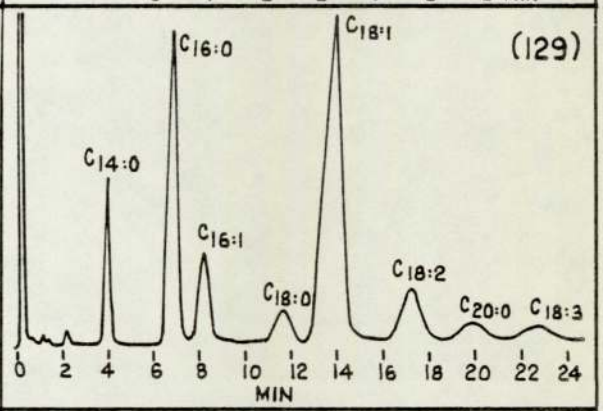
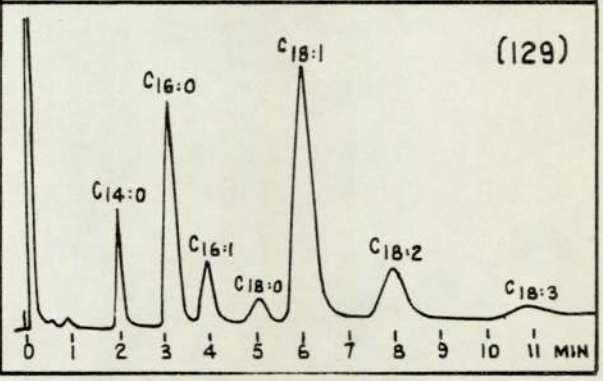
Adsorption is recognized as the worst problem in the separation of free fatty acids, generally giving rise to "tailing" of the acid peaks, irregular shaped peaks and "ghosting".

"Ghosting" is the phenomenon referring to the formation of peaks with an elution time corresponding to fatty acids when water alone is injected. This is due to the removal of free fatty acids, previously adsorbed in the chromatographic column, by the water samples.

The majority of the adsorption effects seems to occur on the support surface, since the modification of the support material usually results in reduced "tailing". However, adsorption may also rise from the metal tubing used for the column, metal injection ports, glass wool used to plug the ends of the column or metal anywhere in the chromatographic system (138). In addition, Martin (139) has proposed that adsorption also occurs on the surface of the liquid phase.

In general, adsorption (138) appears to be related to the ability of the solute to hydrogen bond, with adsorption increasing as

TABLE 2·4 LISTINGS OF PREFERRED LIQUID PHASES FOR THE SEPARATION OF FREE FATTY ACIDS

REF.	STATIONARY PHASE	TYPE	RECOMMENDED USE	REYNOLDS NUMBER X	MIN/MAX TEMPERAT.	TYPICAL CHROMATOGRAM
(130) (131) (134) (135)	F. F. A. P. INTRODUCED BY VARIAN AEROGRAPH IN 1964	CARBOWAX 20M + 2-NITROTEREPHTHALIC ACID	GENERAL PURPOSE	340	50/250°C	
(132) (136) (133)	SP-1200 INTRODUCED BY SUPELCO, INC. IN 1971	ESTER	FOR SHORT CHAIN FATTY ACIDS	67	25/200°C	
(125) (129) (137)	D.E.G.S.-PS	POLYESTER	FATTY ACIDS/FATTY ESTERS	496	20/200°C	
(129)	SP-216-PS INTRODUCED BY SUPELCO. INC. IN 1974	POLYESTER	FOR LONG CHAIN FATTY ACIDS	632	20/200°C	

as the ability to hydrogen bond increases. Consequently, it is expected that fatty acids will show high adsorption properties with their lowest members showing the most severe adsorption.

2. Dimerization of the acids in the liquid phase

James and Martin (3) studying the G.L.C. separation of free fatty acids, proposed that the "tailing" of the acid peaks was caused by dimerization of the acids in the liquid phase as well as by an interaction between the sample and the support. They reported that peak symmetry was improved by including stearic acid in the stationary phase as the acids would tend to associate with the column packing rather than dimerize.

On the contrary some workers (132,140) have reported that an acid additive was not found to be needed when working with more inert supports, e.g. teflon support. The conclusion drawn was that the acid additive in the liquid phase acts as a tail reducer not by eliminating dimerization of the acids but by deactivating active sites on the support.

3. The relative low volatility of fatty acids

The fatty acids have quite high boiling points, particularly their higher members, being in the region of 400°C. This results in the requirement to operate the chromatograph at fairly high temperatures, usually in the region of 200°C for the long chain fatty acids.

Unfortunately, most of the recommended liquid phases for the separation of free fatty acids seem to suffer from thermal instability. Kruppa et al. (137) who had extensively studied G.L.C. separations on polyester columns (E.G.S. and D.E.G.S.) found significant liquid phase losses with operation at 180°C.

Obviously this problem becomes particularly important in preparative and production-scale chromatography.

4. The long elution times of acids

The time required for the analysis of the free fatty acids, particularly of the higher ones, is relatively very high. However, much faster separations can be obtained using their esters for analysis.

Several methods (133,136,141,142) have been proposed in order to eliminate some of the problems encountered with the G.L.C. of free fatty acids, such as the following:

a. Deactivation of the support material

The most recommended support treatment for removing its adsorption sites, involves acid washing combined with silanization of the support material (see Section 3.4.1).

b. Use of formic acid in the carrier gas

As formic acid is the strongest acid, among all the fatty acids, it is obvious that if the analysis of free fatty acids is carried out in the continually polar atmosphere of formic acid, the difficulties associated with adsorption effects will be overcome.

c. Acid-additive in the liquid phase

The addition of a non-volatile acid into the liquid phase acts as a tail reducer by deactivating active sites on the support and by eliminating acid dimerization in the liquid phase. This has led many chromatographic phase suppliers to modify their products by introducing phosphoric acid or other non-volatile acid into the liquid phase.

It is interesting to note that due to the difficulties mentioned above, free fatty acids are often analysed after conversion into their esters which results in better separations. However, it is important

that no incomplete conversion of the fatty acid to the desired ester and no alteration of the structure of the fatty acid occurs during the esterification or transesterification process. Various esterification or transesterification procedures for the preparation of the fatty esters have been described in the literature (126,127, 143-145).

2.5.1.3 G.L.C. OF FATTY ESTERS

The most successful early report in the G.L.C. of fatty esters was obtained by James and Martin (146), who using the non-polar liquid phase Apiezon-L separated fatty esters in the C_1-C_{18} range.

Apiezon-L remains in use, mainly for the separation of the long chain fatty esters, since it is capable of high temperature operations, as it is quite a heat stable phase. However, Apiezon-L lacks selectivity and is found incapable of resolving methyl linoleate and methyl linolenate (127). To accomplish this difficult separation it is necessary to use polar liquid phases.

Among the polar phases, polyesters such as E.G.S., D.E.G.S. and B.D.S. have found the greatest use. Generally, polyesters exhibit higher resolution capacities and faster fatty ester separations than Apiezon-L, but they have rather poor heat stabilities.

Also the F.F.A.P. liquid phase, which has higher thermal stability but less selectivity power than the polyesters, has been successfully used for the separation of fatty esters (131).

The SP-2300 series cyanosilicones were introduced in 1974 by Supelco, Inc., having separating characteristics similar to the polyesters, but having the capability of much higher temperature operations. Among them the SP-2340 cyanosilicone, the most polar phase of the series,

appears to give very fast separations with resolution capacity similar to the D.E.G.S. polyester (152,153).

During 1974 a more polar cyanosilicone, the OV-275 phase, has been introduced with higher cyano-content and similar thermal stability. Ottenstein et al. (147), who extensively studied the G.L.C. separation of methyl elaidate/methyl oleate esters, using various liquid phases, have shown that OV-275 is the superior column in terms of resolution and speed of analysis.

Table 2.5 summarizes some of the most preferred phases for the G.L.C. of fatty esters with their properties and some of their applications given.

A more comprehensive review about the presently used liquid phases for the separation of fatty esters was recently reported by Haken (148).

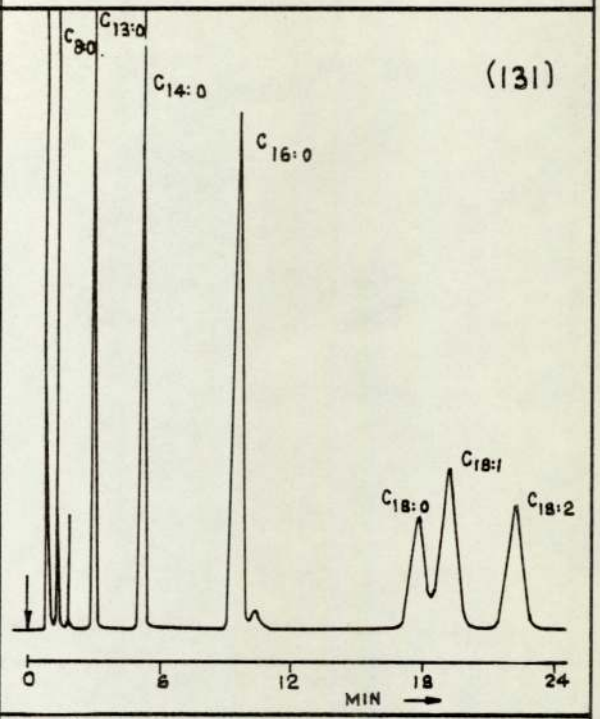
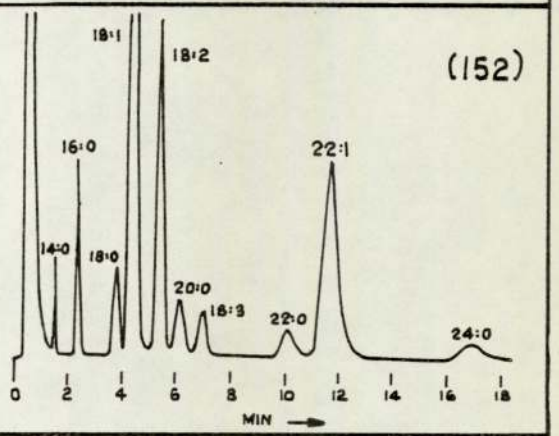
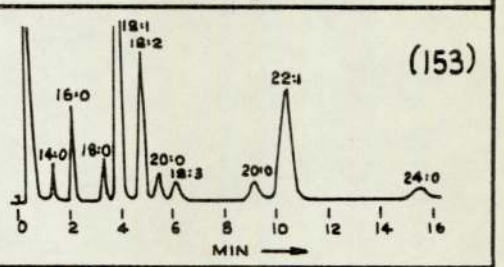
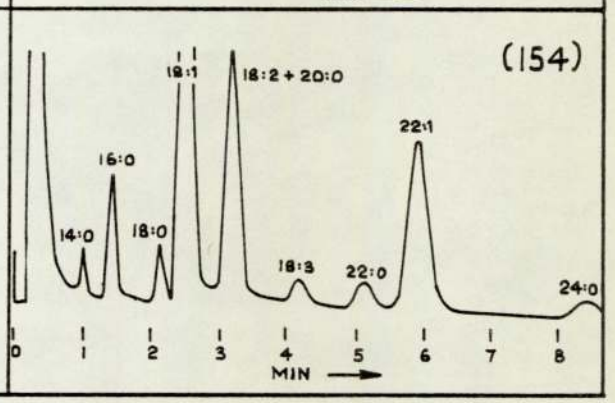
2.5.2 INDUSTRIAL SEPARATIONS OF FATTY ACIDS AND THEIR IMPORTANCE

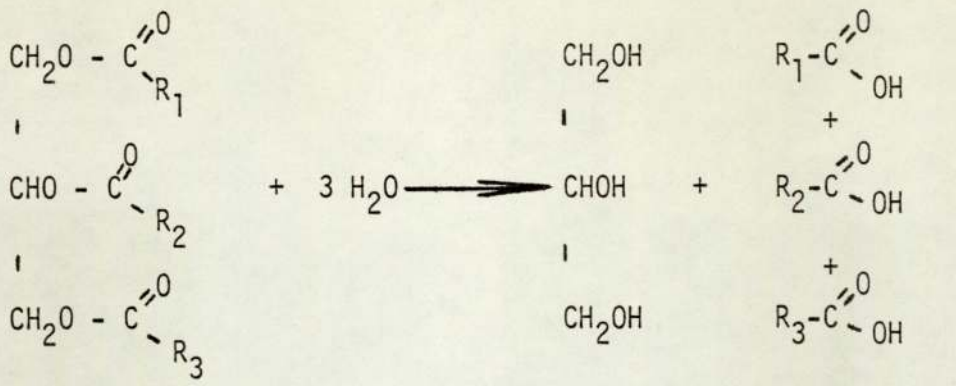
The importance of fatty acids is very well appreciated in biology and the chemical industry today.

In biochemistry, fatty acids are important in the body's metabolic processes. Food fats are hydrolyzed and the acids oxidized for fuel, while at the same time other fats characteristic of the particular organism are being synthesized within the body tissue. As it has been found impossible to modify to any significant extent the fat composition of a specific animal or oil-bearing plant, most fatty acid product processes start with a complex mixture of triglycerides found in natural fats and oils.

The hydrolysis of those triglycerides will produce a mixture of fatty acids, as shown.

TABLE 2·5 LISTINGS OF PREFERRED LIQUID PHASES FOR THE SEPARATION OF FATTY ACID ESTERS

REF.	STATIONARY PHASE	TYPE	RECOMMENDED USE	MIN/MAX TEMPERAT.	REYNOLDS NUMBER X	TYPICAL CHROMATOGRAM
(131)	F.F.A.P. INTRODUCED BY VARIAN AEROGRAPH IN 1964	CARBOWAX 20M + 2 - NITROTEREPHTHALIC ACID	GENERAL PURPOSE	50/250°C	340	
(147) (148) (149) (150)	D.E.G.S.-PS	POLYESTER	FATTY ACIDS / FATTY ESTERS	20/200°C	496	
(147) (148 (151)	SP-2340 INTRODUCED BY SUPELCO, INC. IN 1974	CYANOSILICONE	FATTY ACID ESTERS	0/275°C	520	
(147) (148) (151)	OV-275 INTRODUCED BY SUPELCO, INC. IN 1974	CYANOSILICONE	FATTY ACID ESTERS	0/275°C	629	



(triglyceride) (glycerine) (mixture of fatty acids)

Fatty acids have a very wide range of industrial applications (123,155). The food, pharmaceutical, rubber, soaps and detergents, resins and plastics, greases and paint industries use a large amount of fatty acids, which increases every year. In order to maintain uniform quality of the above products, commercial fatty acids have to be sold on rigid specification. This can be achieved by separating or purifying the complex fatty acid mixtures, obtained from the hydrolysis of triglycerides.

It is interesting to note that the above discussion was mainly concerned with naturally obtained fatty acids which have at least six carbon atoms and are the most important in the fatty acid industry. However, the term "fatty acid" as it is used in this work is applied to the entire family of straight-chain carboxylic acids, having the formula R - C^{O}_{OH} with R as an alkyl or alkenyl group, including the short-chain acids.

2.5.2.1 COMMON MEANS FOR THE SEPARATION OF FATTY ACIDS IN INDUSTRY

In order to choose a separation process for industrial use, a number of factors has to be considered (81,156). King in his text (81) has documented the factors influencing the choice of a separation

process such as production rate, required product purities, product heat stabilities, product values, and specific molecular properties and relative volatilities of the components to be separated.

In general, fatty acids are difficult compounds to be separated, particularly the higher members when high purity products are required. The problems associated with their separations are due to the high boiling points of acids, the low relative volatilities which some of their members have and finally their thermal decomposition.

The most common separation methods used in the fatty acid industry today, are the following.

1. Distillation

Because of the high boiling point of the acids (see Table 2.6) the most widely used procedure is vacuum distillation. However, even under these low operated pressures, 0.666-6.666 kN m^{-2} (5-50 mm Hg abs), moderately high temperatures are required, 200-250°C, and the more highly unsaturated acids, especially those with conjugated unsaturation or those longer than C_{20}, are prone to polymerization, cyclization and stereomutation of double bonds (157).

At higher than 250°C temperatures, most of the fatty acids decompose, first lose water forming anydrines and later break down into ketones and hydrocarbons (155).

At pressures below 0.666 kN m^{-2}, molecular distillation can best be employed which is reported to find industrial application in the manufacture of fatty acids (158).

TABLE 2.6: VAPOUR PRESSURES OF SOME FATTY ACIDS (158)

	boiling point (°C)					
Pressure ($kN\ m^{-2}$)	Capric acid C_{10}	lauric acid C_{12}	Myristic acid C_{14}	Palmitic acid C_{16}	Stearic acid C_{18}	Oleic acid $C_{18:1}$
0.133	125.0	121.0	142.0	153.6	173.7	176.5
0.666	142.0	150.6	174.1	188.1	209.0	208.5
1.333	152.0	166.0	190.8	205.8	225.0	223.0
5.333	179.9	201.4	223.5	244.4	263.3	257.2
13.33	200.0	227.5	250.5	271.5	291.0	286.0
53.33	240.3	273.8	294.6	326.0	343.0	334.7
101.3	268.4	299.2	318.0	353.8	370.0	360.0

Despite the above mentioned problems, distillation is still considered an economical and successful method of producing high purity fatty acids and finds many industrial applications (155,159). However, since the effectiveness of distillation depends on differences of boiling points, chain length is more important than degree of unsaturation (see Table 2.6). Thus, while the separation of C_{10},C_{12},C_{14},C_{16},C_{18} fatty acids is relatively easy, the separation of saturated and unsaturated acids with the same carbon atoms or unsaturated acids with different degree of unsaturation cannot be accomplished by the distillation procedures described earlier. In fact it is reported that stearic (C_{18}), oleic ($C_{18:1}$), linoleic ($C_{18:2}$) and linolenic acid ($C_{18:3}$) are not separable by distillation (157).

With the technological development of distillation, other distillation procedures such as extractive vacuum distillation or

azeotropic vacuum distillation have been developed, which overcome some of the problems met with the fatty acid separations. However, at present most of the relevant reports (159) referred to analytical-scale units, mainly because of the high investment and operating cost of such processes for industrial-scale applications.

2. Crystallization

Solvent processes such as liquid-liquid extraction have been used without success in the fatty acid industry, since the mutual solubility of mixed fatty acids in solvents usually results in an inefficient separation (155).

In contrast, crystallization is considered as a classical procedure for the separation of fatty acids, particularly for the acids having very close boiling points (acids with the same chain length and different degree of unsaturation).

Several crystallization procedures have been applied for fatty acid separations such as crystallization of lead salts, crystallization of lithium salts, urea crystallization and low temperature crystallization (155,157,159,160). Among these the latter is the most successful and has been reported to find industrial applications in the manufacture of fatty acids (155,161,162). However, there are some drawbacks (157,160) with this separation process:

1) sometimes incomplete separation of the mother liquid from crystals occurs.
2) dissolvent acids act sometimes as excellent solvents for those which should crystallize.
3) sometimes one gets the formation of mixed crystals.
4) it is a very slow process; cooled solutions come to equilibrium very slowly and must be held at the crystallizing temperature for several hours.

2.5.2.2 THE FUTURE OF CHROMATOGRAPHY FOR LARGE-SCALE FATTY ACID SEPARATIONS

The successful use of G.L.C. for the analysis of fatty acids is well known. In fact chromatography was introduced by James and Martin in 1952 through this particular analysis of fatty acids and today the best known analytical methods for fatty acids involve the use of G.L.C. (122,123). In addition liquid-liquid chromatography (L.L.C.) with the latest development of high-pressure L.L.C. and with their complementary techniques, paper chromatography and thin-layer chromatography, are found to be very successful in the analysis of fatty acids.

With the development of preparative-scale chromatography several workers have attempted to extend these analytical-scale fatty acid separations to large-scale applications.

Rose et al. (163,164) reported the successful use of a preparative, batch G.L.C. unit for the separation of saturated fatty acid methyl esters at production rates up to 100 cm^3h^{-1}.

In addition Scholfield (165) using a preparative, batch L.L.C. system has successfully separated saturated and unsaturated fatty acid methyl esters. However, the injection sample sizes used were very small (0.01-0.4 cm^3) and the reported elution times were relatively very high (15-100 min).

Recently, Szepesy et al. (114) reported the use of a preparative continuous L.L.C. system for the separation of saturated and unsaturated fatty acid methyl esters in the range of C_{16}-C_{22}, and high purity products at feed rates of about 5 cm^3h^{-1} were obtained.

In Section 2.3.3. comparing G.L.C. with other common separation methods it was shown that large-scale G.L.C. has several advantages over the other methods, particularly for difficult separations heat sensitive materials, when high purity products are required. In fact chromatography can be considered closely related to extractive vacuum distillation. As a result of this added degree of freedom over ordinary distillation, chromatography has a much higher potential for selectivity. Secondly, the efficiency of chromatographic columns is greater than that of a distillation column of equivalent size, again indicating that chromatography should be able to achieve more difficult separations (10,57,60,80).

A comparison of G.L.C. with L.L.C. would not be meaningful as G.L.C. is mainly concerned with volatile components while L.L.C. to non-volatile ones. However, in those few cases where either G.L.C. or L.L.C. can handle the same mixture such a comparison would be helpful.

Giddings (24) and McNair (166) comparing G.L.C. with L.L.C. have shown that G.L.C. is faster than L.L.C. while L.L.C. has the potential of performing more difficult separations, and that L.L.C. has better capability of performing preparative-scale separations but is also more expensive than G.L.C.

Although at this stage it is difficult to state which of G.L.C. or L.L.C. is the most suitable process for large-scale fatty acid separations we are in favour of G.L.C. based on Barker's (6-21) experience who has successfully used preparative G.L.C. systems over the last 10 years for the separation of essential oils, hydrocarbons etc. Consequently, the separation of some fatty acids have been studied on a continuous G.L.C. system, the SCCR-2 machine, and the obtained results are shown in Section 8.

Concluding we should note that the difficulties associated with the fatty acid separations by the common separation methods, has encouraged the investigation of chromatography for such separations. In spite of this very few large-scale applications of chromatographic methods for the separation of fatty acids have been reported in the literature, although the situation is expected to change based on anticipated requirements of the food and pharmaceutical industries.

CHAPTER 3

Analysis Unit

3.1 GENERAL LAYOUT

Gas-liquid chromatography (G.L.C.) analysis units were used for the following purposes.

(1) The determination of vapour-liquid equilibrium data. This in turn helped in the design and operation of the sequential-continuous -chromatographic-refiner-two (SCCR-2).

(2) The rapid qualitative and quantitative analysis of products of separation of the SCCR-2 unit.

(3) The column to column concentration profile analysis of solutes, during the SCCR-2 operation (Section 7.3).

(4) To evaluate when the pseudo-steady state condition was achieved in the sequential unit, during an experimental run (Section 7.4).

On the basis of these requirements two G.L.C. analysis units were used. The first was a Perkin-Elmer F11 chromatograph , with a twin flame ionization detector (F.I.D.) system, employed for the thermodynamic measurements and for the products of separation and concentration profile analysis. The second analysis unit involved a Gow-Mac Katharometer detector with a relatively high susceptibility to flow, pressure and temperature fluctuations. This was used to monitor the product II stream in the SCCR-2 unit and for evaluating the time to pseudo-steady state condition.

Finally both the analysis units were connected to a Perkin-Elmer/Hitachi, model 159, recorder and to a Hewlett-Packard, series 3370B, integrator.

3.2 FLAME IONIZATION DETECTOR

F.I.D. detectors consist essentially of an ionization chamber containing two electrodes across which an electric potential is applied.

A steady hydrogen flame is maintained between these electrodes. When an organic solute in the carrier gas is burned in the hydrogen flame, a change in the electrical conductivity of the gases in the ionization chamber occurs, this change in conductivity being measured and recorded.

The main features of the F.I.D. detector is its high sensitivity and the wide concentration range over which its response is linear. In fact the sensitivity of F.I.D. changes considerably with the flow of hydrogen to the flame and there is an optimum flowrate for maximum sensitivity, which varies with the carrier gas flowrate. Control of the oxygen flow need not be so precise; detector sensitivity increases slowly as the flowrate is increased until the rate is such that the flame becomes unstable. However high oxygen flowrates produce the most linear detector response.

The optimum conditions for the operation of the F11 chromatograph used in this work, determined experimentally are as shown in Fig. 3.1. Therefore, knowing these conditions the maximum F.I.D. response could be obtained for an analysis.

The main components of the Perkin-Elmer F11 (167) chromatograph were:

(1) a dual F.I.D. system

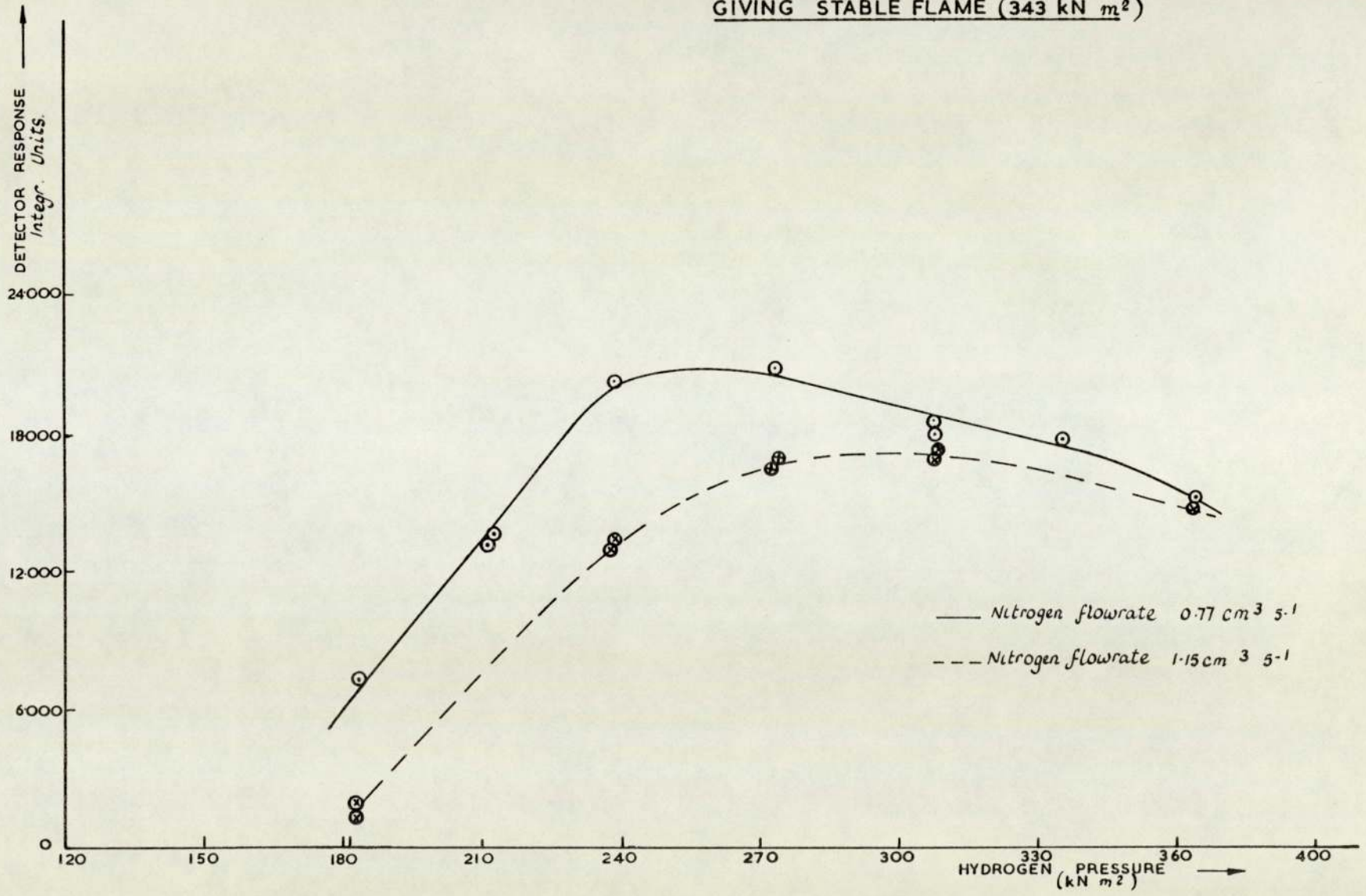
(2) an accurate pressure and flow control unit

(3) an oven with an accurate control device for temperatures up to 500°C

(4) a high signal sensitive ionization amplifier

(5) a dual injection system with heating facilities and analytical chromatographic columns.

FIGURE 3.1 RESPONSE OF F.I.D. (DETECTOR B OF F11 CHROMATAGRAPH) TO HYDROGEN PRESSURE AND CARRIER FLOWRATE AT THE MAXIMUM OXYGEN PRESSURE GIVING STABLE FLAME (343 kN m^2)



3.3 KATHAROMETER

In the Katharometer or thermal conductivity detector an electrically heated filament is inserted in the gas stream. Heat losses from the filament are determined mainly by the thermal conductivity, specific heat and flowrate of the gas surrounding it. As the solute passes through the detector, some of these factors change and result in a different filament temperature. This is detected as a resistance change from which an indication of the amount of solute passing through is obtained.

Normally four filaments are used, connected in a Wheatstone's bridge circuit, two of the filaments being suspended in the sample stream and two in a similar reference stream. In general, Katharometers are considered not to be as sensitive as detectors like F.I.D.

A Gow-Mak, model 10-454, Katharometer was used in this work, which has been found most suitable for preparative chromatography (169). This had four rhenium-tungsten filaments which exhibit very good corrosion resistant characteristics. The Katharometer was installed in the SCCR-2 oven, inside a mild-steel box filled with fibre-glass, to monitor the product II stream (Fig. 5.8).

The associated Wheatstone bridge circuitry was constructed in the department's electronic workshop by M. Lea. Setting the bridge at 18 V and 115 mA was found to give adequate sensitivity and only moderate susceptibility to fluctuations in gas flow, pressure and oven temperature.

In addition both reference (Nitrogen) and product II streams passing through the Katharometer blocks were regulated by two stainless-steel needle valves, normally at 5.0 $cm^3 s^{-1}$.

Finally, the obtained Katharometer traces in the recorder were used to indicate the pseudo-steady state condition in the SCCR-2 unit during a run (Section 7.3.2).

3.4 ANALYTICAL CHROMATOGRAPHY COLUMN

3.4.1 THE CHROMATOGRAPHIC SUPPORT

The basic function of the support is to hold the stationary phase in the column. Ideally, it should be an inert material that holds the stationary phase on its surface as a thin film. But frequently, this is not the case. Instead of obtaining symmetrical peaks, the peaks show severe assymetry or tailing mainly caused by an interaction between the sample and the support (141).

Except for hydrocarbons most classes of compounds exhibit some degree of tailing. In particular, for homologous series of compounds it is the lowest member of the series that tails the most severely; i.e. for fatty acids, formic and acetic acids are the most difficult to work with (138).

There are three major methods of deactivating the support, these are:

(1) removal of mineral impurities by acid or base washing of the support

(2) the removal of surface silanol groups by reaction with a silanizing agent to form a silyl ether

(3) saturation of the active sites with an active agent.

Base washing (BW) however, does little to improve the surface that has already been effectively acid washed (AW), while the AW appears to be ineffective in reducing tailing. When the AW is followed by silanization, the support surface is much more inert than a support which has been only silanized (138).

A comparison of the most commercial supports (chromosorb A, chromosorb P, chromosorb W and chromosorb G) by Ottenstein (138,141) has indicated that chromosorb W was the most suitable support in this

experimental study, because of its relatively high inert properties and the high capacity to hold the stationary phase effectively. A second choice, was chromosorb P which was employed for the separation study of "fungal oil". This was less inert but had a higher capacity for the liquid phase support.

The chromatographic support used for both SCCR-2 columns and analytical columns was acid washed (AW) and treated with dimethyldichlorosilane (DMCS) to remove active sites.

A large sized solid support was chosen for the SCCR-2 machine in order to reduce the pressure drop across the separating section. In contrast finer particles were often employed for the analytical columns to improve the column efficiency.

3.4.2 THE STATIONARY PHASE

The stationary phase is the "Key" element in the chromatographic column. There are three fundamental aspects to be considered in the choice of liquid phase:

(1) the vapour pressure of the liquid phase should be negligible at the operating temperature and the liquid should possess an adequate heat stability

(2) no interaction should take place between the sample components and the liquid phase

(3) It should be a selective solvent for the separating components.

One can evaluate the selectivity of a stationary phase by using the McReynolds constants. The McReynolds constants (128) are determined in a manner similar to the Rohrschneider constants and are used in the same way for liquid phase selection. These constants allow the worker to compare the properties of one stationary phase to another seing both

how they differ and how they are similar, based on the liquid phase polarity. A list of McReynolds constants for a wide range of stationary phases is given by Supelco, Inc. (153).

For the separation of fatty acids which was the main concern of this work, F.F.A.P., D.E.G.S., SP-2340 and OV-275 liquid phases were selected as most suitable (Chapter 2.5).

F.F.A.P. (free fatty acid phase) has been found a very effective phase for the G.L.C. separation of free fatty acids (130); and since most compounds yield symmetrical peaks on F.F.A.P. columns (135), it seems to be one of the most convenient general-purpose liquid phases.

D.E.G.S. (diethylene glycol succinate) is the most common used polyester for the separation of fatty acid esters. But its poor heat stability (137) makes it a less attractive phase, particularly in preparative chromatography.

The SP-2340 and OV-275 are cyanosilicones, having separating characteristics similar to D.E.G.S., but possessing much longer column life.

In choosing a liquid phase for the SCCR-2 machine, we had to consider capacity and economics in addition to efficiency. Generally, in preparative chromatography, larger diameter columns are involved which require more liquid phase to better accommodate the larger samples. Therefore, lower cost liquid phases of maximum versatility and higher upper temperature limit are preferable. Having this in mind, F.F.A.P. was chosen for the SCCR-2 unit. However, recent experimental work has shown the necessity of replacing the F.F.A.P. with OV-275 phase in order for the recovery of γ-linolenic acid from "fungal oil" to be achieved.

Finally, to protect the liquid phases from moisture, Molecular Sieve 5A or Silical gel beds were inserted in the carrier gas (nitrogen) inlet streams of both analysis and SCCR-2 units.

3.4.3 COATING AND COLUMN PACKING PROCEDURE

For coating the support the required amount of stationary phase was carefully weighed and dissolved in about ten times its own volume of an appropriate solvent. An accurately weighted amount of solid support was added to this solution. The whole mixture was then carefully transferred to the flask of a rotary evaporator. A combination of a water bath at slightly above ambient temperature and a water suction pump connected to the rotary evaporator helped to slowly remove the solvent, while the rotating action ensured that the mixture was thoroughly mixed and a uniform coating was obtained. When all the solvent evaporated the content of flask was further dried at about 50°C.

The analytical column was thoroughly washed with acetone and dried with dry filtered nitrogen before it was packed by adding small amounts of packing at a time into the column, applying continuous vibration and occasional gentle tapping, under vacuum. When filled, a plug of glass wool was inserted to both ends of the column. The packed stainless steel column was then coiled to the required shape and fitted into the F11 analysis unit.

Before a packed column was used, it was conditioned for a period of time to get rid of the very volatile portion of the stationary phase and also the last traces of solvent used in the coating step. A chromatographic column should be conditioned for at least 10 hours at 20°C above the maximum operating temperature but below the maximum temperature limit for the stationary phase (168).

Particularly for the analysis of "fungal oil" or "evening primrose oil" glass columns were employed, since significant loss in column efficiency was found to be caused by the stainless steel columns. These were fitted to a Pye 104 chromatograph, because the F11 unit was unable to accommodate glass columns.

3.5 SAMPLING VALVE

The most commonly used gas sampling device is a gas tight syringe. The major drawback of this instrument is its confinement to low boiling compounds, otherwise condensation will occur. Heating the syringe would not overcome this problem as it would render the actual amount injected uncertain.

With fatty acids, whose boiling points are relatively high, the use of a gas syringe was clearly impossible. Therefore, a sampling valve was used, supplied by Pye Unicam (170). This was a six-port pneumatic diaphragm valve, made from stainless steel and P.T.F.E. with a maximum operating temperature of 200°C.

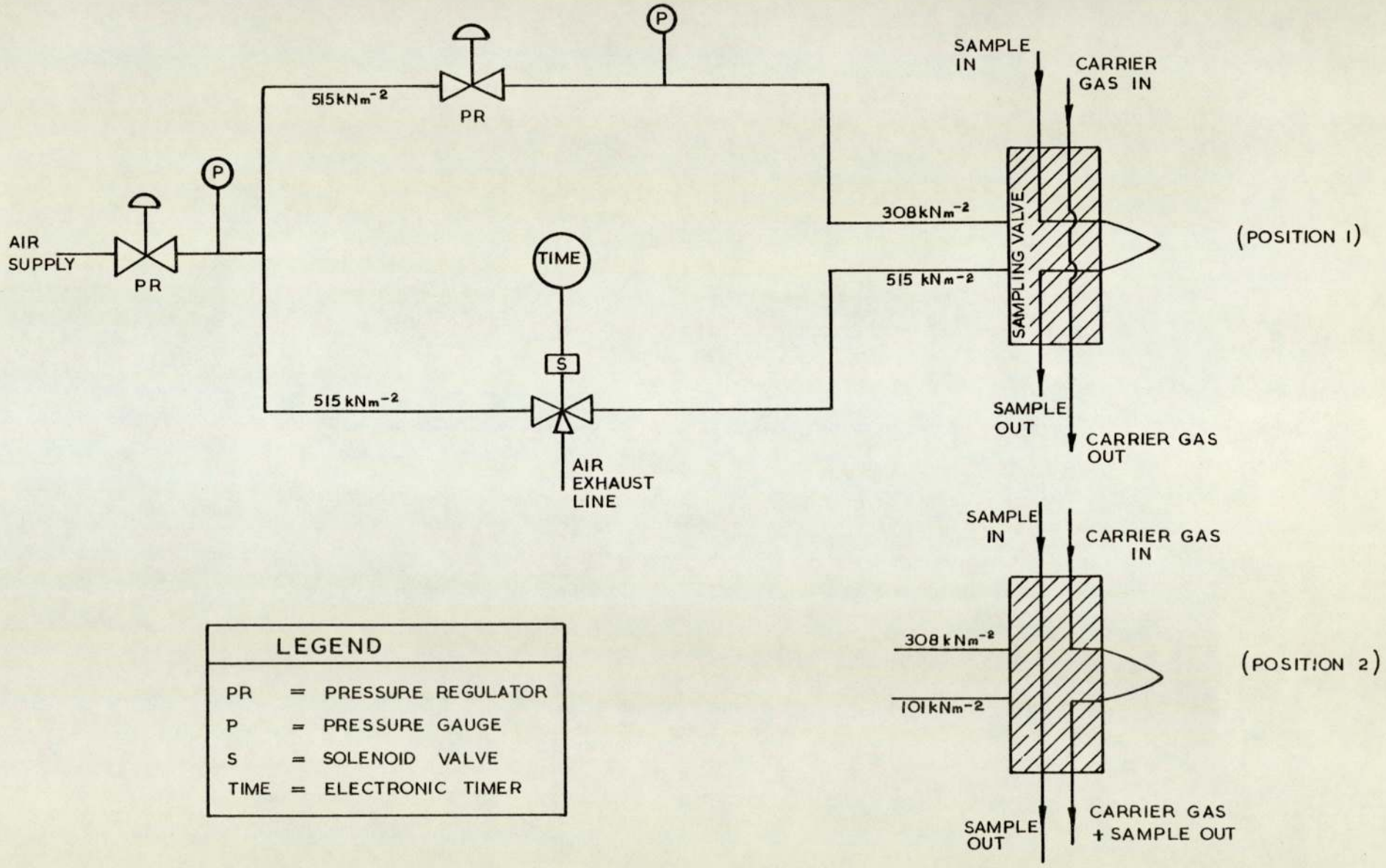
The actuation of the sampling valve was achieved by a solenoid actuated, pilot-operated 5-port spool valve which required a 207 kNm^{-2} (30 psia) pressure differential to switch the sampling valve between its two positions. Also the timing of actuation was automatically achieved by an electronic timer connected to the solenoid, which could repeat the operation at pre-set time intervals. (Fig. 3.2).

The operation of the sampling valve is shown in Fig. 3.3. In position 1, the carrier gas flows in at A, through pad hole 4, and out at B to the F11 chromatograph. Sample flows in at E, through pad groove 2, out at C, through the sample loop, in at D through pad groove 3 and out to the condensing trap at F. In position 2, carrier gas flows in at A, through pad groove 2, out at C, through the sample loop in at D, through groove 3 and out to the F11 chromatograph at B. The volume of sample contained in the sample loop was thus injected into the carrier stream, while in the meantime fresh sample flows in at E, through hole 1 and out to exhaust at F.

The Pye sampling valve was installed in the SCCR-2 unit as shown in Fig. 5.8, housed in an oven capable of maintaining the valve at a temperature of up to 200°C with an accuracy of 1°C. The inlet and outlet lines of the sampling valve were heated by heating tape connected to a variac.

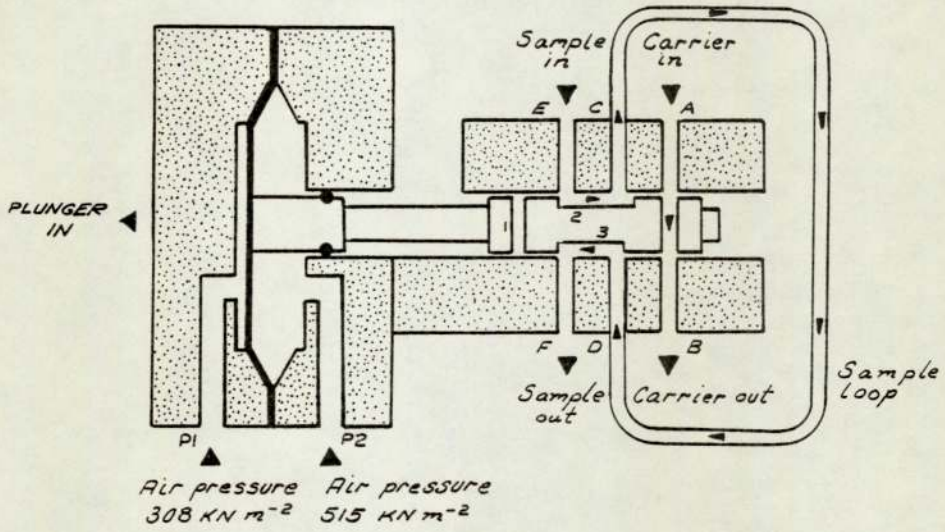
Using the sampling valve, the volume of sample which is actually passed into the gas chromatograph is equal to the volume of sample loop and that of the connecting tubing and dead space of the valve. This volume was experimentally found to be 0.26 cm^3, by feeding the Pye valve with a low concentration level nitrogen - "Arklone"-P, high volatile vapour stream, whose concentration could be predetermined by sampling with a gas tight syringe. Cuddeback, Birch and Burg (171) describe a similar method for determining the sample volume of a sampling valve.

FIGURE 3·2 CIRCUIT FOR OPERATION OF PYE SAMPLING VALVE

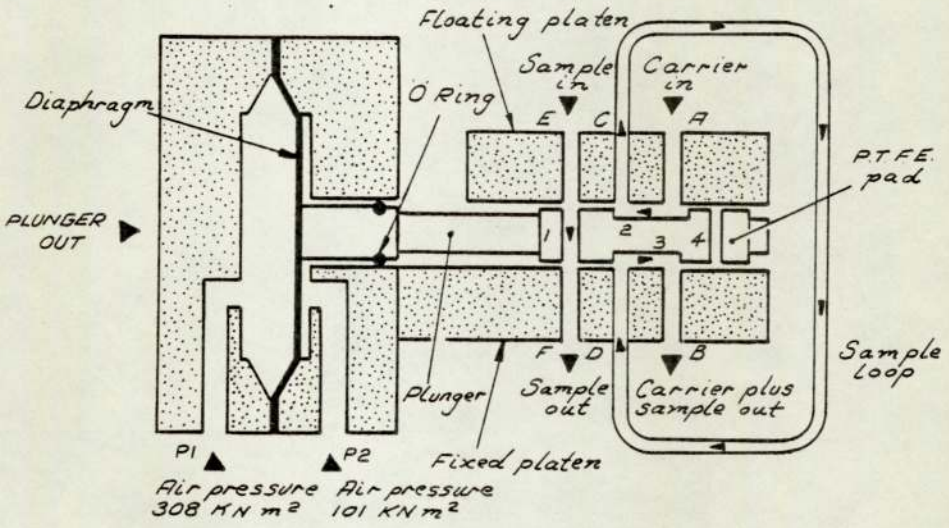


LEGEND		
PR	=	PRESSURE REGULATOR
P	=	PRESSURE GAUGE
S	=	SOLENOID VALVE
TIME	=	ELECTRONIC TIMER

FIG. 3.3. THE OPERATION OF A PYE SAMPLING VALVE



(a) Position 1 (normal)



(b) Position 2 (operate)

3.6 DETECTOR CALIBRATION

The detector of the F11 chromatograph was calibrated under specific operating conditions (column temperature, chemical species, nitrogen, oxygen and hydrogen flowrates) in preparation for quantitative analysis. Therefore, the response of the detector to different solute amounts was determined using a Hewlett-Packard, model 3773B, integrator.

The technique used in the preparation of samples for calibration depended on the volatility of the solute. Thus, for volatile solutes gas samples were prepared by the vaporization of a known quantity of the solute into a known volume of air. A three-necked glass flask connected to a manometer was used for this purpose. Gas samples of known volume and concentration were then drawn from the sealed flask by a gas tight 1.0 cm^3 syringe and injected into the F11 chromatograph for calibrating the detector. This technique was used for all volatile solutes employed in the present work such as "Arklone" P and "Genklene" P.

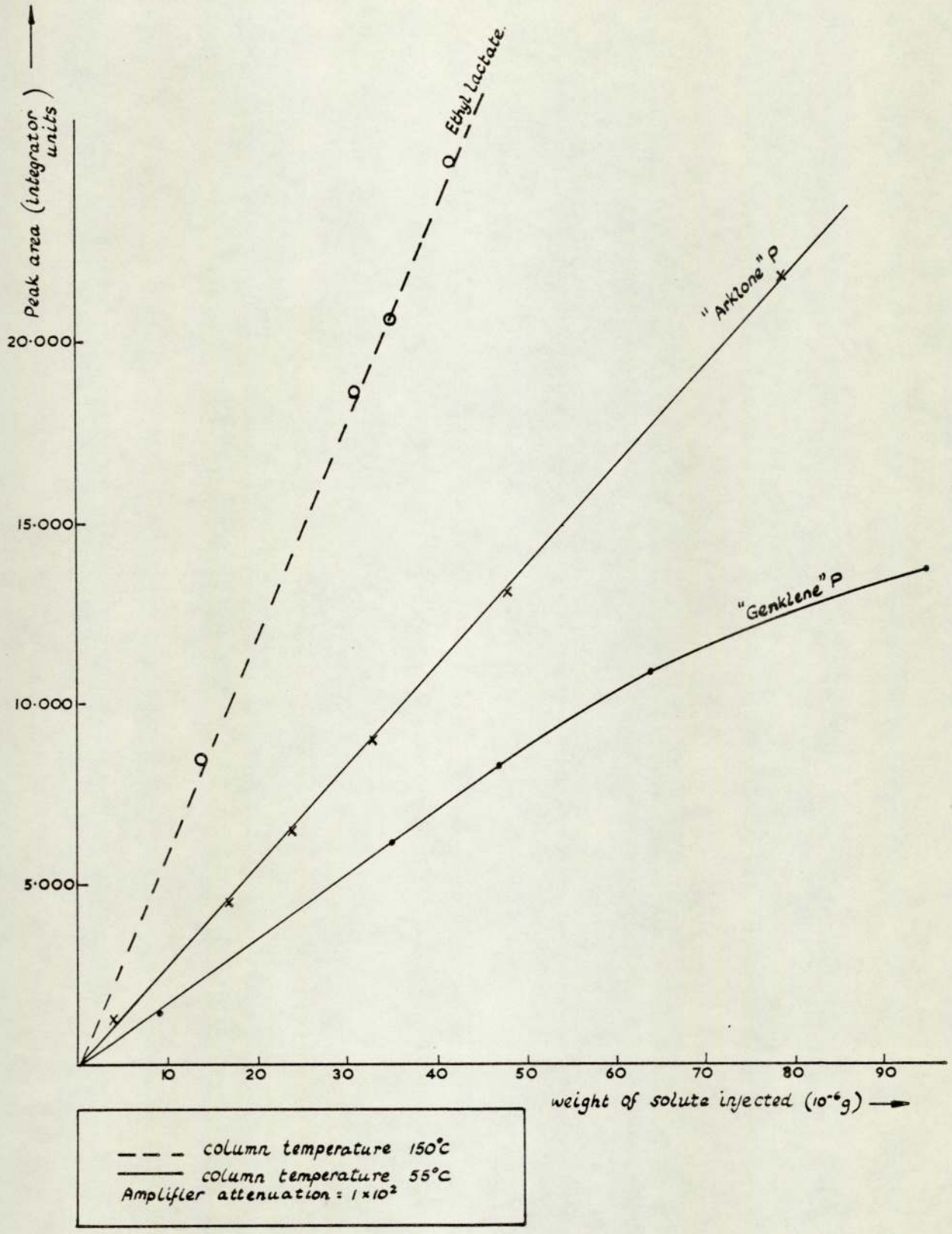
For low volatile solutes like methyl chloroacetate, ethyl lactate, acetic acid and γ-methyl linolenate, hexane solutions of concentrations varying between 1% to 10% v/v were prepared. Adequate volumes of these solutions were injected by a S.G.E. 1.0 mm^3 liquid syringe into the F11 chromatograph to determine the detector response to the specific solute amount.

For each injected sample the attenuation of the ionization amplifier and peak area, as measured by the Hewlett-Packard integrator, were recorded together with the sample volume and solute concentration. Each injection of a specific volume and concentration was repeated 3-4 times and reproducible results within ±2% were obtained.

A linear relationship was found to exist between the amount of solute and detector response in terms of integrator units, the correlation

falling off slightly at higher values as the limit of the linear response of F.I.D. was approached. Calibration curves under one set of conditions are shown in Fig. 3.4. Since the response of the detector was found to vary slightly with time, regular recalibration of the detector, normally once per week, was required.

FIGURE 3.4 TYPICAL CALIBRATION OF THE F11 ANALYSIS UNIT



CHAPTER 4

Thermodynamic Measurements by G.L.C.

It is obvious that a knowledge of vapour-liquid equilibrium data is essential in the design and operation of a preparative G.L. chromatograph as in other unit operations. Such information can be obtained from an analytical scale G.L. chromatograph. More than 200 papers dealing with thermodynamic measurements by G.L.C. have established G.L.C. as a good method for the determination of thermodynamic data (Section 2.2).

In preparative chromatography problems like the choice of a suitable stationary phase or the selection of chemical systems for separation study, the required operating conditions for separation and the determination of the mass transfer efficiency of the equipment, cannot be answered without the use of vapour-liquid equilibrium data.

The present work was initiated with the aim of providing vapour-liquid equilibrium data for the SCCR-2 equipment.

4.1 DETERMINATION OF PARTITION COEFFICIENT AT INFINITE DILUTION

According to James and Martin G.L.C. theory (3), the partition coefficient of a solute is given by

$$V_N^\circ = J_3^2 . V_N = J_3^2 (V_R - V_m) = K . V_L \qquad (4.1)$$

where $V_R = F^\circ . t_R$

$V_m = F^\circ . t_m$

and $$J_3^2 = \frac{3}{2} \quad \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}$$

V_N° : the corrected net retention volume

V_R : the retention volume

V_m : the gas "hold up" in the column and associated fittings

J_3^2 : the gas phase compressibility factor

P_i : the column inlet pressure

P_o : the column outlet pressure

t_R : the retention time

F° : the flowrate of the mobile phase measured at the column outlet pressure

V_L : the volume of stationary phase

K : partition coefficient of the solute, defined as

$$K = \frac{q}{C} = \frac{\text{concentration of solute in the stationary phase}}{\text{concentration of solute in the mobile phase}}$$

There are several assumptions in the derivation of the equation 4.1.

(1) The value of the partition coefficient is constant.

(2) The concentration of the solute in the gas phase must be such that no significant contribution is made to the retention volume. So the "sorption" and "enthalpic overloading" effects are negligible.

(3) The gas phase behaves ideally.

(4) There is no liquid or solid surface adsorption.

(5) The pressure drop through the column is negligibly small.

In G.L.C. the partition coefficient has been found to be approximately constant at constant temperature, when the solute volume is not exceedingly large and the column pressure not too far below the ambient pressure. The second assumption requires infinite solute dilution, while the third and fourth can be approximated by carrying out the measurements of retention time at near ambient pressures on a column pre-treated to saturate the active sites. Finally the fifth condition requires very low flowrates of the carrier gas.

The partition coefficient at infinite dilution is then calculated from the rearranged form of the equation 4.1.

$$K^{\infty} = \frac{F.(T_{co}/T_a).(P_a/P_o).J_3^2.(t_R-t_m)}{W_L/\rho_L} \qquad (4.2)$$

where

T_{co} : column temperature (°K)

T_a : ambient temperature (°K)

P_o : column outlet pressure

P_a : ambient pressure

W_L : weight of liquid phase in the column

ρ_L : density of liquid phase

F : flowrate of carrier gas, measured under the ambient conditions.

4.1.1 EXPERIMENTAL PROCEDURE

Based on the James and Martin equation and using a standard "model F11 Perkin-Elmer chromatograph", the partition coefficients of various solutes at infinite dilution (K^{∞}) were experimentally determined for a wide range of temperatures.

In order to carry out accurate K^{∞} measurements, the employed operating conditions, i.e. carrier gas flowrate, mean column pressure and injected sample size were such as to remove the assumptions taken for the derivation of the James and Martin equation. These conditions were accurately measured and recorded.

K^{∞} data were determined for several fatty acids (acetic acid, propionic acid), fatty esters (ethyl acetate, ethyl butyrate, ethyl caproate, ethyl caprylate, methyl linoleate, methyl γ-linolenate), derivatives of fatty esters (methyl chloroacetate, ethyl chloroacetate, ethyl lactate, methyl acetoacetate, ethyl acetoacetate) and isoprenoids, constituents of essential oils, (camphene, tricyclene, α-pinene, β-pinene), using some of the most recommended stationary phases for the G.L.C. separation of fatty acids (F.F.A.P., D.E.G.S., SP-2340, OV-275).

Examples of the analytical chromatograph columns employed in this work are given below.

(1) 121.9 cm long, 0.3 cm O.D. stainless steel column packed with 1.0544 g chromatographic packing material, consisting of 16.67% by weight of F.F.A.P. on 500-353 μm chromosorb W, AW-DMCS.

(2) 121.9 cm in length and 0.3 cm in O.D. stainless steel column packed with 1.0625 g chromatographic material, 16.67% by weight of F.F.A.P. on 500-353 μm chromosorb W, AW-DMCS.

(3) 45.7 cm long, 0.3 cm O.D. stainless steel column with 0.3806 g packing material, consisting of 16.67% by weight of F.F.A.P. on 500-353 μm chromosorb W, AW-DMCS.

(4) 121.9 cm long, 0.3 cm O.D. stainless steel column packed with 0.9042 g chromatographic material, consisting of 20% by weight of D.E.G.S. on 250-177 μm chromosorb W, AW-DMCS.

(5) 182.9 cm long, 0.6 cm O.D. glass column packed with 1.6862 g chromatographic material, 14.86% by weight of OV-275 on 149-125 μm chromosorb P, AW-DMCS.

For the latest column a Pye 104 chromatograph was used, because the F11 unit was unable to accomodate glass columns.

4.1.2 ESTIMATION OF EXPERIMENTAL ERRORS

The main errors involved for the determination of K^{∞} data were the following:

(1) The fluctuations in the carrier gas flow rate and errors in the flowrate measurements

Day to day reproducibility of flowrate was found to be better than 1%. A soap-bubble meter was used to measure the nitrogen flowrate with accuracy better than 2%.

(2) The column temperature fluctuations and measurements

The error was very small. The temperature of the oven, set by a dial calibrated in degrees centigrade, was controlled to 0.1°C.

(3) Errors for determining the packing weight and liquid phase loading

The error was negligible. The support material and stationary phase required for the preparation of chromatograph packing were weighed with an accuracy of 0.0001 g.

(4) The fluctuations in the column pressure and errors in the column pressure measurements

The inlet and outlet pressures were measured by a mercury manometer with an accuracy of 0.1333 kN m^{-2} (1 mm Hg). No fluctuations in column pressure have been noticed.

(5) Errors in the measurements of retention time

The retention times were measured by an accurate 30-second stopwatch. The introduced error in the recorded time was negligible, unless solutes with very short retention times were used.

There is also another systematic error, which is the slow loss of stationary phase from the column. This error becomes important only when operating the chromatograph at temperatures near the maximum recommended temperature for the liquid phase.

The factors mentioned above indicate that K^{∞} values should be measured with a precision better than 3%.

In addition a systematic study of the reproducibility of the determined K^{∞} data has been carried out by using three different size chromatographic columns containing different quantities of the same packing material (16.67% F.F.A.P. on chromosorb W, AW-DMCS). The employed operating conditions also varied within the limits of the application of the James and Martin equation (carrier gas flowrate low i.e. 0.6 $cm^3 s^{-1}$, mean column pressure near to ambient i.e. 136 kN m^{-2}, low pressure drop across the column i.e. 69 kN m^{-2} and small injected sample volume i.e. 0.1 mm^3). The results were always found to be reproducible to within ± 2%.

4.1.3 RESULTS

The experimentally measured K^{∞} values are summarized in Tables 4.1, 4.2, 4.3 along with the operating temperatures under which they were determined. A plot of log K^{∞} versus 1/T yielded straight line relationships as shown in Figures 4.1-4.7. From these plots K^{∞} values can be obtained at any other intermediate temperature, without the necessity of employing further experimental work. It should be noted that the linear relationship between log K^{∞} and 1/T is only exact for the limited temperature range with which no variation in the stationary phase volume occurs.

A plot of log K^{∞} against the number of carbon atoms, for aliphatic ethyl esters on F.F.A.P. and D.E.G.S. stationary phases, is demonstrated in Fig. 4.4. This plot may be used for a rough estimation of K values for other fatty solutes belonging in the same homologous series.

Finally Table 4.4. represents a typical set of conditions applied in the James and Martin equation for K^{∞} determinations.

4.1.4 DISCUSSION

As was already mentioned the purpose of this experimental work was to provide equilibrium data for a preparative G.L.C. chromatographic unit, the SCCR-2 machine.

Generally in preparative columns large quantities of packing materials are required which involve high costs. Therefore, a careful selection of the liquid phase is of prime importance. K^{∞} determinations are particularly useful for this to be achieved.

Since the SCCR-2 unit was mainly intended for fatty acids separations the employed liquid phases for these K^{∞} determinations were some of the most recommended in the field of G.L.C. of fatty acids, such as F.F.A.P., D.E.G.S., SP-2340 and OV-275.

TABLE 4.1 K^{∞} DATA OF SOME FATTY SOLUTES ON F.F.A.P. AND D.E.G.S. STATIONARY PHASES AT VARIOUS TEMPERATURES

Liquid Phase	FATTY ACIDS			FATTY ESTERS					DERIVATIVES OF FATTY ESTERS									
	Column Temp.	K^{∞}		Column Temp.	K^{∞}				Column Temp.	K^{∞}		Column Temp.	K^{∞}			Column Temp.	K^{∞}	
		Acetic acid	Propionic acid		Ethyl acetate	Ethyl butyrate	Ethyl caproate	Ethyl caprylate		Methyl linoleate	Methyl γ-linolenate		Methyl chloroacetate	Ethyl chloroacetate	Ethyl lactate		Methyl acetoacetate	Ethyl acetoacetate
	°C			°C					°C			°C				°C		
	92	1349	2175	80.5	71	209	655		193	1828	2199	84	629		995	85.5	1556	2000
F	100	939	1478	91.5	53	138	435	1422	197	1478	1813	93	460		714	92	1183	1482
F	108	706	1102	95	49	126	388	1252	204.5	1155	1322	97	391	479	602	98	943	1169
A	120	452	684	102	38	100	295	903	206.5	1061	1271	106	291	329	443	102	806	991
P	130.5	329	482	110.5	32	81	225	655	211.5	870	1044	112	239	279	357	108	661	810
	142	234	338	121	26	62	164	456	216	748	881	118		228		112		661
												120	184		275	120		503
												125		185				
												135		145	170			
				78.5	44	91	272	817	169.5	1831	2526					107		633
D				89	33	69	185	529	174	1603	2082					116.5		467
E				98	28	55	146	366	179	1293	1738					122.5		384
G				107	22	44	105	270								127		324
S				117	18	35	77	188								131.5		283
				127	14	28	59	142										

TABLE 4.2 K^{∞} DATA OF METHYL LINOLEATE-METHYL γ-LINOLENATE SYSTEM ON VARIOUS LIQUID PHASES

Liquid Phase	Column Temp.	K^{∞}		Separation Factor
		Methyl Linoleate	Methyl γ-Linolenate	
	°C			
FFAP	193	1828	2199	1.20
	197	1478	1813	1.23
	2045	1155	1322	1.14
	206.5	1061	1271	1.20
	211.5	870	1044	1.20
	216	748	881	1.18
DEGS	169.5	1831	2526	1.38
	174	1603	2082	1.30
	179	1293	1738	1.34
SP/2340	165	1350	1755	1.30
	169	1118	1464	1.31
	176.5	808	1040	1.29
	182.5	604	775	1.28
	191	425	532	1.25
OV/275	178	367	451	1.23
	186	264	320	1.21
	195	179	218	1.22
	203	144	172	1.19
	212	99	119	1.20

TABLE 4.3 K^{∞} DATA OF SOME ISOPRENOID COMPOUNDS ON F.F.A.P. STATIONARY PHASE

Liquid Phase	Column Temp.	K^{∞}			
		Tricyclene	Camphene	α-pinene	β-pinene
	°C				
	78	234	320		
	83	197	269		
FFAP	88	170	232	183	289
	93	149	198	160	250
	98	129	170	139	215
	103			121	186
	107	102	134	105	160
	117	82	107	85	128
	127	61	79	66	101

TABLE 4.4 TYPICAL SET OF CONDITIONS FOR THE DETERMINATION OF K^{∞} DATA

F	0.81 $cm^3 s^{-1}$	t_R	73 s
T_{co}	379.15°K	t_m	6 s
T_a	295.15°K	W_L	0.17578 g
P_a	101.15 kN m^{-2}	ρ_L	1.12 g cm^{-3}
P_o	101.15 kN m^{-2}	solute	methyl chloroacetate
J_3^2	0.655	packing	16.67% F.F.A.P. on 500-353 μm chromosorb w, AW-DMCS
K^{∞} = 291			

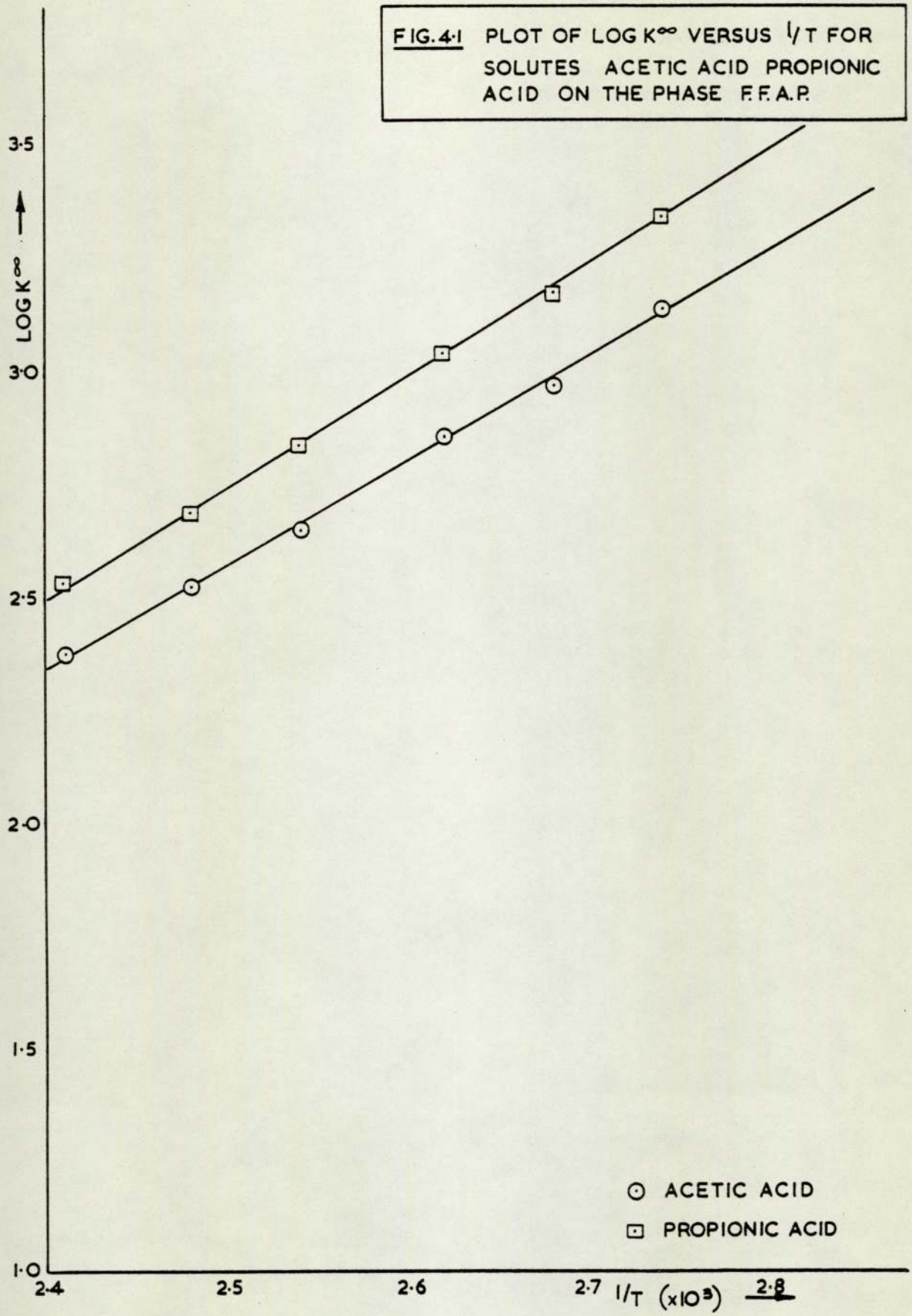


FIG. 4·1 PLOT OF LOG K∞ VERSUS 1/T FOR SOLUTES ACETIC ACID PROPIONIC ACID ON THE PHASE F.F.A.P.
LOG K∞
3·5
3·0
2·5
2·0
1·5
1·0
2·4
2·5
2·6
2·7
2·8
1/T (x10³)
ACETIC ACID
PROPIONIC ACID

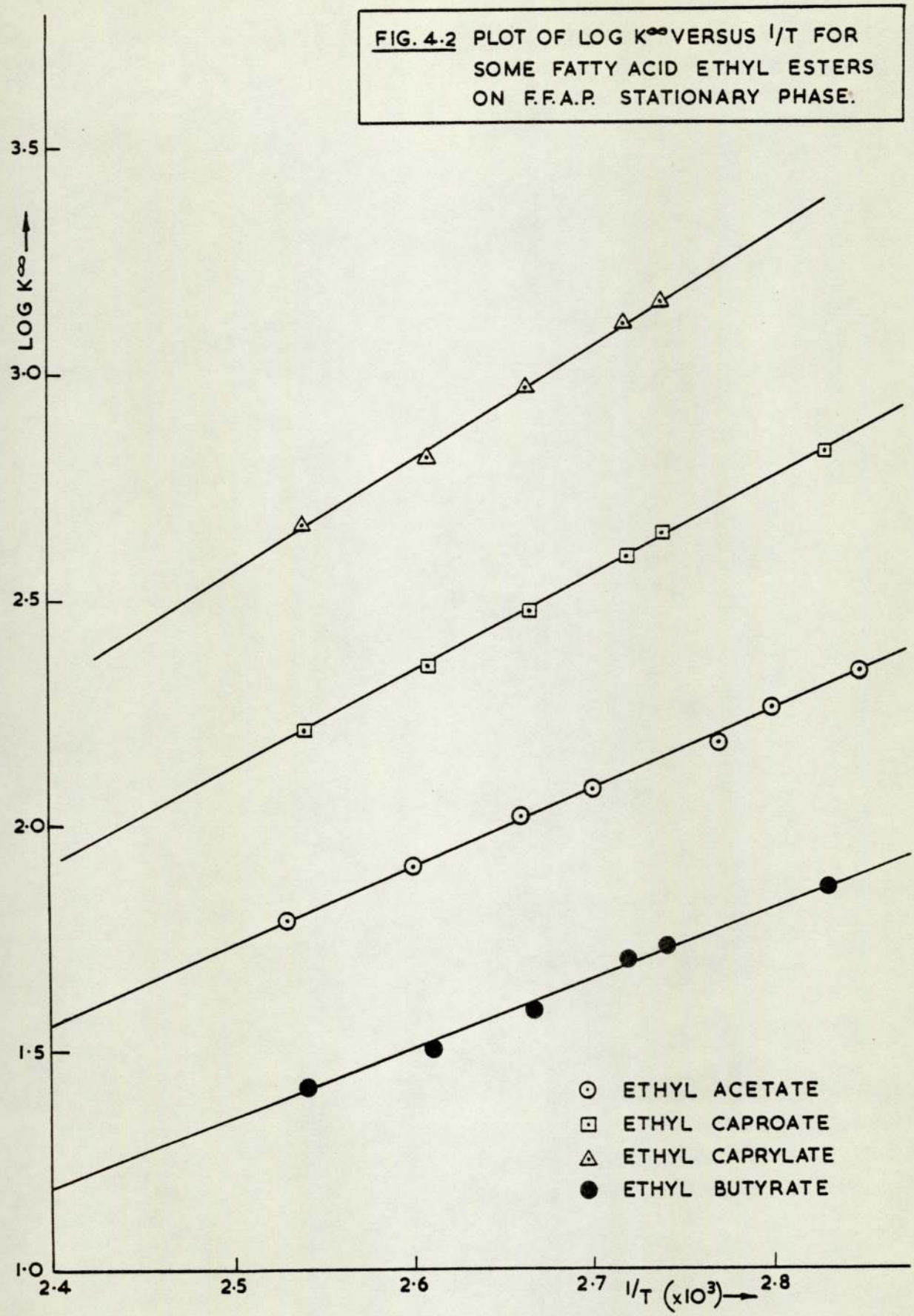


FIG. 4.2 PLOT OF LOG K∞ VERSUS 1/T FOR SOME FATTY ACID ETHYL ESTERS ON F.F.A.P. STATIONARY PHASE.
3·5
3·0
2·5
2·0
1·5
1·0
LOG K∞
2·4
2·5
2·6
2·7
2·8
1/T (x10³)
ETHYL ACETATE
ETHYL CAPROATE
ETHYL CAPRYLATE
ETHYL BUTYRATE

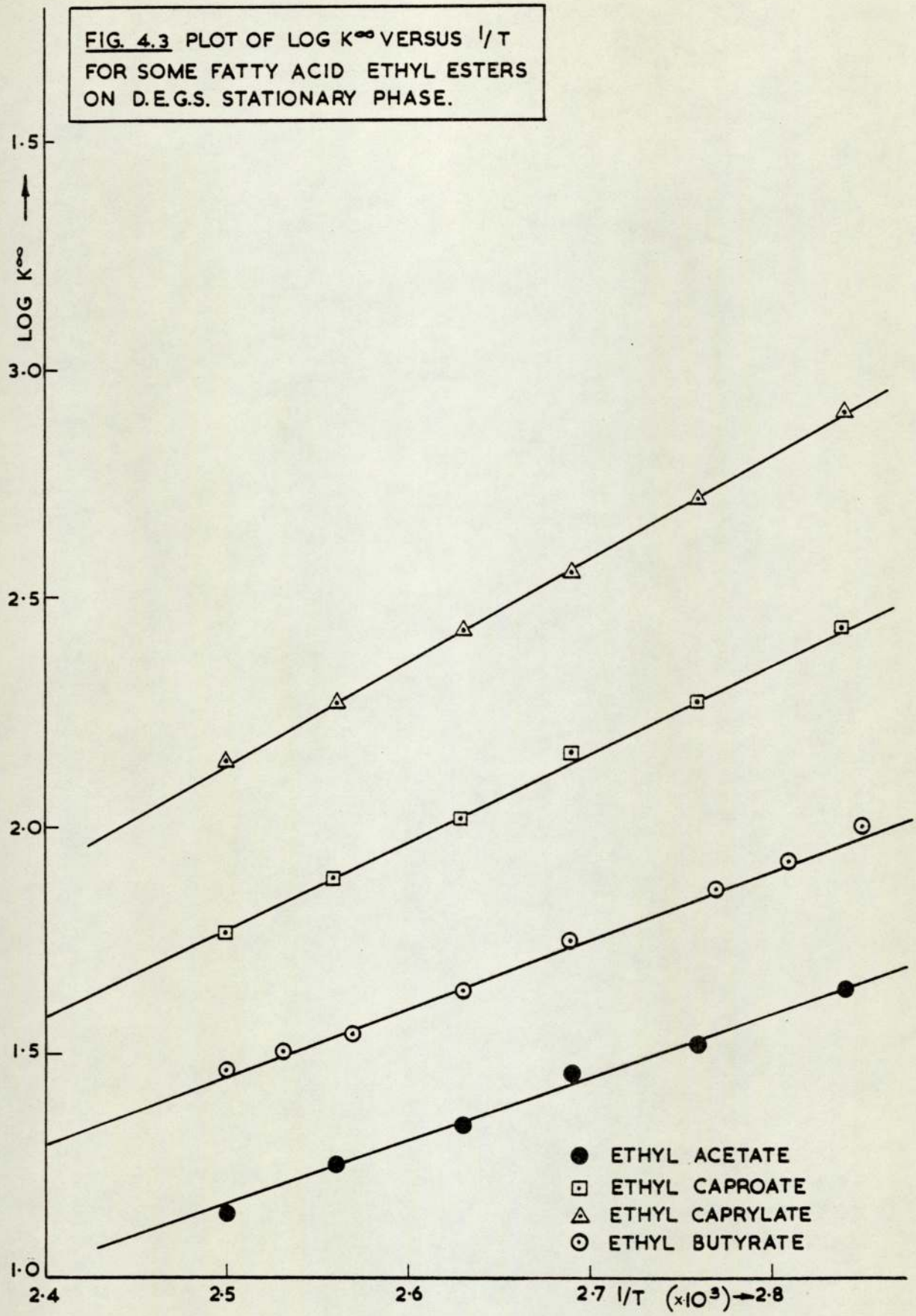


FIG. 4.3 PLOT OF LOG K∞ VERSUS 1/T FOR SOME FATTY ACID ETHYL ESTERS ON D.E.G.S. STATIONARY PHASE.
LOG K∞ ⟶
1·5
3·0
2·5
2·0
1·5
1·0
2·4
2·5
2·6
2·7
1/T (×10³) ⟶ 2·8
ETHYL ACETATE
ETHYL CAPROATE
ETHYL CAPRYLATE
ETHYL BUTYRATE

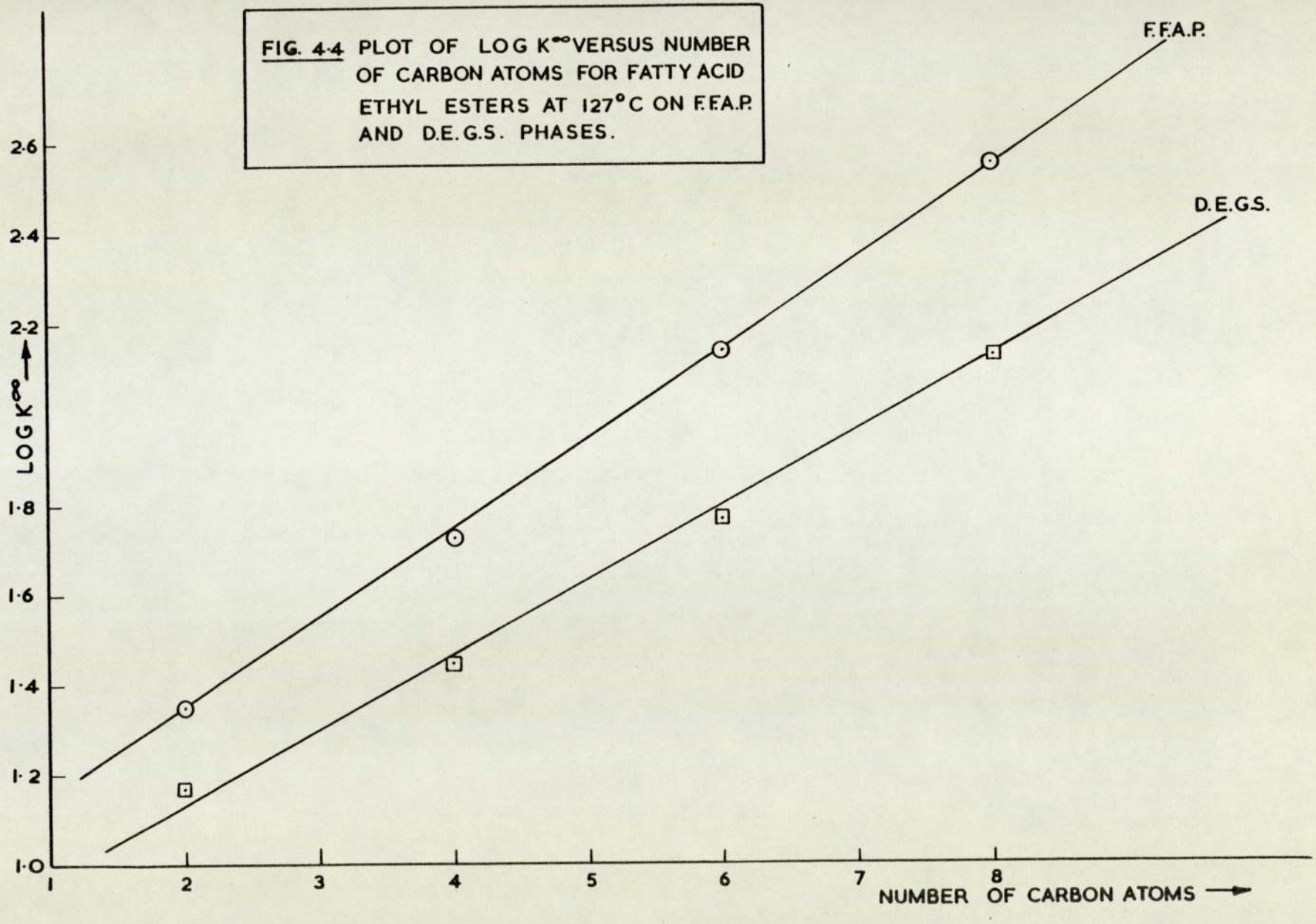


FIG. 4·4 PLOT OF LOG K° VERSUS NUMBER OF CARBON ATOMS FOR FATTY ACID ETHYL ESTERS AT 127°C ON F.F.A.P. AND D.E.G.S. PHASES.

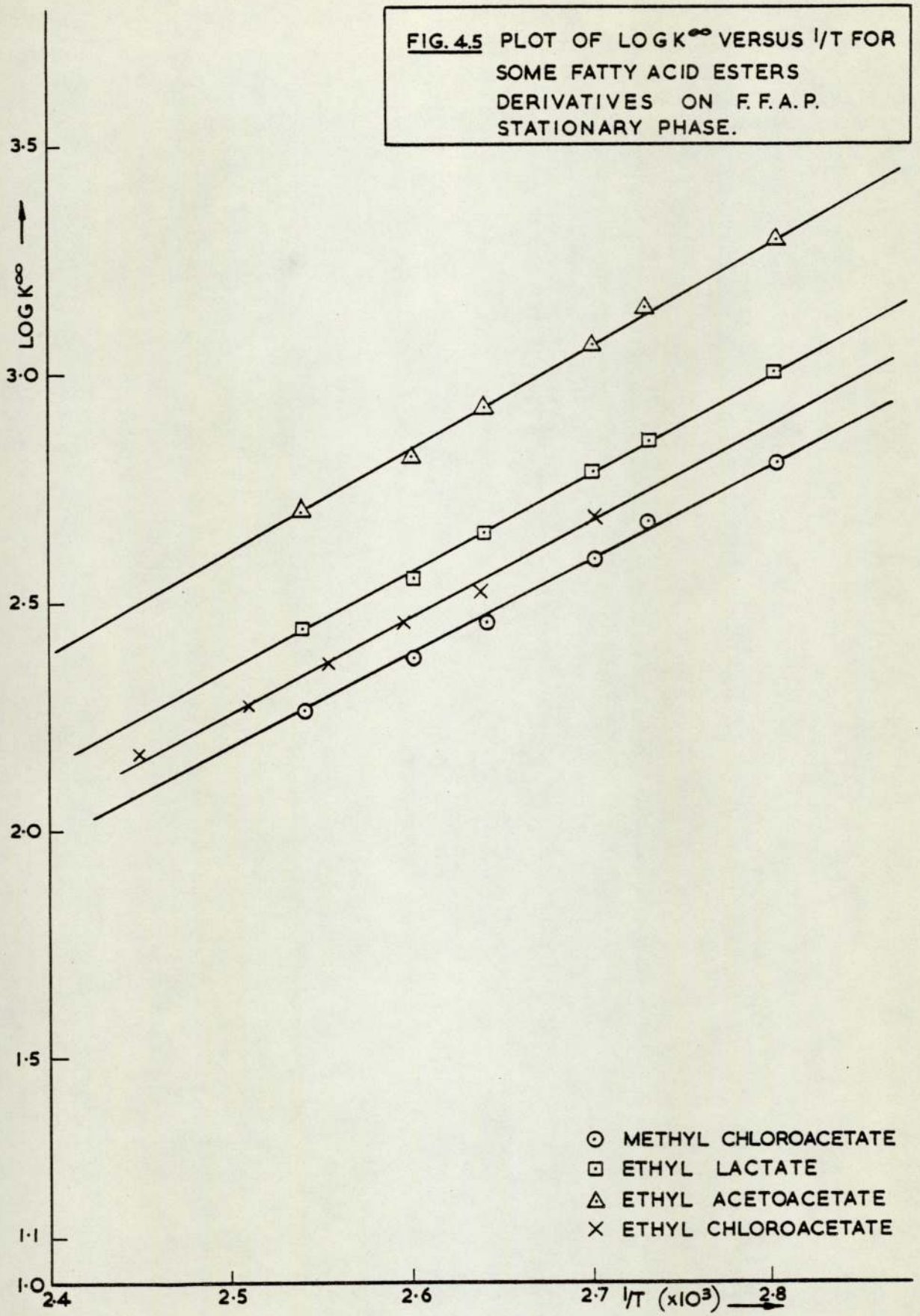
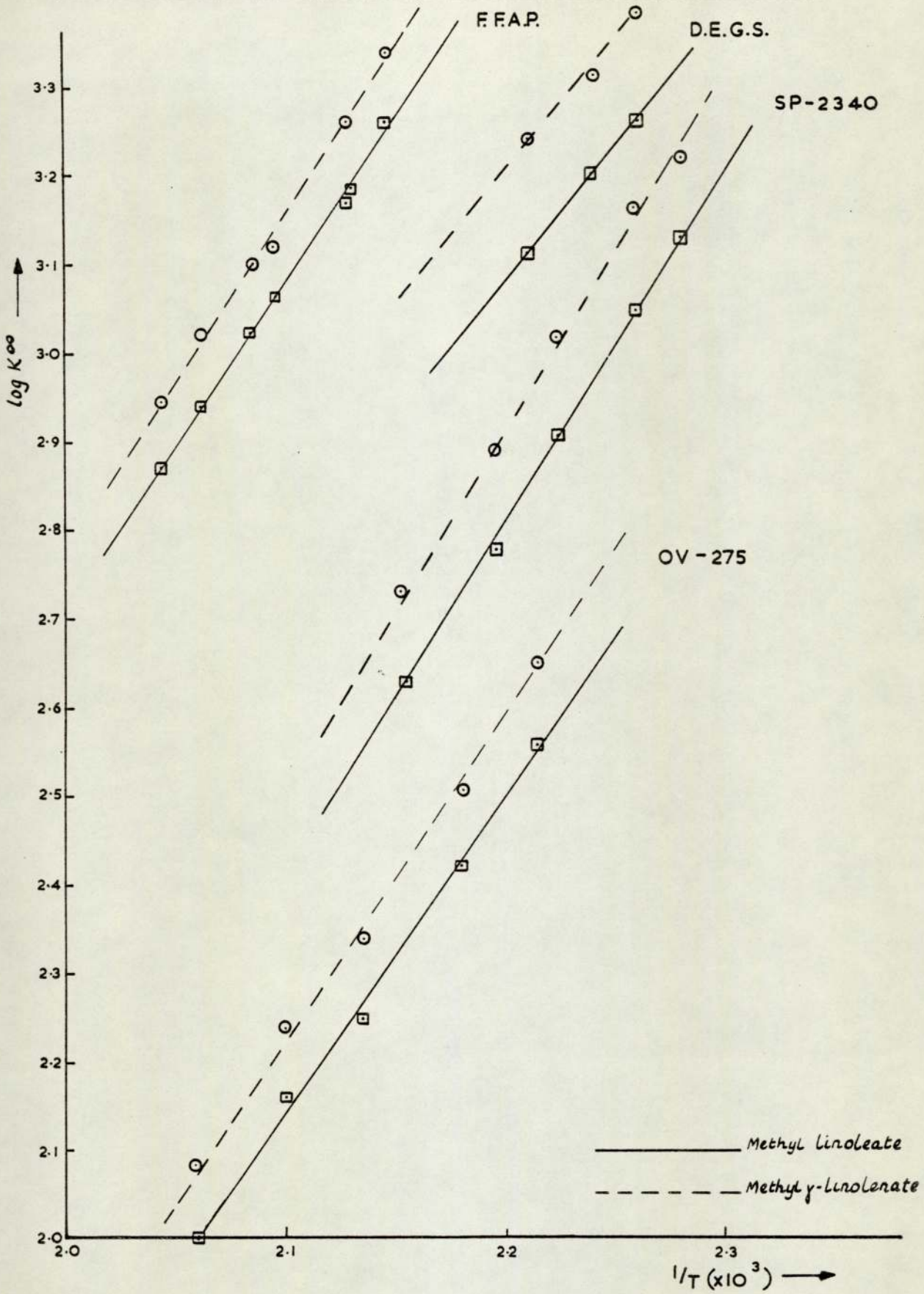


FIG. 4.5 PLOT OF LOG K∞ VERSUS 1/T FOR SOME FATTY ACID ESTERS DERIVATIVES ON F.F.A.P. STATIONARY PHASE.
LOG K∞
3·5
3·0
2·5
2·0
1·5
1·1
1·0
2·4
2·5
2·6
2·7
2·8
1/T (x10³)
METHYL CHLOROACETATE
ETHYL LACTATE
ETHYL ACETOACETATE
ETHYL CHLOROACETATE

FIGURE 4.6 PLOT OF LOG K^{∞} VERSUS $^{1}/_{T}$ FOR SOLUTES METHYL LINOLEATE -METHYL γ-LINOLENATE ON VARIOUS STATIONARY PHASES



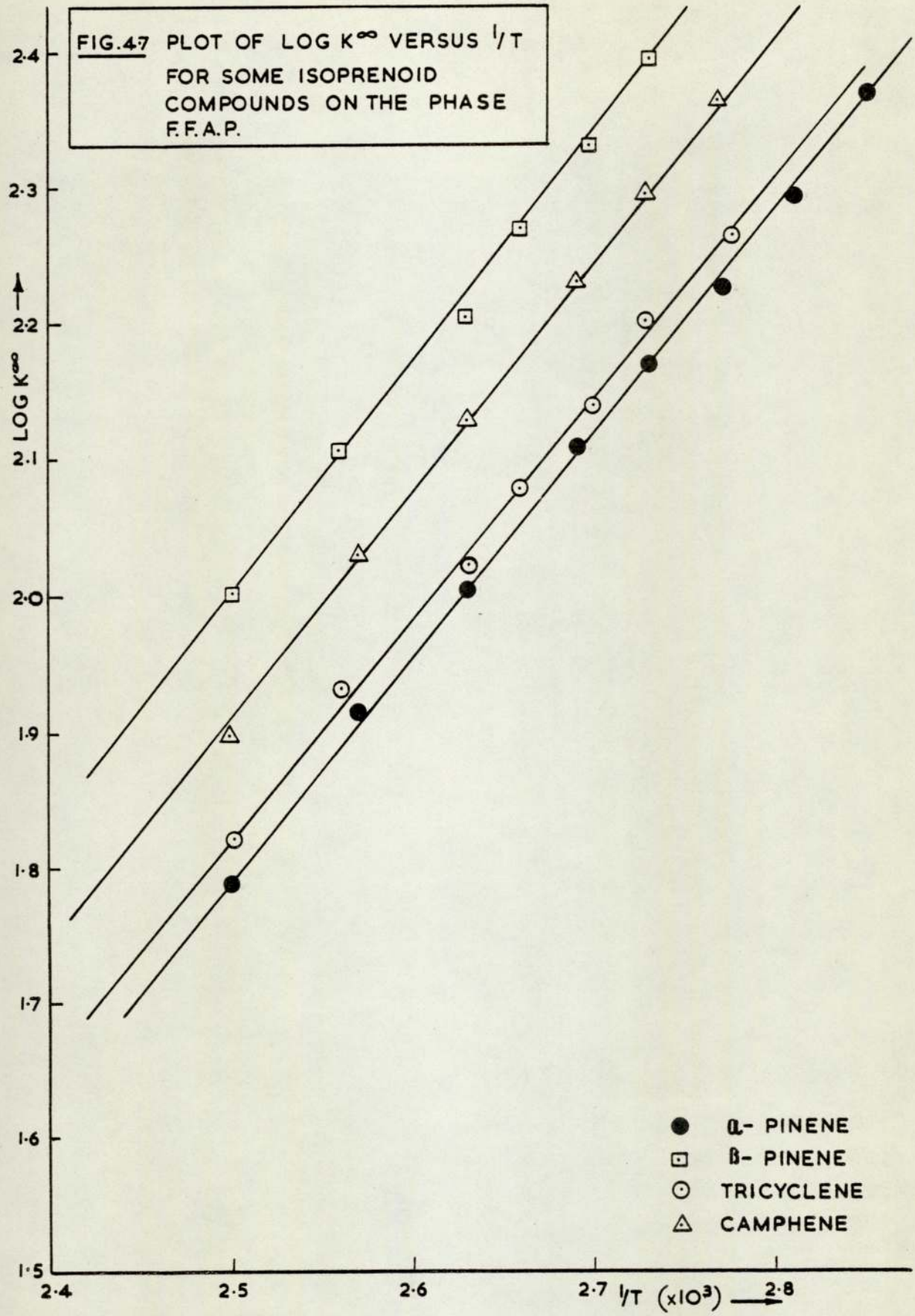


FIG.47 PLOT OF LOG K∞ VERSUS 1/T FOR SOME ISOPRENOID COMPOUNDS ON THE PHASE F.F.A.P.
2·4
2·3
2·2
2·1
2·0
1·9
1·8
1·7
1·6
1·5
LOG K∞
2·4
2·5
2·6
2·7
2·8
1/T (x10³)
α- PINENE
β- PINENE
TRICYCLENE
CAMPHENE

Among them F.F.A.P. (free fatty acid phase) was found to be the most convenient general purpose liquid phase, as most of the employed solutes (free fatty acids, fatty esters, derivatives of fatty esters and essential oils) gave symmetrical elution peaks on F.F.A.P. columns. In addition it is a relatively cheap phase with high thermal stability.

D.E.G.S. (diethylene glycol succinate) has been found very effective for the separation of fatty acid esters. A comparison of fatty esters K^{∞} values on F.F.A.P. and D.E.G.S. phases, at the same temperature (Table 4.1) indicates that much lower K^{∞} values can be obtained on D.E.G.S. columns. This in preparative chromatography is quite important, since the required carrier gas flowrates and operating temperatures for separation can be significantly decreased, also the loading of stationary phase may be increased with a significant gain in throughputs. But the poor heat stability of D.E.G.S. (137) makes this phase less attractive particularly for preparative use.

The SP-2340 phase was introduced in 1974 by Suppelco Inc., having separating characteristics similar to D.E.G.S. but having the capability of a much longer column life.

OV-275 is like the SP-2340 a cyanosilicone but with higher cyano-content and higher polarity.

Comparing these four phases for the separation of methyl linoleate/methyl γ-linolenate esters found that OV-275 is the most effective phase in terms of resolution and speed of analysis. As shown in Table 4.2, the K^{∞} values of these esters on OV-275 are much lower than those corresponding on the other stationary phases, at the same temperature. Consequently, OV-275 seems to be the preferred phase for this application, although the separation factor of the esters were found to be higher on D.E.G.S. columns (Table 4.2).

Comparison of K^{∞} data for free fatty acids and fatty esters with about the same number of carbon atoms, on F.F.A.P. liquid phase, shows that much lower K^{∞} values can be obtained with the fatty esters (Table 4.1). The drawback of high K^{∞} values of free fatty acids along with some other problems associated with their separations (Section 2.5) lead to the conclusion that in preparative chromatography the separation of fatty acids after conversion into their esters is the preferred procedure.

In addition these K^{∞} value determinations were found very useful for selecting chemical systems suitable for separation studies on the SCCR-2 machine (see Section 6). Also the K^{∞} data determined in this work were used for selecting the experimental conditions required for the operation of the SCCR-2 unit (Section 7).

4.2 PRELIMINARY STUDIES FOR THE DETERMINATION OTHER THERMODYNAMIC DATA

4.2.1 ACTIVITY COEFFICIENT AT INFINITE DILUTION

Following the James and Martin basic G.L.C. equilibrium theory, the equation 4.3 may be derived (44) which relates activity with partition coefficients. This equation is true when the vapour phase obeys the ideal gas laws and the solute is at infinite dilution.

$$\gamma_1^{\infty} = \frac{R_g.T.\rho_L}{P_1^{\circ}.K^{\infty}.M_L} \qquad (4.3)$$

Using the above relationship, activity coefficients at infinite dilution, γ^{∞}, for ethyl acetate, ethyl acetoacetate and methyl chloroacetate on F.F.A.P. stationary phase, have been calculated by using the experimental determined K^{∞} data, the known molecular weight of F.F.A.P. (M_L = 15,000), and the corresponding vapour pressures of the solutes (see Appendix A.2).

Table 4.5 γ^{∞} DATA FOR ETHYL ACETATE, ETHYL ACETOACETATE, METHYL CHLOROACETATE ON THE F.F.A.P. PHASE

Column Temper.	γ^{∞} x 10 ethyl acetate on F.F.A.P.	Column Temper.	γ^{∞} x 10 ethyl acetoacetate on F.F.A.P.	Column Temper.	γ^{∞} x 10 methyl chloro-acetate on F.F.A.P.
°C		°C		°C	
57.5	0.300	115.5	0.367	92.2	0.170
60.5	0.289	120.5	0.355	94.5	0.169
67.5	0.278	123.5	0.349	96.5	0.169
74.5	0.281	125.5	0.351	97.8	0.167
79.0	0.274	130.5	0.347	101.5	0.169
81.7	0.269	135.5	0.338	105.0	0.166
				107.7	0.166

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°C		°C		°C	
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60.5	0.289	120.5	0.355	94.5	0.169
67.5	0.278	123.5	0.349	96.5	0.169
74.5	0.281	125.5	0.351	97.8	0.167
79.0	0.274	130.5	0.347	101.5	0.169
81.7	0.269	135.5	0.338	105.0	0.166
				107.7	0.166

4.2.2 SECOND VIRIAL COEFFICIENT

As is shown in the equations of Table 2.2 the second, cross virial coefficient (B_{12}) may be obtained by measuring the variation of net retention volume of a solute with the pressure of the carrier gas. Although these equations are quite similar, and over small ranges of pressure it is unlikely that experimental data will be able to distinguish between them, the latter equations are considered the most accurate as more factors have been considered for their development.

Based on the Cruickshank, Windsor and Young theory (see Table 2.2) and using a standard "model F11 Perkin-Elmer chromatograph" the determinations of B_{12} for ethyl acetate and methyl chloroacetate with nitrogen as carrier gas have been attempted. But the difficulty of measuring the small differences in retention volume involved with this reduced pressure gas chromatography which the standard F11 chromatograph permitted, have led to significant errors. In order to carry out accurate B_{12} determinations the F11 chromatograph had to be modified to meet the apparatus requirements for these measurements, i.e. the column pressure must be variable over a range of several atmospheres. Young (32), Wicăr and Novák (49) have described specially designed G.L.C. apparatus for B_{12} measurements.

The second, cross virial coefficients for ethyl acetate-nitrogen and methyl chloroacetate-nitrogen mixtures were finally determined using the O'Connell-Prausnitz method (172), which is an empirical method correlating B_{12} with critical constants through the equations given in Appendix A.2. The critical constants and vapour pressures required for these calculations are also given in Appendix A.2.

A summary of the calculated B_{12} values is demonstrated in the following Table.

TABLE 4.6 SECOND, CROSS VIRIAL COEFFICIENTS FOR ETHYL ACETATE-NITROGEN, METHYL CHLOROACETATE-NITROGEN MIXTURES

Temperature °C	B_{12} ethylacetate-nitrogen $cm^3\ mol^{-1}$	Temperature °C	B_{12} methyl chloroacetate-nitrogen $cm^3\ mol^{-1}$
57.5	-677	92.2	-766
59.6	-666	93.5	-761
60.5	-656	94.5	-754
64.9	-640	96.5	-745
67.5	-628	97.8	-738
74.5	-605	101.5	-720
75.4	-593	105.0	-701
79.0	-572	107.7	-690
80.7	-571	118.0	-644
81.7	-561	130.2	-597
96.6	-508	154.7	-517
128.2	-422	191.3	-426
149.4	-374	215.8	-378
202.2	-279	276.9	-284

Using this B_{12} data the contribution of the gas phase imperfections on the determination of the γ^{∞} values, for ethyl acetate and methyl chloroacetate solutes on F.F.A.P. phase, was estimated by the Everett equation (31):

$$\ln \gamma_1^{\infty}(T,0) = \ln\left(\frac{\rho_L . R_g . T}{K^{\infty} . M_L . P_1^{\circ}}\right) - \frac{(B_{11}-V_1^{\circ})P_1^{\circ}}{R_g . T} + \frac{(2\,B_{12}-\bar{V}_1^{\infty})}{R_g . T} . \bar{P} \qquad (4.4)$$

The non-logarithmic terms in the above equation are the corrections for the non-ideality of the vapour mixture.

Also,

$\bar{P}$: mean column pressure, $\bar{P} = J_3^2/P_o$

V_1° : the molar volume of the solute

$\bar{V}_1^{\infty}$: the partial molar volume of the solute at infinite dilution in the stationary liquid

B_{11}: second virial coefficient of solute

$\gamma_1^{\infty}(T,0)$: activity coefficient at infinite solute dilution and zero column pressure.

In the calculations, $\bar{V}_1^{\infty}$ was assumed equal to V_1°, and B_{11} was determined using the O'Connell-Prausnitz empirical equation (see Appendix A.2.3). The operating conditions employed for the application of equation 4.4, were identical as those in the previous section (Section 4.2.1), which meet the requirements (infinite solute dilution, no significant mean column pressure variation) for the applicability of the above equation. Finally the determined γ^{∞} data are summarized in Table 4.7, and a typical set of conditions used for these calculations is shown in Table 4.8.

The purpose of this work was to estimate the significance of the gas phase imperfections in the determination of thermodynamic data which is so often discussed by many workers.

TABLE 4.7: ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR ETHYL ACETATE, METHYL CHLOROACETATE SOLUTES ON F.F.A.P. LIQUID PHASE

Temperature°C	ETHYL ACETATE ON F.F.A.P. PHASE WITH N_2 AS CARRIER GAS	
	γ^{∞} GAS PHASE IDEAL	γ^{∞} GAS PHASE NON-IDEAL
57.5	0.0300	0.0289
60.5	0.0289	0.0280
67.5	0.0278	0.0272
74.5	0.0281	0.0277
79.0	0.0274	0.0273
81.7	0.0269	0.0269
Temperature °C	METHYL CHLOROACETATE ON F.F.A.P. PHASE WITH N_2 AS CARRIER GAS	
	γ^{∞} GAS PHASE IDEAL	γ^{∞} GAS PHASE NON-IDEAL
92.2	0.0170	0.0161
94.5	0.0169	0.0161
96.5	0.0169	0.0161
97.8	0.0167	0.0159
101.5	0.0169	0.0162
105.0	0.0166	0.0160
107.7	0.0166	0.0161

TABLE 4.8 : TYPICAL SET OF CONDITIONS FOR THE APPLICATION OF EVERETT THE EQUATION

$\gamma^{\infty} = \frac{R.T.\rho_L}{P_1^{\circ}.K^{\infty}.M_L}$		P_o	101,325 Nm^{-2}
"ideal" γ^{∞} data as determined in Section 4.2.1	0.0278	J_3^2	0.781
		$\bar{V}_1^{\infty}$	It is assumed equal to V_1°
T	340.65 °K	V_1°	97.85 $cm^3 mol^{-1}$
B_{11}	-1430 $cm^3\ mol^{-1}$	P°	73,066 N m^{-2}
B_{12}	- 628 $cm^3\ mol^{-1}$		

4.2.3 DISCUSSION

Examining the effects of solute concentration, mean column pressure and gas phase imperfections on the gas-liquid equilibrium data is of importance particularly when difficult separation problems are studied on a preparative G.L.C. chromatograph. Certainly the above thermodynamic studies may be considered less important when relatively easy G.L.C. separations are required, but these will become of crucial importance when operating the chromatograph near to its separating limits. Thus, a decrease in the operating pressure or the use of helium instead of nitrogen as carrier gas may increase the separation factor from 1.10 to 1.20, which could be enough to facilitate the design and operation of a preparative chromatograph.

The effect of solute concentration on K values has been experimentally studied by previous workers (46) and found quite significant. Such a study would be useful in relating the separation efficiency with the feed throughput of a preparative chromatograph, from which the maximum overall efficiency of the equipment could be obtained. Also γ^{∞} data may be found useful in determining equilibrium data at finite concentrations by using the solution theories (see Section 2.2.3).

Unfortunately only limited experimental work on the above was performed because of limitations of the analytical equipment (F11 Perkin-Elmer Chromatograph) that was available for thermodynamic measurements. The modifications that the standard "model F11 Perkin-Elmer chromatograph" required for K values determinations at finite solute concentrations are outlined by A. Sunal (47). Also Young (32) and Wicăr and Novák (49) describe the apparatus requirements for high pressures G.L.C. thermodynamic measurements.

CHAPTER 5

The Design and Construction of the Sequential Continuous Chromatographic Refiner (SCCR-2)

5.1 INTRODUCTION

5.1.1 PRINCIPLE OF OPERATION

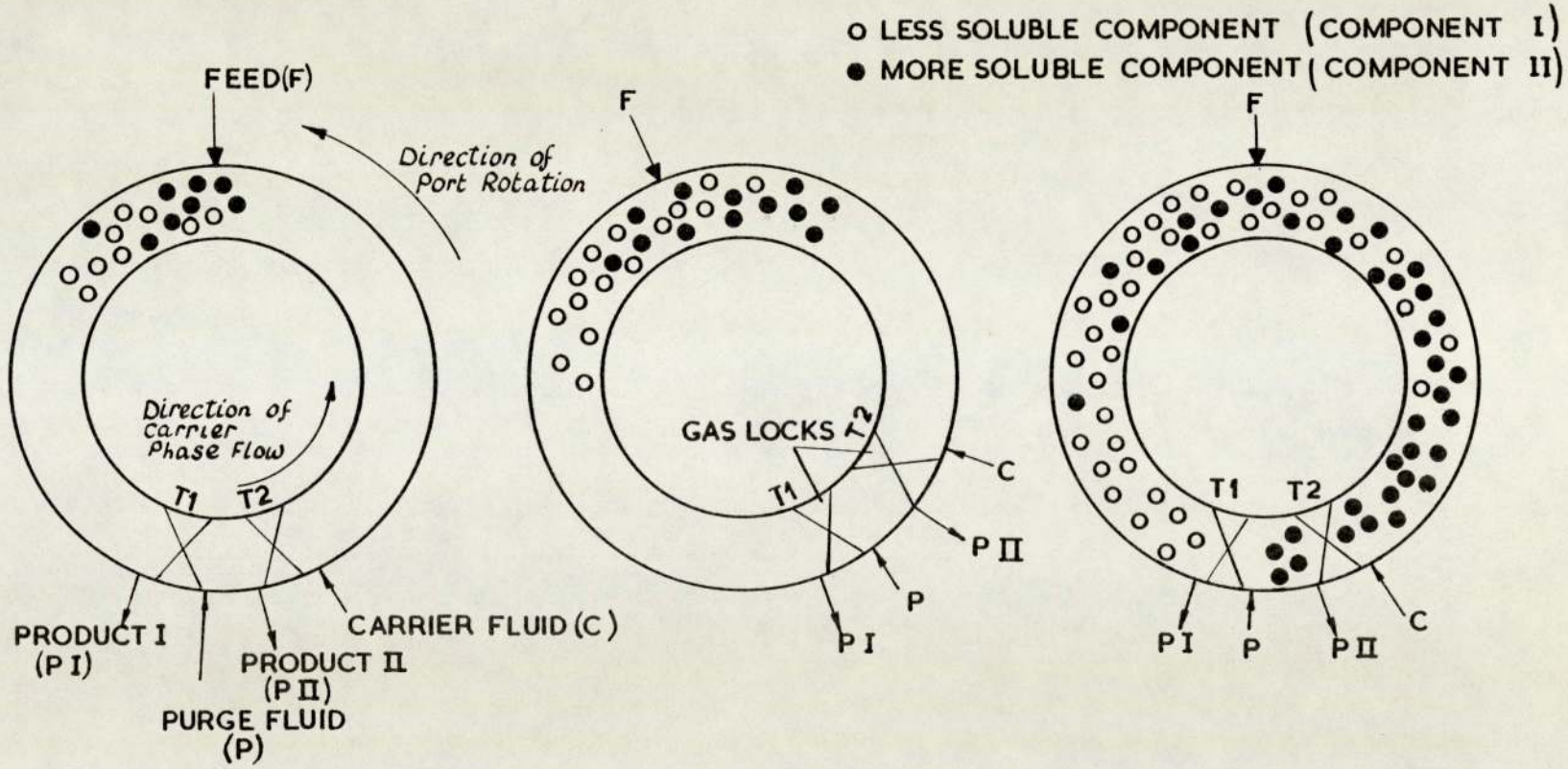
The principle of operation of the sequential continuous chromatographic refiner (SCCR) is illustrated in Fig. 5.1, using a binary feed mixture for separation.

Fig. 5.1a schematically shows the distribution of two components within the system soon after "starting-up" the operation. Feed enters the system at port F, while the carrier fluid is introduced at port C and then flows through the chromatographic packed column. Component I, the least soluble component to the stationary phase of packing, travels with the carrier fluid moving towards the product I offtake port, PI. In contrast, component II which is the most soluble component is "held" preferentially on the stationary phase. A section of the closed loop is isolated by the gas locks T1 and T2 in which an independent fluid stream (purge stream) enters at port P and exi ts from PII.

Fig. 5.1b shows the two components distribution soon after all the port functions have been advanced one position around the static chromatographic column. The movement of the ports has the same general direction as the carrier fluid therefore, simulating the counter-current movement between chromatographic column and carrier phase flow met in the field of moving column chromatography.

The final diagram in Fig. 5.1 represents the fully established operating condition of the system. The less soluble component is now issuing from port PI, as "pure" product I. Meanwhile, the more soluble component is contained in the isolated section which is purged at such a rate as to ensure the complete removal of "pure" product II.

FIGURE 5.1 DIAGRAMATIC PRESENTATION OF THE PRINCIPLE OF THE SCCR OPERATION



(a)
THE DISTRIBUTION OF TWO COMPONENTS SOON AFTER "STARTING-UP" THE OPERATION

(b)
THE TWO COMPONENTS DISTRIBUTION AFTER ONE SEQUENCING ACTION OF THE PORT SYSTEM

(c)
THE SOLUTES DISTRIBUTION WHEN THE PSEUDO-STEADY STATE CONDITION IS ESTABLISHED IN THE SCCR UNIT

The described system is capable of producing only two products. But obviously for a multicomponent feed mixture, the products may be collected and re-run, if more than two fractions are required.

Based on the above principle, the SCCR-2 was built for preparative, high temperature, gas-liquid chromatography applications. The SCCR-2 unit was designed in 12 discrete sections linked together to form a closed symmetrical ring. Each section was a 61 cm long and 2.54 cm in diameter chromatographic column, provided with the necessary port functions (feed inlet, carrier gas inlet and outlet, purge gas inlet and outler and gas lock) by six pneumatically operated valves.

5.1.2 DEVELOPMENT OF THE SCCR-2 DESIGN

Experience gained on the unreliability of moving seals (47,110) in the field of moving column chromatography led Barker and Deeble (17,18) to the development of the SCCR type of chromatograph. The latest scheme provides fixed-bed, moving-port operation, instead of the fixed-port, moving-bed operation involved in moving column chromatography. With this scheme the mechanical movement of the chromatographic columns and the large moving face seals are avoided, to facilitate the scale-up of the process to industrially important levels.

The first SCCR unit (SCCR-1), designed and constructed by Barker and Deeble (18,20), consisted of 12 chromatographic columns, each 7.6 cm in diameter and 61 cm long, arranged vertically and linked together so as to form a closed symmetrical ring. The port rotation movement, was achieved by using solenoid valves, placed at the inlet/outlet and in the transfer lines of the columns. These were energized in a programmed sequence, according to the required pattern, by an automatic

timing device. The SCCR-1 unit has been successfully used by Barker, Deeble and Bell (19-21) to separate binary halocarbon mixtures at feed rates of up to 1500 cm^3 h^{-1}.

But the construction of the SCCR-1 was limited by economic considerations such as:

(1) its materials of construction (brass and copper) since these corroded and act as decomposition sites for many organic chemicals.

(2) the use of air as a carrier gas, so many organic substances are either oxidized or degraded in this atmosphere. In addition the use of highly flammable chemicals was forbidden, for safety reasons.

(3) the lack of heating facilities, hence the SCCR-1 can only be used to separate substances which are easily volatilized at ambient temperature.

These limitations have led to the development of a new sequential continuous chromatographic refiner (SCCR-2) to work at 200°C, using nitrogen as the carrier gas and being constructed of 316 stainless steel and P.T.F.E. (see Plate 5.1). Twelve chromatographic columns were employed, each 61 cm long and 2.54 cm in diameter. However, it is expected that by increasing the number of columns, the discontinuity imposed by the discrete operating nature of the unit will be reduced and an increased separating power will be obtained. The diameter of the columns, was chosen as 2.5 cm, only one third the diameter of the SCCR-1 unit, because of the high cost of building an all stainless steel/P.T.F.E. unit and the necessity of keeping carrier gas costs down when using nitrogen.

In general, the SCCR-2 unit was constructed for high temperature separations of low-volatile organic chemicals and is mainly intended for industrially based problems such as the separation of fatty acids and essential oils.

PLATE 5.1 THE SCCR-2 EQUIPMENT

CAB = charcoal adsorption bed

CU = central unit

FCP = flow control panel

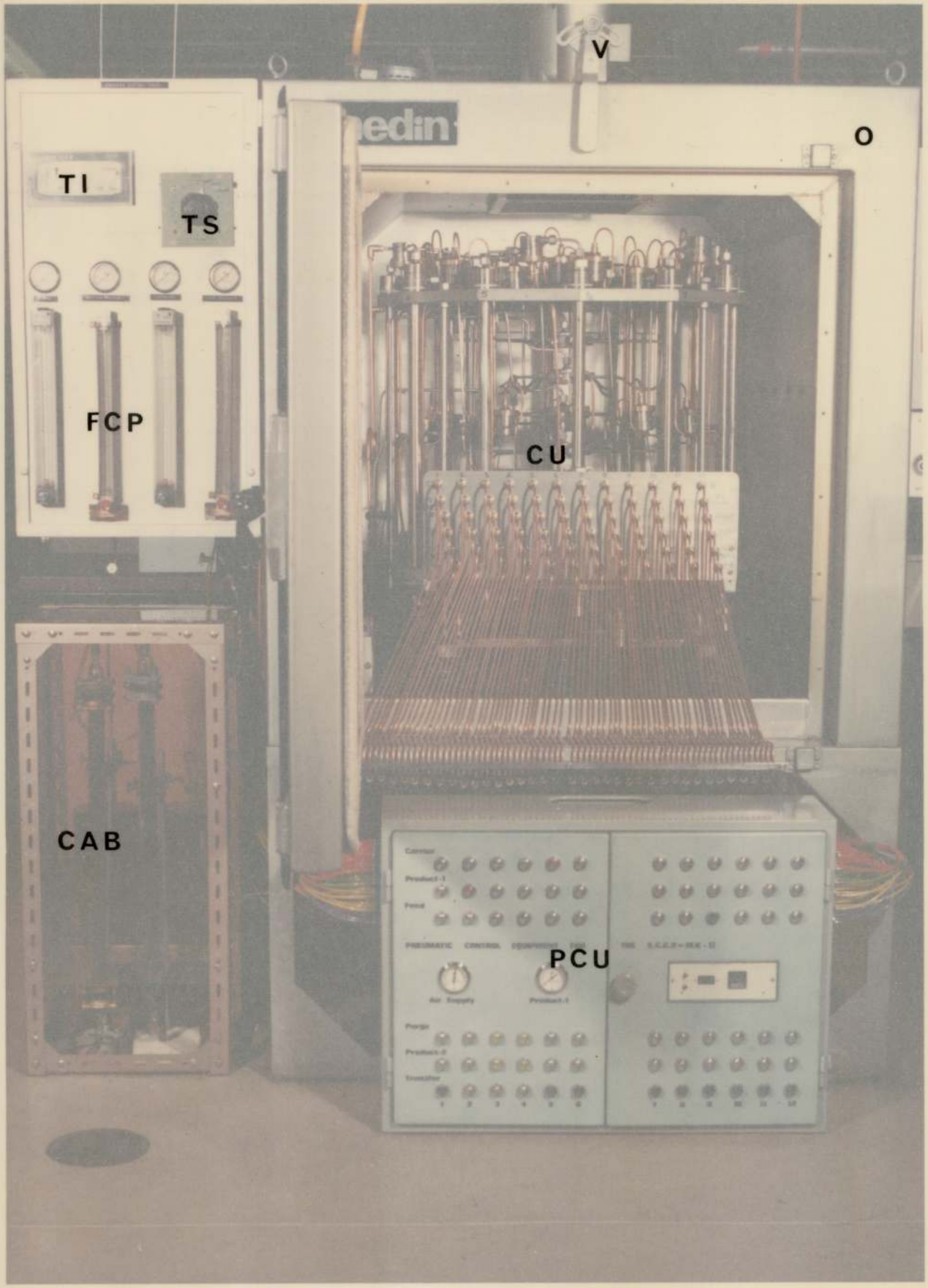
O = oven

PCU = pneumatic control unit

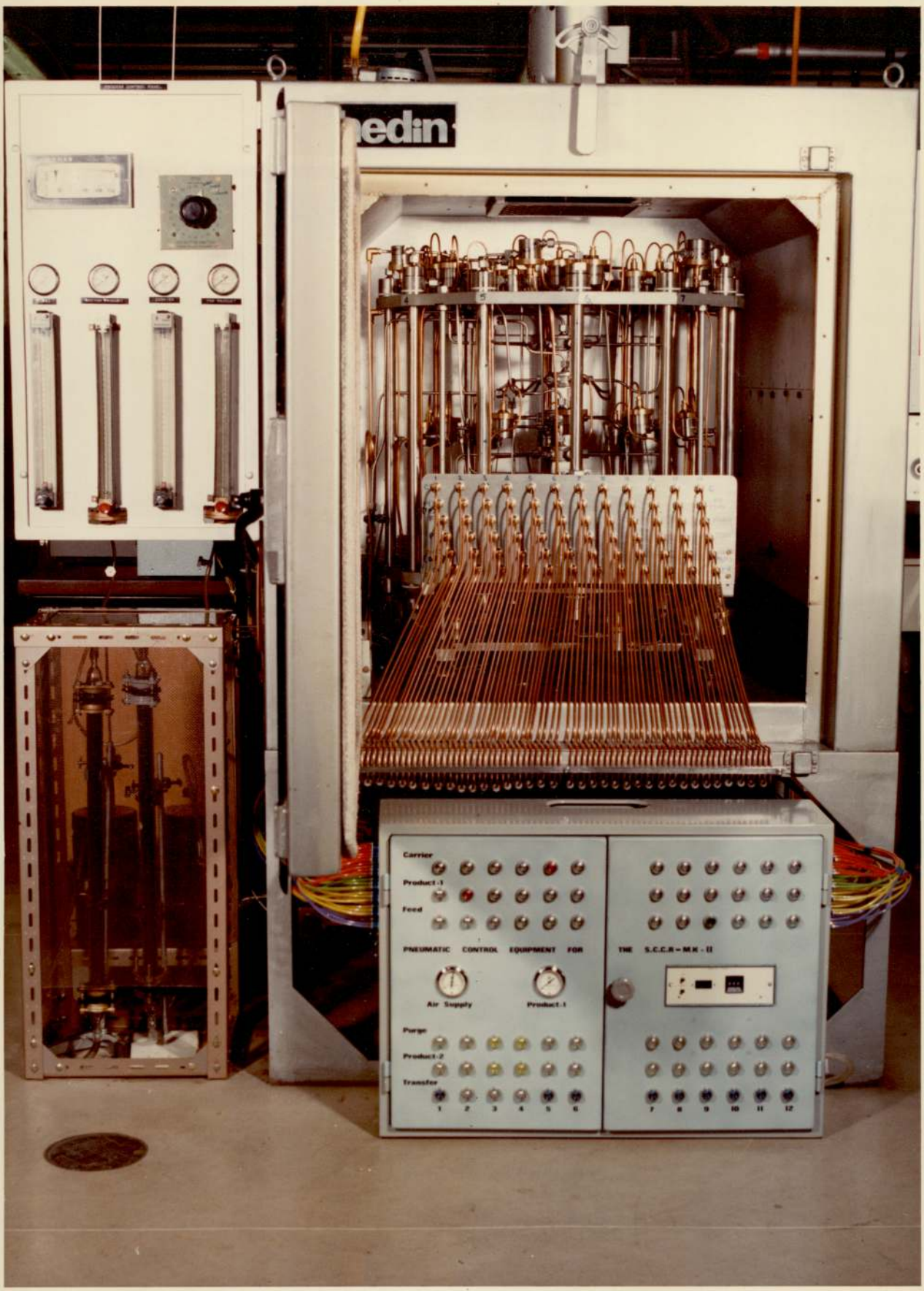
TI = temperature indicator

TS = thermocouple switch

V = vent to extractor fan



THE SCCR-2 EQUIPMENT



THE SCCR-2 EQUIPMENT

5.1.3 DESCRIPTION OF THE SCCR-2 EQUIPMENT

The central unit of the SCCR-2 machine (see Plate 5.2) consisted of 12 chromatographic columns connected alternatively at top and bottom to form a closed symmetrical ring. Each of the 12 columns made from stainless steel, was 61 cm long, 2.54 cm in diameter and was packed with 16.67% F.F.A.P. (free fatty acid phase) on chromosorb W, AW-DMCS, chromatographic packing material.

Six pneumatically operated, normally closed, diaphragm valves were arranged in each column to give the required operating functions: feed inlet (F), carrier gas inlet (C), product I outlet (PI), purge gas inlet (P), product II outlet (PII) and a gas lock (T). Fig. 5.2 shows diagrammatically the relative position of diaphragm valves on 4 consecutive columns, with the numbers 1 to 12 assigned to the individual columns.

The 12 gas locks (transfer valves), being situated in the transfer line between each pair of columns, were used to form the purge section in the unit, by isolating two consecutive columns (double column purge operation). Isolation of an individual column was achieved by having closed two consecutive transfer valves.

The other 12 valves of each type (F, C, PI, P, PII), were connected via stainless steel tubing to an independent, centrally situated, distributor system. Lines from the gas distributors then passed to the relevant control and measuring devices, while the feed distributor was connected to a positive displacement pump.

The system of the 12 chromatographic columns with their respective valves, pipe and distribution networks was housed in an oven, capable of operating at temperatures of up to 300°C.

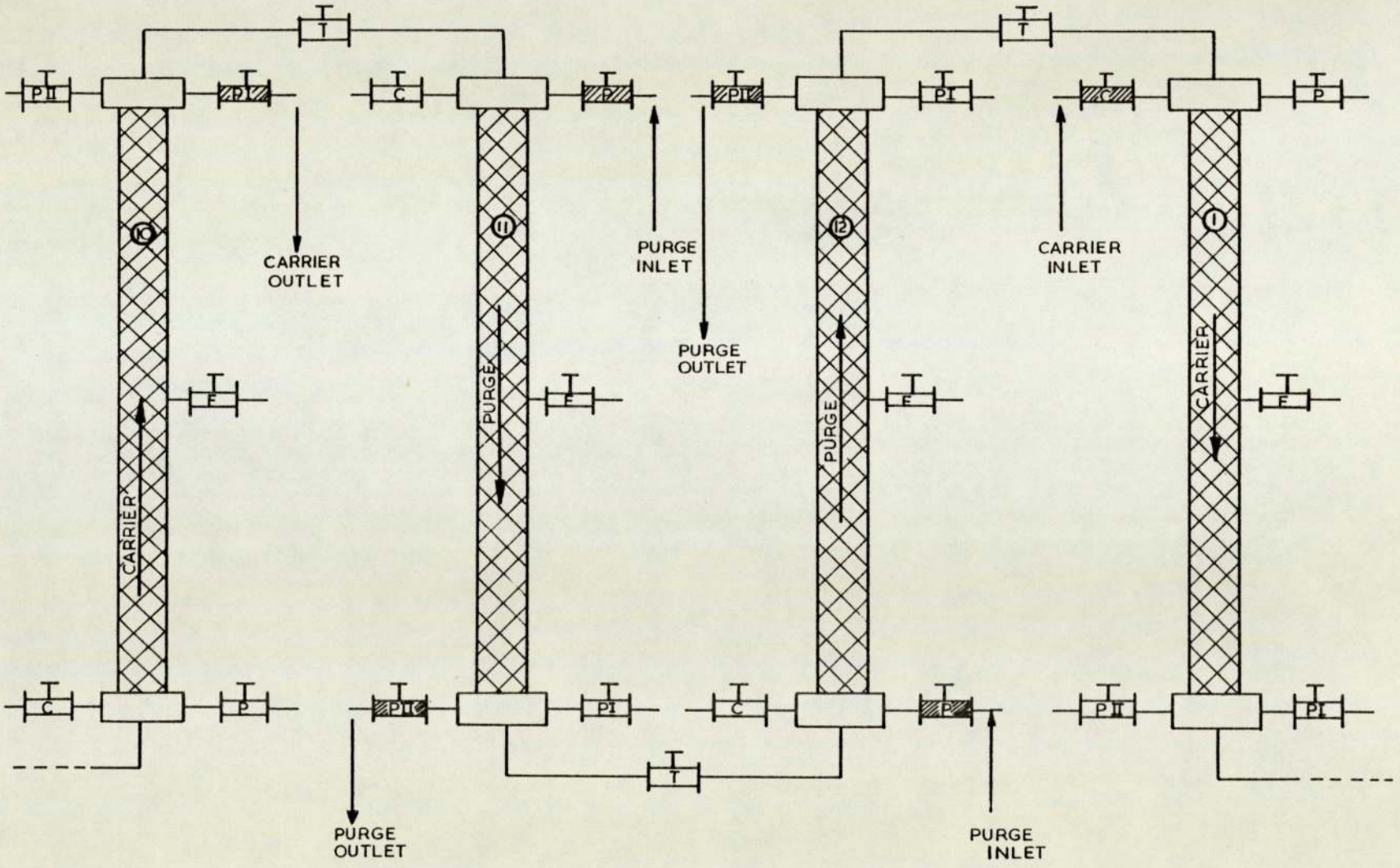
The port rotation required for this sequential type of equipment, was achieved by a pneumatic control unit which sequenced the position of the energized valves around the unit in the required pattern, at the desired time interval.

During the SCCR-2 operation and within a particular sequencing interval, the carrier gas enters the system via the energized to open valve C on column 1, travels through 10 columns and exits with the less soluble component from column 10, where the valve PI is energized to open (see Fig. 5.2). The 11 and 12 columns meanwhile are isolated by having closed (de-energized) the valves T on the transfer lines 10/11, 11/12, 12/1. Also the valves P and PII on columns 11 and 12 are energized to open, effecting purging of the more soluble component. Finally the feed mixture is introduced into the column 5 through the energized to open F valve.

In the next sequencing action of the valves, columns 12 and 1 are isolated. Purge gas enters columns 12 and 1 to remove product II. Carrier flows from column 2 round the unit to exit from column 11 with the product I. Feed is now entering column 6.

Twelve sequencings complete the cycle, which continues automatically.

FIGURE 5·2 SCHEMATIC DIAGRAM SHOWING THE POSITION OF DIAPHRAGM VALVES ON 4 CONSECUTIVE COLUMNS



LEGEND

C = CARRIER GAS INLET VALVE

P = PURGE GAS INLET VALVE

PI = CARRIER GAS (PRODUCT I) OUTLET VALVE

PII = PURGE GAS (PRODUCT II) OUTLET VALVE

F = FEED VALVE

T = TRANSFER VALVE

NOTE

ALL VALVES ARE NORMALLY CLOSED. AT A PARTICULAR SEQUENCING INTERVAL, T ARE THE ENERGIZED VALVES AND T THE DE-ENERGIZED ONES. ALL THE OTHERS (NON-SHOWN VALVES) ARE DE-ENERGIZED, EXCEPT THE TRANSFER VALVES AND FEEDS (FS).

PLATE 5.2 THE CENTRAL UNIT

C = central distributor

CC = chromatographic column

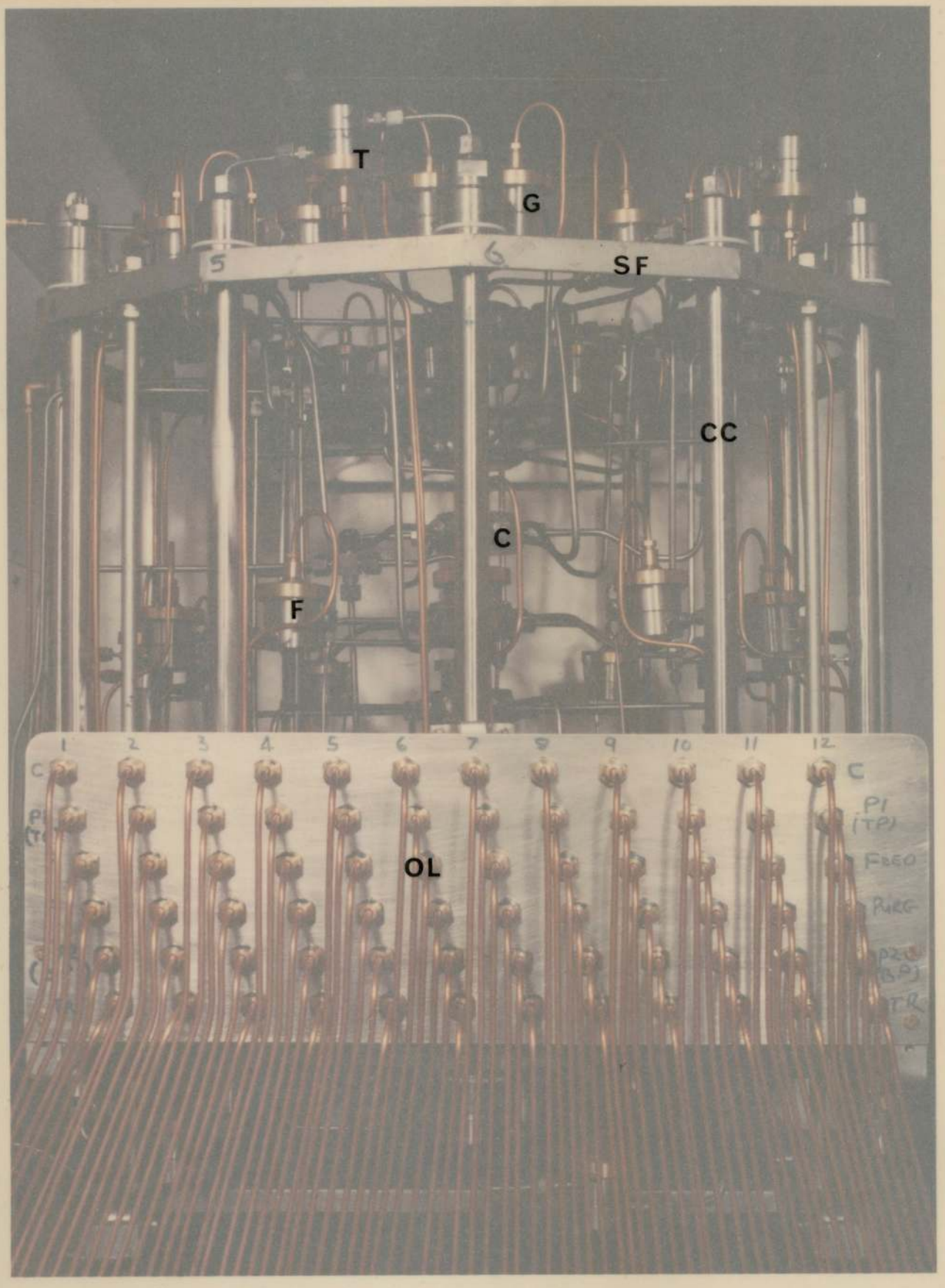
F = feed valve

G = gas inlet/outlet valve

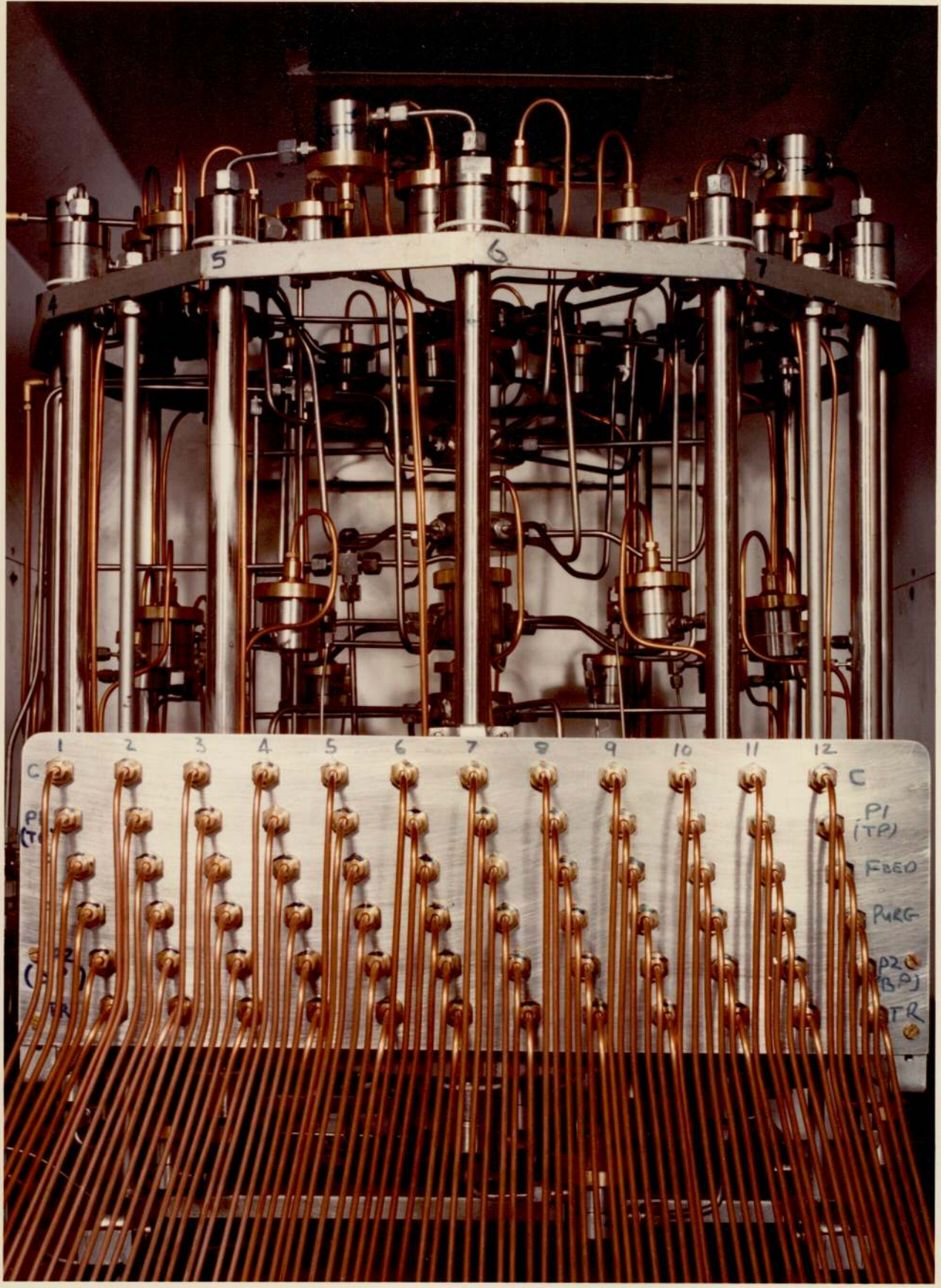
OL = output line circuit from the control unit

SF = support frame

T = transfer valve



THE CENTRAL UNIT



THE CENTRAL UNIT

5.2 DETAILED DESIGN AND CONSTRUCTION

5.2.1 VALVES

The operation of a sequential chromatographic unit relies on the valves which provide the six required functions for each column: feed inlet (F), carrier gas inlet (C) and outlet (PI), purge gas inlet (P) and outlet (PII) and an intercolumn lock (T).

The valves on the SCCR-2 unit had to fulfil the following requirements.

(1) Be capable of operation at temperatures up to 200°C. This high temperature was necessary for the chromatographic separation of some fatty acids and essential oils to be achieved by the SCCR-2 unit.

(2) All materials of construction in contact with the working fluids to be resistant to most organic chemicals, to increase the range of possible separations by the sequential unit.

(3) Capable of withstanding a differential forward or back pressure in excess of 446 kN m^{-2} (50 psig). A value of 446 kN m^{-2} was considered to give adequate flexibility in the flow and pressure settings.

Unfortunately it very quickly became evident that very few commercially available valves were capable of operation at 200°C and any suitable valve would be very expensive. Moreover the valves required had to be small with inlet and outlet ports in positions to enable a compact equipment to be built. On an industrial scale there would be no difficulty in obtaining standard high temperature valves.

Initially solenoid-operated stainless steel valves, supplied by Dewrance Controls Ltd. were chosen by my predecessor Mr. M. Lynham for the SCCR-2 machine. These valves consisted of a high temperature (class H) solenoid coil, which on being energized caused a magnetic plunger to lift off the P.T.F.E. valve seat allowing flow. On

de-energizing the solenoid, a small spring returned the plunger to the seat thereby preventing flow.

Preliminary experimental studies with the SCCR-2 unit indicated that the solenoid valves were ineffective and despite the modifications made by M. Lynham had to be replaced with more suitable ones (173).

The main problems that arose with the solenoid type valves were as follows.

(1) Their maximum operating temperature was only 100°C, since the maximum recommended temperature of the coils was 180° and the inherent temperature rise of the coils themselves, due to the passage of electrical current was approximately 80°C. Incorrect information given by a Dewrance representative caused these solenoid valves to be recommended.

(2) They were incapable of sealing at high back pressures (377 $kN\ m^{-2}$).

(3) The use of P.T.F.E. for the valve seats was unsatisfactory because it was found not to be resilient enough to give a tight seal, while the alternative choice silicone rubber had to be regularly replaced to promote successful operation.

All these problems have led to the development of a new valve which could operate under the desired conditions. Thus, a new 2-way pneumatic diaphragm operated poppet valve was designed by Dr. B. Jones (174) to meet our requirements based on a stainless steel to stainless steel flow process seal.

This diaphragm valve, essentially consisted of two sections. The pneumatic control section, made from brass and the process fluid section made from stainless steel. By applying air pressure onto the

pneumatic section of the valve, the stainless steel diaphragm was deflected causing the poppet to move downwards, thus allowing flow (see Fig. 5.4). Otherwise, the valve was normally closed.

A prototype valve was made by Aston Technical Services Ltd. which was extensively tested using the equipment illustrated in Figure 5.3. The testing conditions were more arduous than the expected operating conditions for the SCCR-2 unit. Thus, temperatures as high as 230°C and line pressures as high as 446 kN m^{-2} (50 psig) were used, while the frequency of the valve operation was set as to simulate many days of actual operation in a short time.

During testing the following faults became apparent and modifications were made as indicated.

(1) The stainless steel to stainless steel seal provided by the poppet and valve seat, on the valve being de-energized, was found to be quite unreliable on the prototype valve. By grinding and lapping the sealing surfaces the leaking problem was reduced but not adequate for our needs. Thus a P.T.F.E. ring was inserted into the top side of the valve poppet which was then found sufficiently resilient to ensure a satisfactory gas tight seal (see Fig. 5.4).

(2) The tests have also indicated that the pressure drop across the valve was increased considerably by increasing the thickness of P.T.F.E. poppet ring. In contrast decreasing the thickness of P.T.F.E. ring resulted in a less reliable seal. Long term experiments finally determined the minimum thickness of P.T.F.E. required to provide a satisfactory seal without any significant pressure drop across the valve at the required flow conditions.

(3) Slight imperfections or scratches on the P.T.F.E. poppet ring caused by any solid particles present in the fluid stream were subsequently found to be sufficient to prevent satisfactory sealing. Thus, special care was taken to remove any solid particles from the flow process section of the valve before assembling. In addition the use of a stainless steel gauze in the inlet/outlet ports of the valve to ensure the trapping of any particulate solid present in the fluid stream was found to be necessary.

(4) The twelve valves used as the inlet ports for the liquid feed (feed valves) were redesigned so as to have the flow process feed line with the smallest possible internal volume, thus reducing the "dead volume" of liquid held up in each valve after closure. If this were not done, any trapped feed could diffuse into the mobile gas stream causing contamination after switching. Consequently 0.3 cm orifices, "1/8 in B.S.P." ports were used for the feed valves compared to the 0.6 cm orifices, "1/4 in B.S.P." ports employed for the other sixty gas valves.

(5) Slight leaking was found to occur from the process fluid section to the pneumatic section of the valve via the poppet/diaphragm contact points. This was of particular importance since the material of construction of the pneumatic section (brass) could be corroded by organic chemicals. Trials by using P.T.F.E. washers, P.T.F.E. paste or P.T.F.E. tape finally indicated that the most reliable seal was obtained by inserting a piece of P.T.F.E. tape on the threads of the poppet, large enough to form a P.T.F.E. washer below the diaphragm.

The modified valve was extensively tested and found very effective with no sign of leakage occurring, at high temperature operations (80-220°C). At lower temperatures slight leakage through

the P.T.F.E. poppet ring was sometimes observed, in particular when the valve had been previously operated near its maximum temperature limit (220°C) and for a long period of time.

It seems that at high temperatures the P.T.F.E. was getting more resilient, thus providing a very satisfactory gas tight seal. But the P.T.F.E. sealing surface could also be slightly deformed under these high temperatures, long term operation causing leaking through the valve at low temperatures.

Account had to be taken of the need to replace a damaged P.T.F.E. ring during a run. Special tools were made to assist this operation so that a rapid replacement could take place.

The valve was tested within the pressure range of 101-446 kN m^{-2} (0-50 psig), dictated by the differential pressure limits of the diaphragm, in both forward and backward directions. In fact the stainless steel diaphragm required a minimum 239 kN m^{-2} (20 psig) differential pressure for its full deflection and had a maximum recommended differential pressure limit of 584 kN m^{-2} (70 psig). No sign of wear or rupture was observed in the diaphragm, during the testing period even after long term operation under the pressure limit conditions.

Another good feature of the valve is its versatility as the stainless steel diaphragm can be changed for a stronger one, giving the possibility of operation at a higher pressure range. This could facilitate future work on the SCCR-2 machine.

The developed valve is illustrated in Fig. 5.4 and Plate 5.3 while its construction details are shown in Table 5.1. Since the SCCR-2 unit consists of 12 columns and each column requires 6 valves to provide the necessary operating functions, the total number of valves used was 72. These were made by Aston Technical Services Ltd. and were

carefully tested before being arranged around the 12-chromatographic column system as shown in Fig. 5.2 and Plate 5.4.

FIGURE 5·3 SCHEMATIC DIAGRAM OF THE APPARATUS FOR TESTING THE DIAPHRAGM VALVE

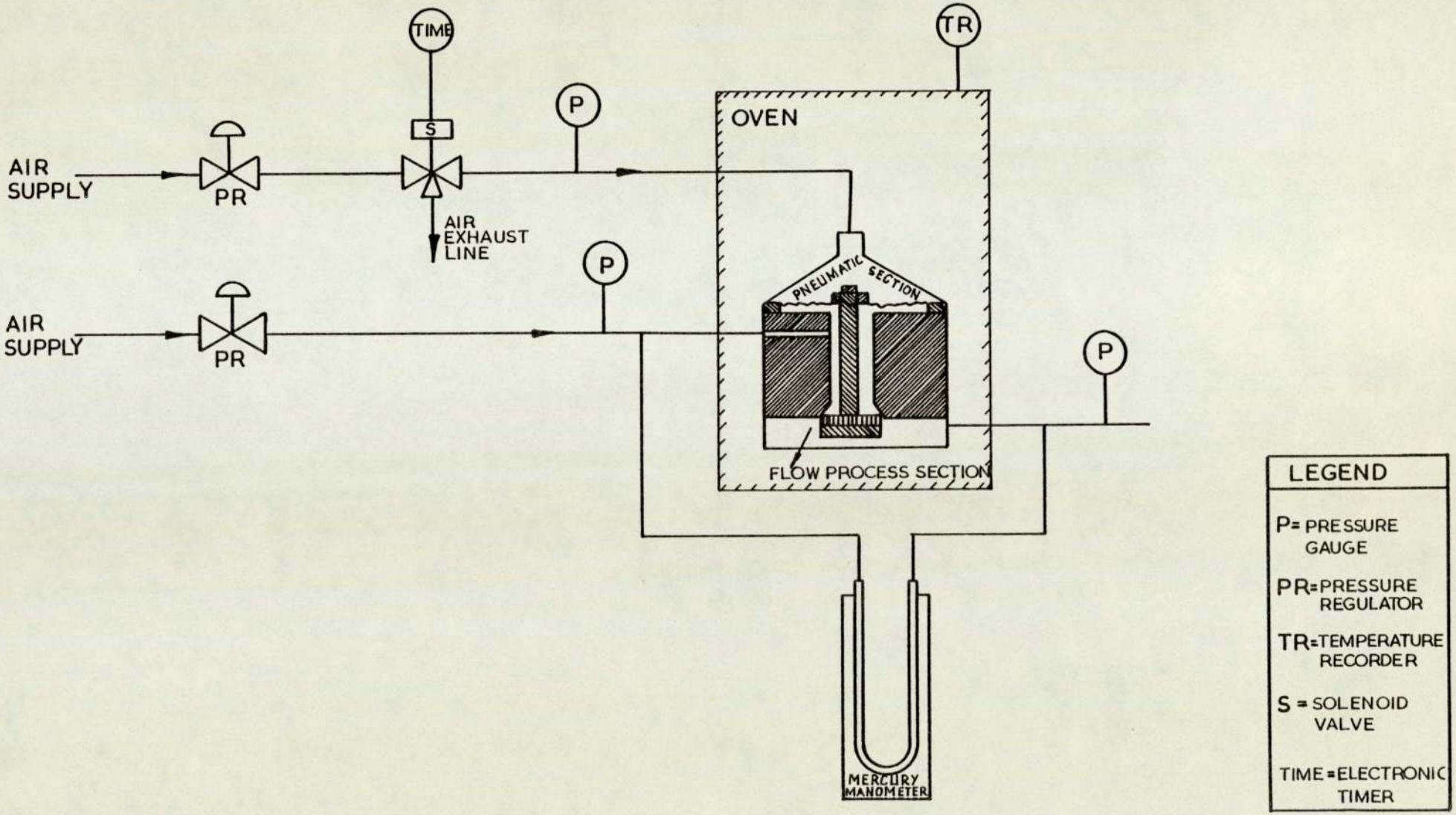


FIGURE 5·4 DIAPHRAGM VALVE DESIGN.

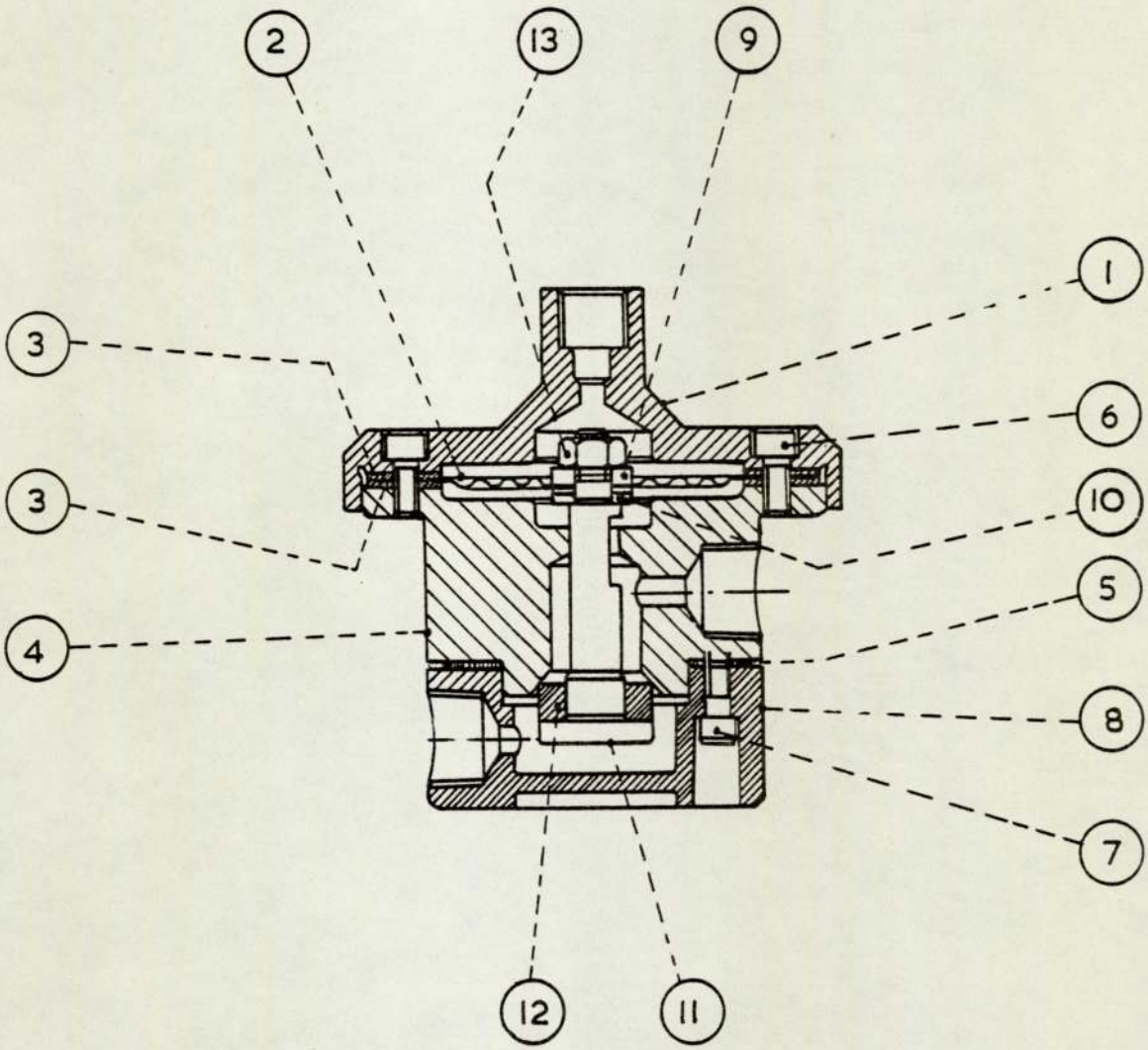


TABLE:5.1 VALVE PARTS LIST

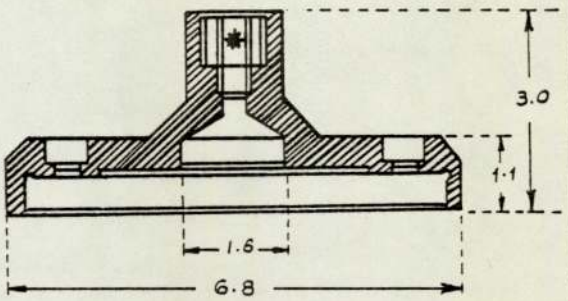
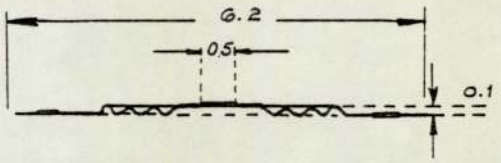
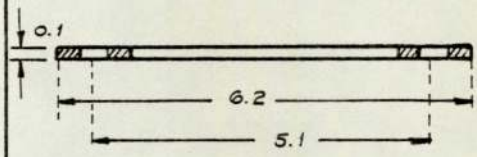
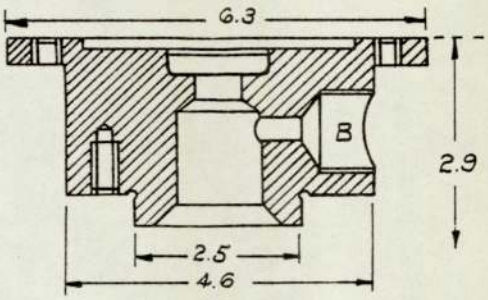
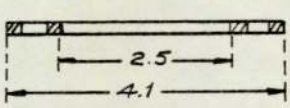
ITEM NUMBER	PART NAME	MATERIAL	REMARKS	DESIGN DIMENSIONS IN CMS
1	VALVE CAP	BRASS	*FEMALE PORT "3/16 IN B.S.P."	
2	DIAPHRAGM	STAINLESS STEEL		
3	DIAPHRAGM SEALING RING	P.T.F.E.		
4	VALVE BODY	STAINLESS STEEL	B FOR GAS VALVES IS A "1/4" IN B.S.P." FEMALE PORT, WHILE FOR THE FEED VALVES IS "1/8 IN B.S.P." A P.T.F.E. RING WAS INSERTED IN THE PORTS OF THE FEED VALVES TO REDUCE THE DEAD VOLUME	
5	BODY SEALING	P.T.F.E.		
6	VALVE CAP SCREWS	STAINLESS STEEL	4BA x 0.8 CM LONG Nº REQUIRED : 6	
7	VALVE BODY SCREWS	STAINLESS STEEL	4BA x 1.3cm LONG Nº REQUIRED : 6	

TABLE 5·1 CONTINUED

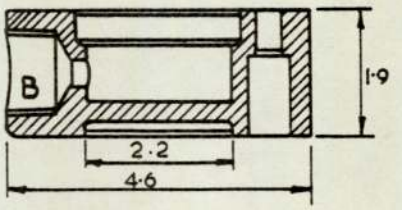
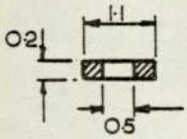
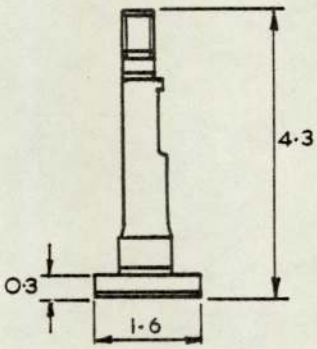
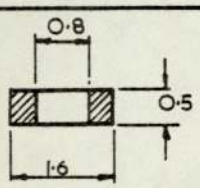
ITEM NUMBER	PART NAME	MATERIAL	REMARKS	DESIGN
8	VALVE LOWER CHAMBER	STAINLESS STEEL	B: "1/4 B.S.P." AND "1/8 B.S.P." FEMALE PORT FOR THE GAS VALVES AND FEED VALVES RESPECTIVELY A P.T.F.E. RING WAS INSERTED IN THE PORTS OF THE FEED VALVES TO REDUCE THE DEAD VOLUME	
9	VALVE WASHER	STAINLESS STEEL		
10	VALVE SHIM	STAINLESS STEEL		AS ABOVE
11	POPPET VALVE	STAINLESS STEEL		
12	VALVE SEATING RING	P. T. F. E.		
13	DIAPHRAGM NUT	STAINLESS STEEL	2 B A	

PLATE 5.3 THE DIAPHRAGM VALVE

AV	=	assembled valve
D	=	diaphragm
N	=	diaphragm nut
P	=	poppet
PSR	=	P.T.F.E. sealing ring in valve cap
VB	=	valve body
VBS	=	valve body sealing
VC	=	valve cap
VLC	=	valve lower chamber
W	=	washer

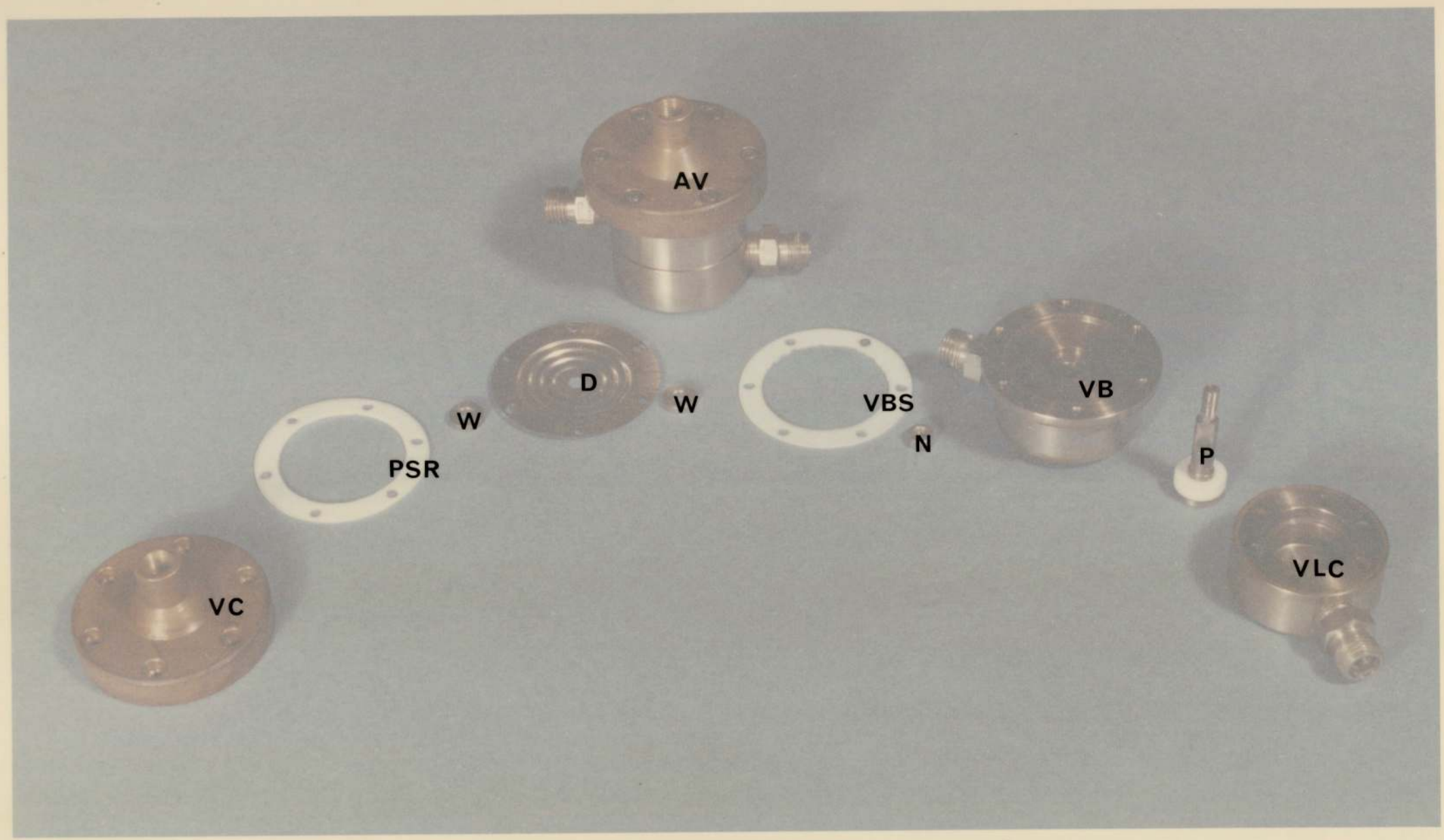

AV
D
W
W
VBS
N
VB
P
PSR
VC
VLC

PLATE 5.4 THE ARRANGEMENT OF DIAPHRAGM VALVES

BT = brass tube to the pneumatic section of diaphragm valve

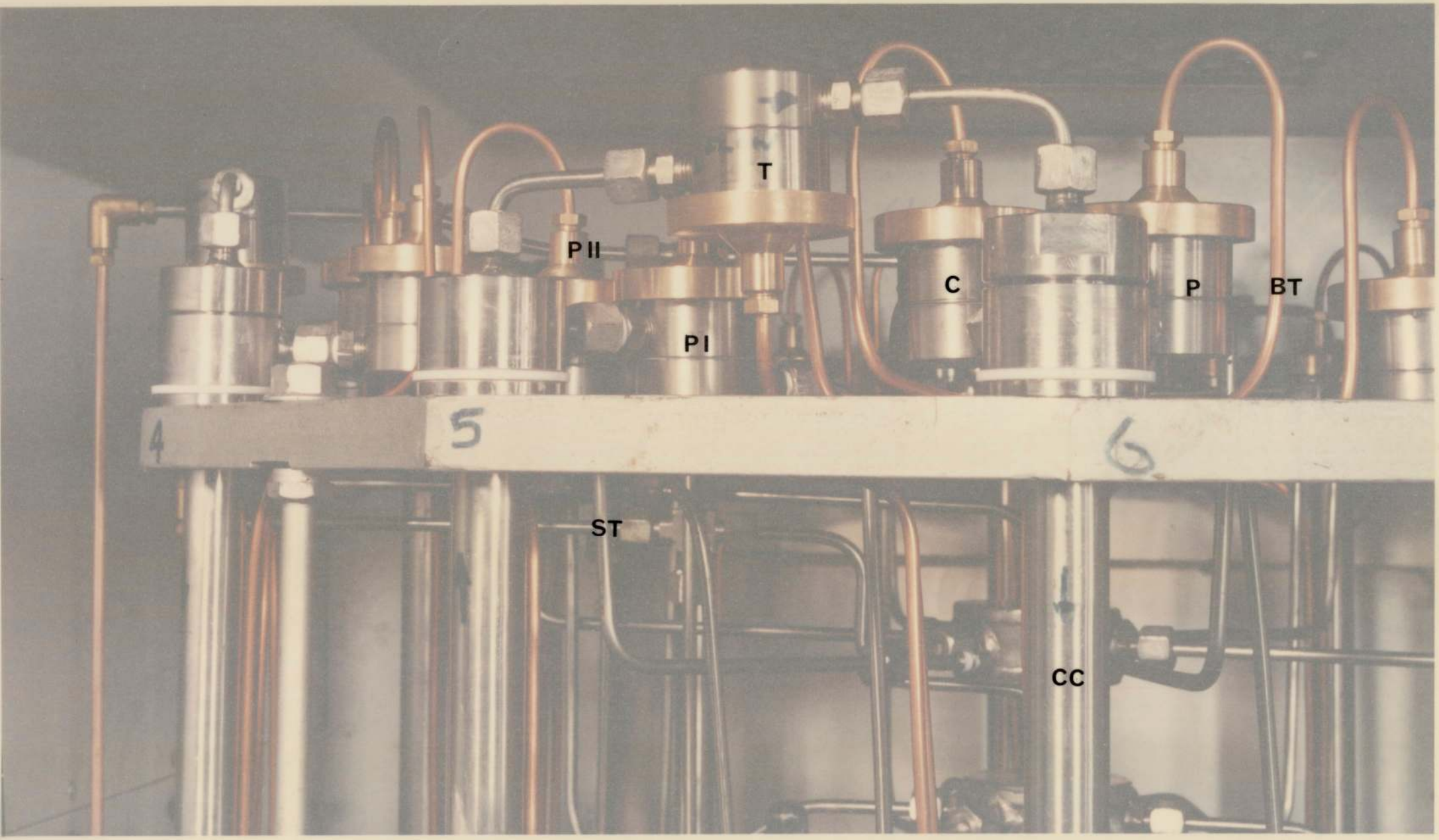
CC = chromatographic column

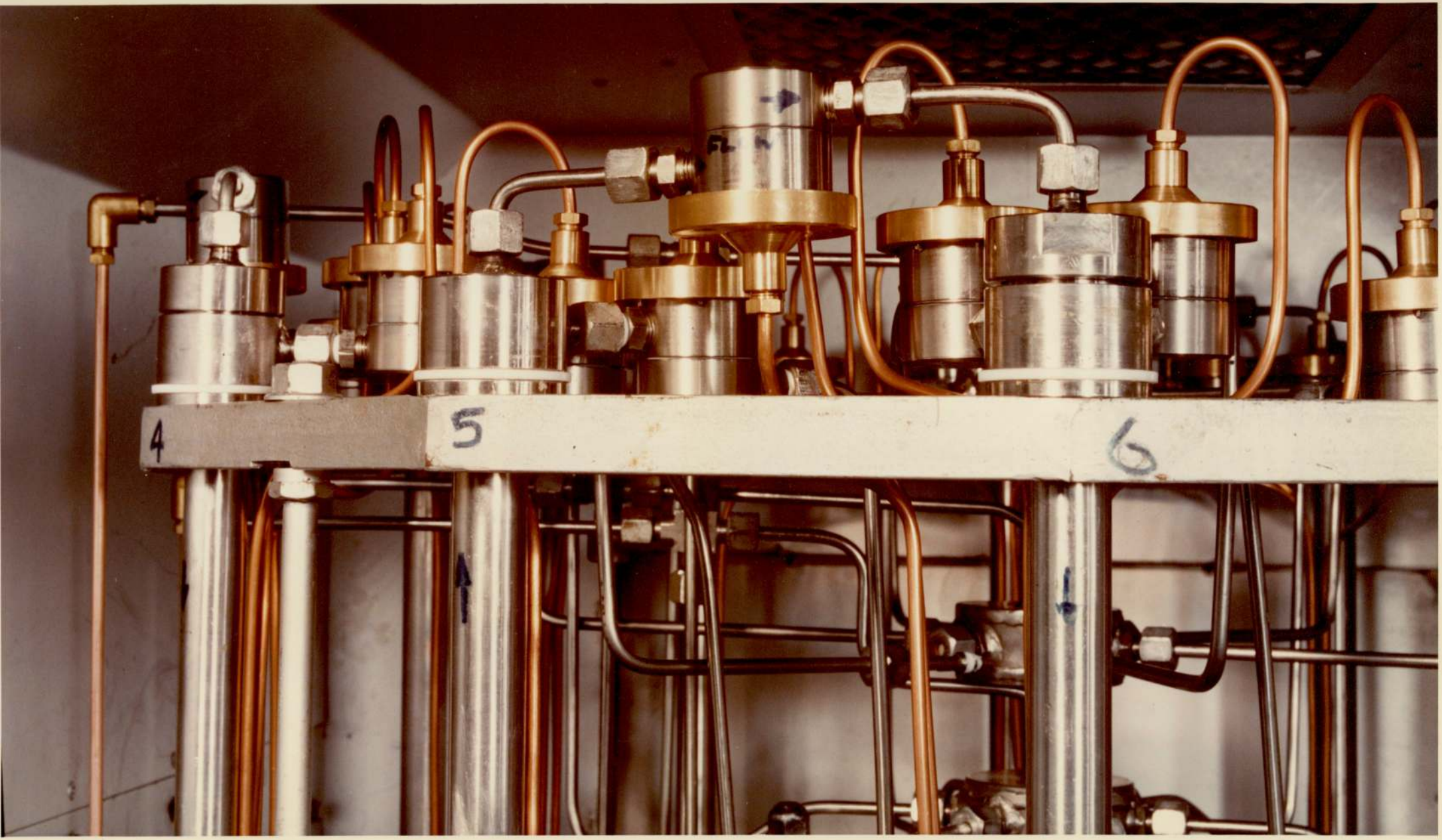
C,P = carrier/purge inlet valves

PI, PII = product I/product II outlet valves

ST = stainless steel tube to the flow process section of diaphragm valve

T = transfer valve


T
PII
PI
C
P
BT
4
5
6
ST
CC


4
5
6

5.2.2 THE PNEUMATIC CONTROL UNIT

The operation and sequencing of the valves according to the required pattern was performed by a pneumatic control unit supplied by Festo Pneumatic Ltd. (Plate 5.1).

Basically the pneumatic control unit consisted of a cam belt unit operating on twenty on/off pneumatic 3-way valves.

The cams were carefully positioned on the links of the belt shaft to suit a particular cam program. By exchanging the position of the cams it was possible to change to another cam operating program without lengthy setting-up time.

The cam belt shaft was driven by a synchromesh gear motor which could be regulated in the torque range of 1-10 r.p.m. These torques were transmitted to the cam belt shaft via a pair of gear wheels. Thus, revolution times of the cam belt from 9 seconds to 24 hours could be obtained.

The cam belt shaft consisted of 48 links and each one of them could accommodate up to 12 cams. For the operation of the SCCR-2 unit, 12 links were employed, each one having a set of 5 cams.

A set of cams in contact with the appropriate 3-way pneumatic valves, energized them for a period of time controlled by a digital timer. After this selected time interval the motor was energized bringing into contact the next set of cams with the 3-way pneumatic valves. In the meantime the digital timer was automatically reset to zero. By the time that the new set of pneumatic valves had been energized the motor was automatically de-energized. After a further time interval the next set of cams was operated and so on until the cycle was completed. Repetition of the cycle continued automatically.

With pneumatic valves there was only one communal connection to the air supply which was required to have a minimum 377 kN m^{-2} pressure. The 3-way, RS-3, pneumatic valves could work as normally opened or normally closed valves. The re-arranging of opening or closing function or vice versa was achieved by simply reversing the upper valve part with the roller lever by 180°.

The sequencing time interval was adjusted by a digital timer constructed by Mr. M.F. Lea, The Department's Chief Electronics Engineer, in the range of 0-999 seconds. In addition the timer was arranged (Fig. 5.5b) so that the motor could be de-energized during the switching time period. At the end of this time interval the motor was energized again causing rotation of the belt shaft for 1 second, when the next set of pneumatic valves was operated.

A diagrammatic presentation of the pneumatic control unit is illustrated in Fig. 5.5a. A shown only the twelve intercolumn (transfer) diaphragm valves were directly connected to the pneumatic control unit. The other sixty diaphragm valves had an indirect control, since the total capacity of the Festo pneumatic unit for direct control was only twenty.

The 12 first pneumatic valves (see Fig. 5.5a) connected to the transfer valves were arranged to be normally opened as the transfer valves were energized almost continuously (9/12 of time) during the SCCR-2 operation. In contrast the next 6 pneumatic valves (see Fig. 5.5a) reserved for the operation of the other sixty diaphragm valves via a secondary circuit of valves, were normally closed.

Two main types of pneumatic valves were used for the secondary circuit. The type ZK-PK3-6/3 (Fig. 5.6) consisted of 3 single pneumatic valves, each with 2 inputs x,y and one output A. The output A was only

exhausted when both the inlet ports were under pressure. The type OS-PK3-6/3 (Fig. 5.6) also consisted of 3 single pneumatic valves each with 2 inputs x,y and one output A. If one or both the inlet ports were under pressure, the output A was exhausted. The arrangement of these pneumatic valves in the secondary circuit, according to the requirements for the operation of the SCCR-2 unit, is shown diagramatically in Fig. 5.6.

The pneumatic control unit had the ability to perform single as well as twin column purge operation. In this work the double column purge operation was employed. The connection pattern of the various set of diaphragm valves to the pneumatic valves of the control unit is demonstrated in Table 5.2.

An indicator light on the display panel appears when air pressure is on a particular diaphragm valve. The 72 indicators were arranged in a display panel on the front of the control unit box, for observing the energized diaphragm valves during the SCCR-2 operation. Also in case of faulty operation the indicator panel could give an immediate indication of the possible cause (see Plate 5.1).

Tubing, tee pieces, fittings and all the necessary accessories for assembling the control unit were supplied by Festo Pneumatic Ltd. The tubing used for the required connections inside the control box, was of white 0.4 cm O.D. nylon, except for the transfer valves piping which was red. For the external output lines various coloured nylon tubing (0.4 cm O.D.) was used in matching with indicators colours for the convenience of installation. Thus, for the feed lines green indicators and tubing were used. For the carrier and product I lines, red. For the purge and product II, yellow and for the transfer lines, blue.

The output lines from the control unit were connected to the diaphragm valves via copper tubing of 0.95 cm O.D. The nylon tubing was connected to the copper one, by a nylon connector unit, 20 cm before the lines entered the oven.

FIGURE 5.5_a DIAGRAMATIC PRESENTATION OF CONTROL UNIT

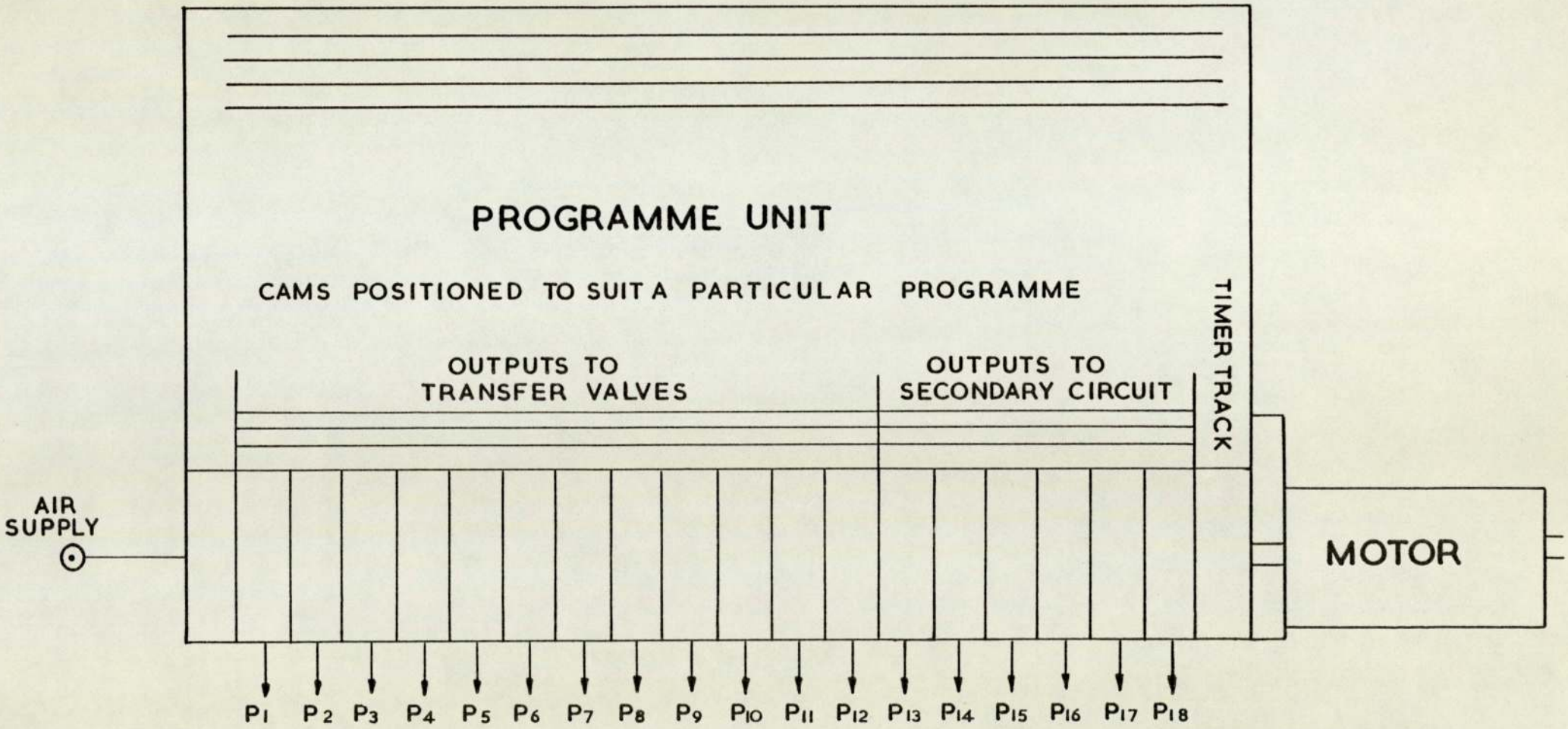
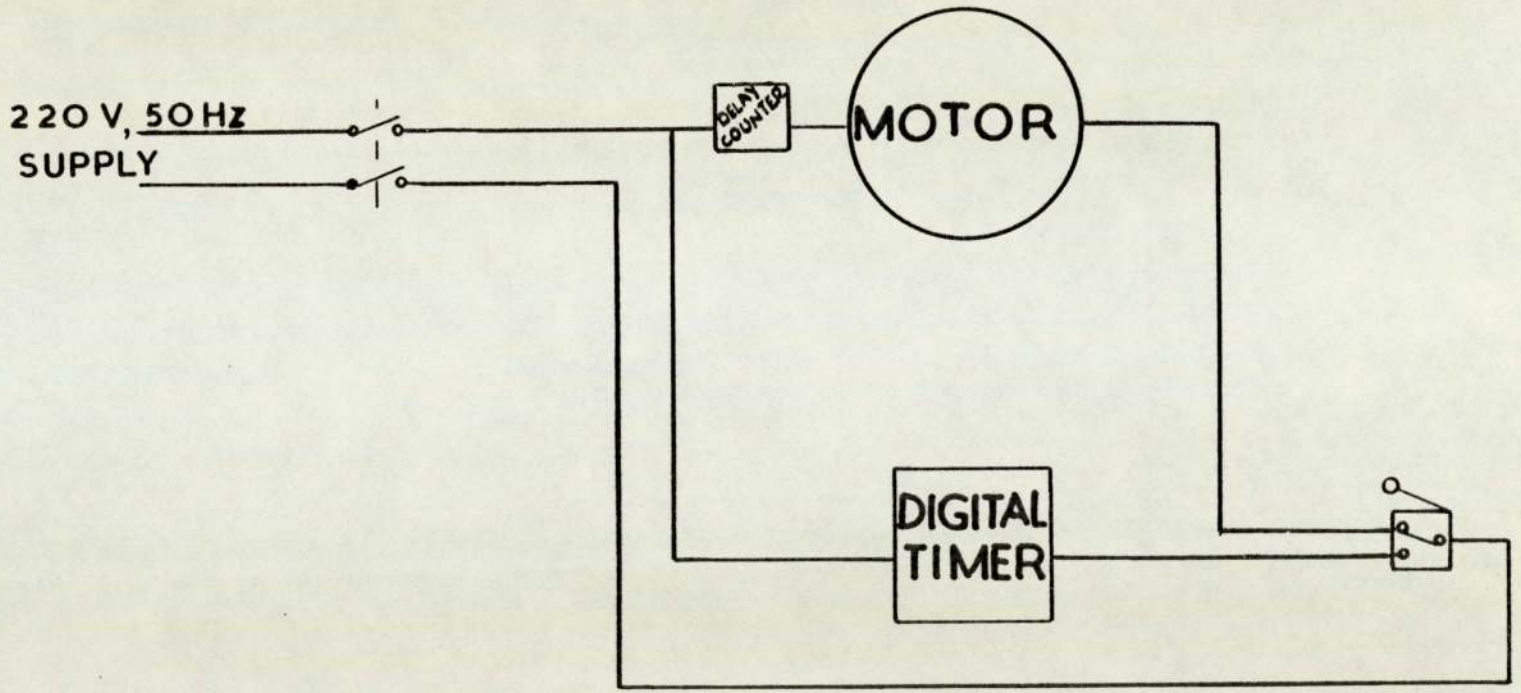


FIGURE 5.5b THE DIGITAL TIMER CIRCUIT



NOTE THE DELAY COUNTER IS A PNEUMATICALLY OPERATED CONTROL DEVICE GIVING INFORMATION FOR THE TIME PERIOD WHICH THE DIGITAL TIMER IS OFF

FIG 5.6 THE SECONDARY PNEUMATIC CIRCUIT

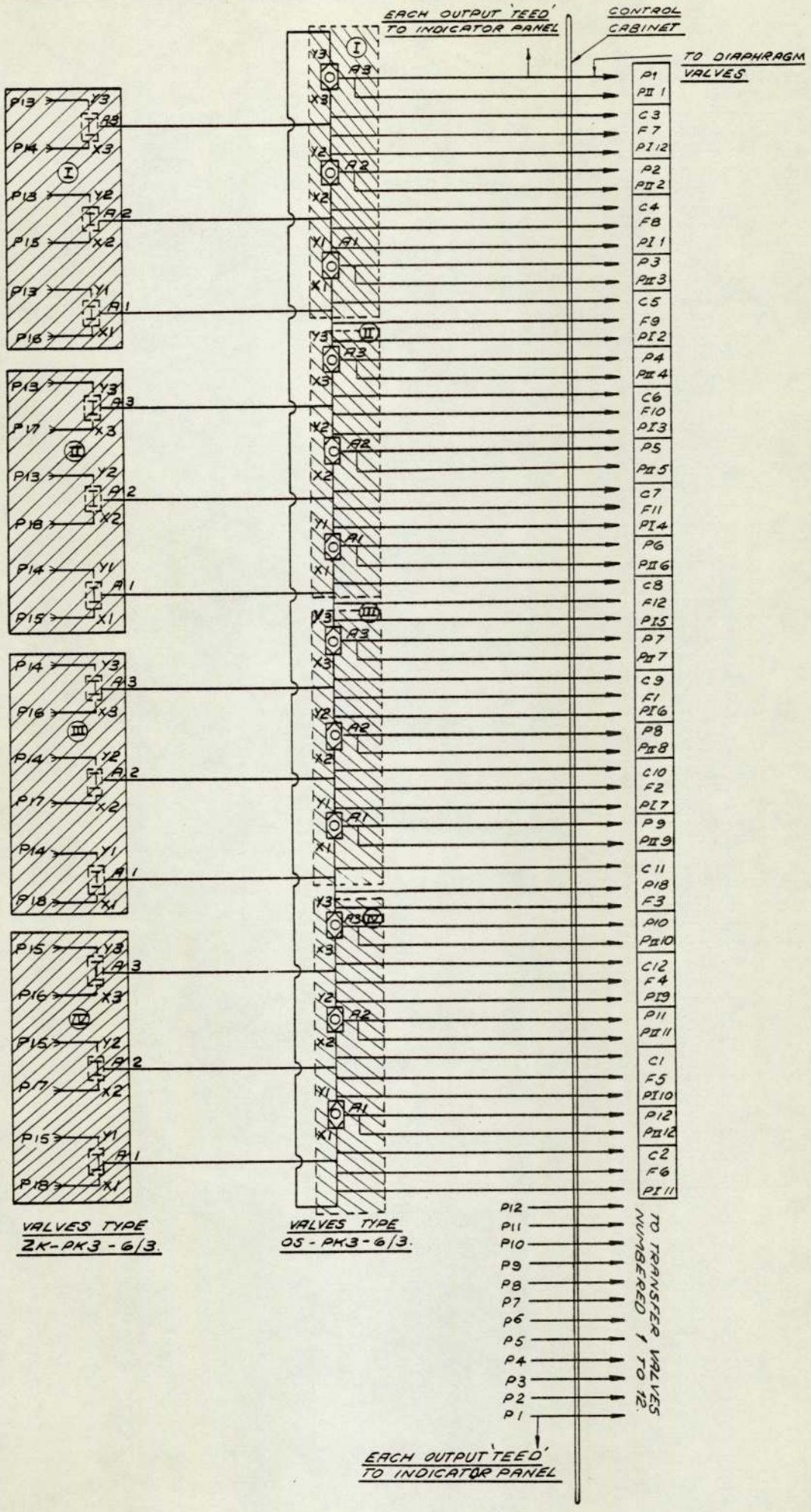


TABLE 5.2: THE SEQUENCING OF ENERGIZED VALVES ACCORDING TO THE SCCR-2 OPERATING REQUIREMENTS

	COLUMNS ISOLATED (Assigned Numbers)	1,2	2,3	3,4	4,5	5,6	6,7	7,8	8,9	9,10	10,11	11,12	12,1
PNEUMATIC CONTROL UNIT	MAIN PNEUMATIC VALVES ENERGIZED Type : RS-3	P_{12} P_1 P_2 P_{13} P_{14}	P_1 P_2 P_3 P_{13} P15	P_2 P_3 P_4 P_{13} P_{16}	P_3 P_4 P_5 P_{13} P_{17}	P_4 P_5 P_6 P_{13} P_{18}	P_5 P_6 P_7 P_{14} P_{15}	P_6 P_7 P_8 P_{14} P_{16}	P_7 P_8 P_9 P_{14} P_{17}	P_8 P_9 P_{10} P_{14} P_{18}	P_9 P_{10} P_{11} P_{15} P_{16}	P_{10} P_{11} P_{12} P_{15} P_{17}	P_{11} P_{12} P_1 P_{15} P_{18}
	SECONDARY PNEUMATIC VALVES ENERGIZED type: ZK-PK-3	IA_3	IA_2	IA_1	IIA_3	IIA_2	IIA_1	$IIIA_3$	$IIIA_2$	$IIIA_1$	IV A_3	IV A_2	IV A_1
	type: OS-PK-3	IA_3, IA_2	IA_2, IA_1	IA_1, IIA_3	IIA_3, IIA_2	IIA_2, IIA_1	IIA_1, $IIIA_3$	$IIIA_3$, $IIIA_2$	$IIIA_2$, $IIIA_1$	$IIIA_1$ IV A_3	IV A_3, IV A_2	IV A_2, IV A_1	IV A_1, I A_3
DIAPHRAGM VALVES	TRANSFER VALVES ENERGIZED (directly controlled)	T3 T8 T4 T9 T5 T10 T6 T11 T7	T4 T9 T5 T10 T6 T11 T7 T12 T8	T5 T10 T6 T11 T7 T12 T8 T1 T9	T6 T11 T7 T12 T8 T1 T9 T2 T10	T7 T12 T8 T1 T9 T2 T10 T3 T11	T8 T1 T9 T2 T10 T3 T11 T4 T12	T9 T2 T10 T3 T11 T4 T12 T5 T1	T10 T3 T11 T4 T12 T5 T1 T6 T2	T11 T4 T12 T5 T1 T6 T2 T7 T3	T12 T5 T1 T6 T2 T7 T3 T8 T4	T1 T6 T2 T7 T3 T8 T4 T9 T5	T2 T7 T3 T8 T4 T9 T5 T10 T6
	INLET/OUTLET VALVES ENERGIZED (indirectly controlled)	F7 C3 PI 12 P1 P2 PII 1 PII 2	F8 C4 PI 1 P2 P3 PII 2 PII 3	F9 C5 PI 2 P3 P4 PII 3 PII 4	F10 C6 PI 3 P4 P5 PII 4 PII 5	F11 C7 PI 4 P5 P6 PII 5 PII 6	F12 C8 PI 5 P6 P7 PII 6 PII 7	F1 C9 PI 6 P7 P8 PII 7 PII 8	F2 C10 PI 7 P8 P9 PII 8 PII 9	F3 C11 PI 8 P9 P10 PII 9 PII 10	F4 C12 PI9 P10 P11 PII 10 PII 11	F5 C1 PI 10 P11 P12 PII 11 PII 12	F6 C2 PI 11 P12 P1 PII 12 PII 1

5.2.3 THE CHROMATOGRAPHIC COLUMNS

The main unit of the SCCR-2 machine is a system of 12 chromatographic columns connected alternatively at top and bottom to form a closed symmetrical ring, 78 cm in diameter.

The support frame to which the columns were assembled was made from 2.54 cm mild steel angle iron in such a way that each column was held rigidly top and bottom but capable of withstanding any differential expansion that might occur at temperatures up to 200°C. (Plate 5.2). For the convenience of "piping", the orientation of the columns on the frame was such that all the inlet/outlet fluid access points were positioned in a horizontal radial direction while all the sample points faced outwards for ease of access.

The support frame rested on six stainless steel wheels which rode on a rail inside the oven. By this means the 12-columns with their respective pipe networks and valves can easily be removed from the oven for maintenance on to an external trolley made from Dexion angle iron.

Each chromatographic column consists of a stainless steel tube with the required fittings and the chromatographic packing material. A detailed description of these, is given in the following sections.

5.2.3.1 COLUMN TUBES AND FITTINGS

The SCCR-2 unit has 12 stainless steel tubes, each 2.54 cm outside diameter, 2.21 cm internal diameter and 61 cm long. Two stainless steel end flanges were silver soldered to the outer wall of each tube, enabling the end fittings to be attached using 6, 2.54 cm x 2 BA cheese headed screws. A fine stainless steel gauze, of nominal aperture size 76 μm (200 B.S. Mesh), was also mounted on both the end

flanges of the tubes so as to hold firm the chromatographic packing material in each tube. The seal between the end flange of the tube and the end fitting was provided by a P.T.F.E. gasket.

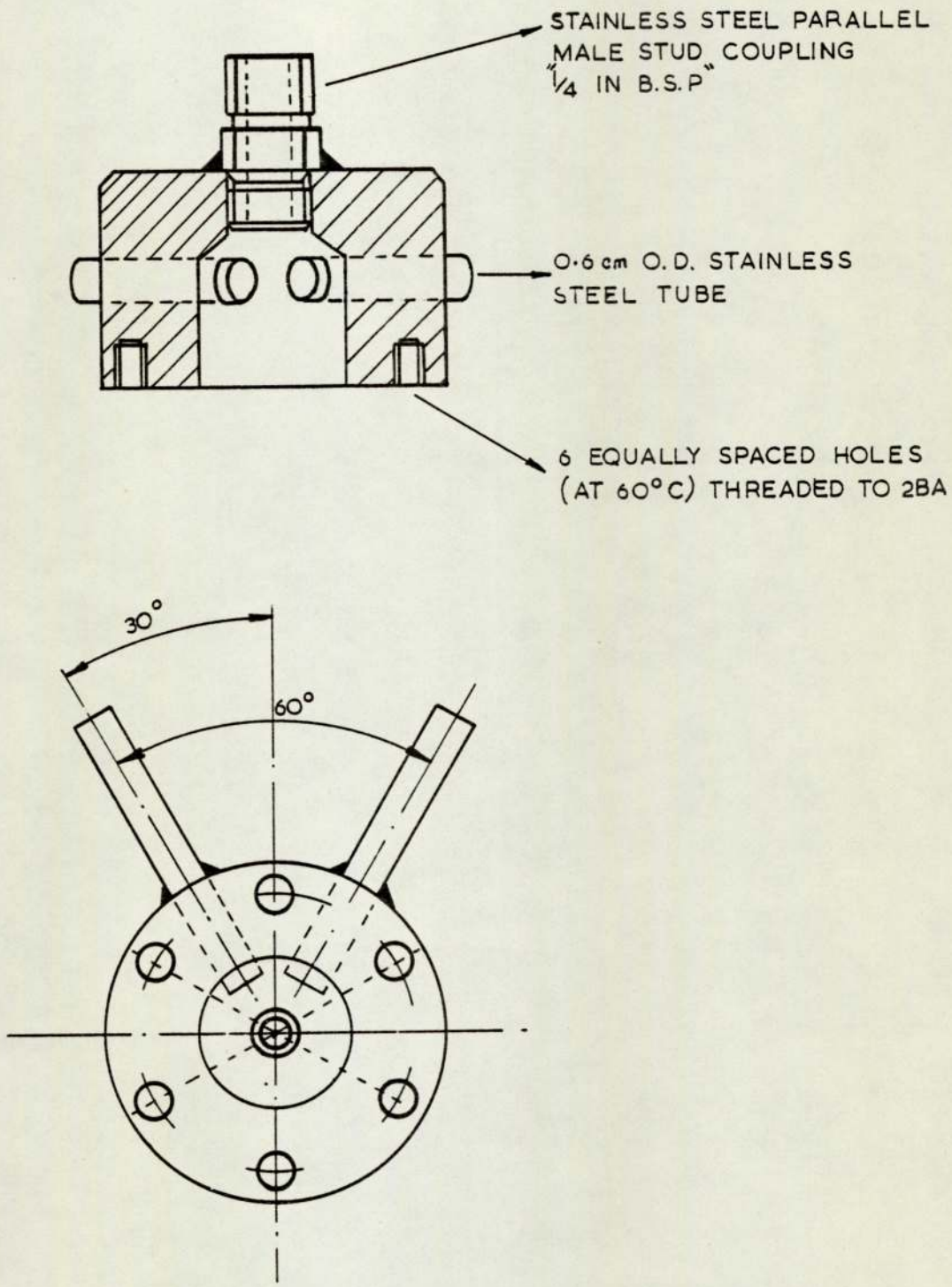
The end fitting shown in detail in Fig. 5.7, was machined from stainless steel rod, being essentially cylindrical and was designed to minimise the internal "dead" volume. A "1/4 in B.S.P." parallel male stud stainless steel coupling was silver soldered into the centre of the top of the end fitting to receive the 0.64 cm O.D. line from the appropriate transfer valve. In addition two stainless steel tubes 2.8 cm long and 0.64 cm O.D., were silver soldered into the cylindrical surface of the end fitting to permit connection with the respective inlet/outlet gas diaphragm valves.

At mid-height of each tube a "1/8 in B.S.P." male stud stainless steel coupling was silver soldered to accommodate the feed diaphragm valve, via a 0.32 cm O.D. stainless steel tube, as close as possible to the column. A capillary tubing was mounted inside the 0.32 cm O.D. tube in order to eliminate the feed hold-up in the line between column and feed valve.

In general the position of the fittings in each chromatographic column was dictated by the space requirements of the diaphragm valves, while their design was made in order to minimise the "dead" volume between column and diaphragm valve and also to give values of low pressure at the gas flowrates to be used.

Finally, a sample point was set at the bottom end fitting, on each of 6 alternate columns of the unit. Each sample point consisted of a "1/16 in B.S.P." male stud coupling, silver soldered to the end fitting and from which samples were drawn from the column by a 0.05 cm I.D. capillary tube to the sampling valve.

FIGURE 5·7 : THE END FITTING
(SCALE 1:1)



5.2.3.2 THE "PACKING"

Each stainless steel column was individually packed with chromatographic packing material consisting of 16.67% by weight of F.F.A.P. (free fatty acid phase) on 500-353 μm chromosorb W, AW-DMCS.

F.F.A.P., a product of the reaction between Carbowax 20M and 2-nitroterephthalic acid, developed by Varian Aerograph, was chosen for the SCCR-2 machine at the commencement of the work, as it seemed to be one of the most convenient general-purpose liquid phases with high heat thermal stability.

Chromosorb W (celite) was used as support, because of its low adsorptivity properties and its high liquid phase capacity. The chromosorb W, supplied by Jones Chromatography Ltd., was acid washed and treated with dimethyldichlorosilane to remove active sites.

Although it is well known that as the particle size is decreased the column efficiency increases, the selected support had particle sizes of 500-353 μm (30-44 B.S. mesh) to keep pressure drop to a minimum.

For the coating process, a rotary evaporator was employed and the solvent recommended by Varian Aerograph namely methylene chloride was used. Further information about chromatographic packing materials, criteria for their selection and details of the coating procedure are given in Sections 3.4.1, 3.4.2, 3.4.3.

The importance of the packing techniques in relation to the performance of a preparative chromatographic column has been already emphasized in Section 2.3.1.3. A modified version of the S.T.P. (Shake, Turn and Pressurise) method (66) was employed for packing the SCCR-2 columns. Basically the columns could be rotated and shaken, at predetermined frequencies, while they were being filled with successive

TABLE 5.3: QUANTITY OF CHROMATOGRAPHIC PACKING MATERIAL USED FOR THE SCCR-2 UNIT

(1) 16.67% F.F.A.P. on 500-353 μm chromosorb W,AW-DMCS		(2)*15% OV-275 on 353-251 μm chromosorb P, AW-DMCS	
Assigned Column Number	Weight of Packing	Assigned Column Number	Weight of Packing
	g		g
1	81.6	1	111.1
2	82.1	2	111.4
3	82.0	3	112.3
4	81.6	4	112.5
5	81.7	5	112.3
6	81.8	6	112.8
7	82.0	7	112.2
8	81.9	8	112.8
9	81.7	9	111.6
10	81.8	10	112.4
11	81.8	11	112.2
12	81.7	12	113.4
Total Weight (g)	981.7	Total Weight (g)	1347.0
Average Weight per column (g)	81.8	Average Weight per column (g)	112.2
Total weight of liquid phase (g)	163.6	Total weight of liquid phase (g)	202.1

* Note The OV-275 on chromosorb P, AW-DMCS packing was only used on the experimental study for the recovery of γ-linolenic acid from "fungal oil".

additions of low quantities of packing material. A special packing device was constructed by M. Lynham in order for this to be achieved (173). Also, during the packing procedure, the walls of the column were periodically tapped with a heavy metal bar and nitrogen pressure was applied to the top of the column.

The exact weights of packing material used for each column of the SCCR-2 unit, are shown in Table 5.3.

Recent experimental work has shown the necessity of repacking the chromatographic columns with 15% OV-275 on 353-251 μm (44-60 B.S. mesh) chromosorb P, AW-DMCS to enable the recovery of γ-linolenic acid from "fungal oil" to be achieved. More details of this work, are given in Section 8.4.2.

5.2.4 THE OVEN

The oven supplied by Hedinair Ltd. was an electrically heated oven with forced air circulation, dimensions 0.915 m x 0.915 m x 0.915 m and internal volume 0.766 m^3.

The heat was provided by Incolloy sheathed mineral insulated rod elements located in ducts along both side of the oven walls, while air was partially recirculated through the oven at least ten times per minute by a centrifugal fan.

The wall and doors of the oven were made from sheet steel and the thermal insulation was from mineral wool 7.62 cm thick.

This oven could provide a maximum operating temperature of 300°C with a maximum energy consumption of 13 kW and was capable of maintaining the temperature with an accuracy of ± 4°C.

The operating temperature was adjusted and clearly indicated by a mercury-in-steel controller. In addition, an excess temperature

thermostat was used to prevent the heaters remaining energized should any fault occur in the control circuit.

A large exhaust vent was fitted on the oven with a setting quadrant for manual control to enable evacuation of fumes to take place. Replacement fresh air entered around the fan shaft and was heated and mixed with the recirculating air before entering the working chamber.

Finally the Hedinair, type VFO, oven was modified from its standard design.

(1) By having a 0.61 m x 0.61 m explosion relief/access door in the centre of rear wall with an adjustable pressure release device.

(2) A horizontal slot 20.3 cm long and 0.95 cm in height was provided in the left hand side wall near the oven's base to allow pipes to pass to the chromatographic unit.

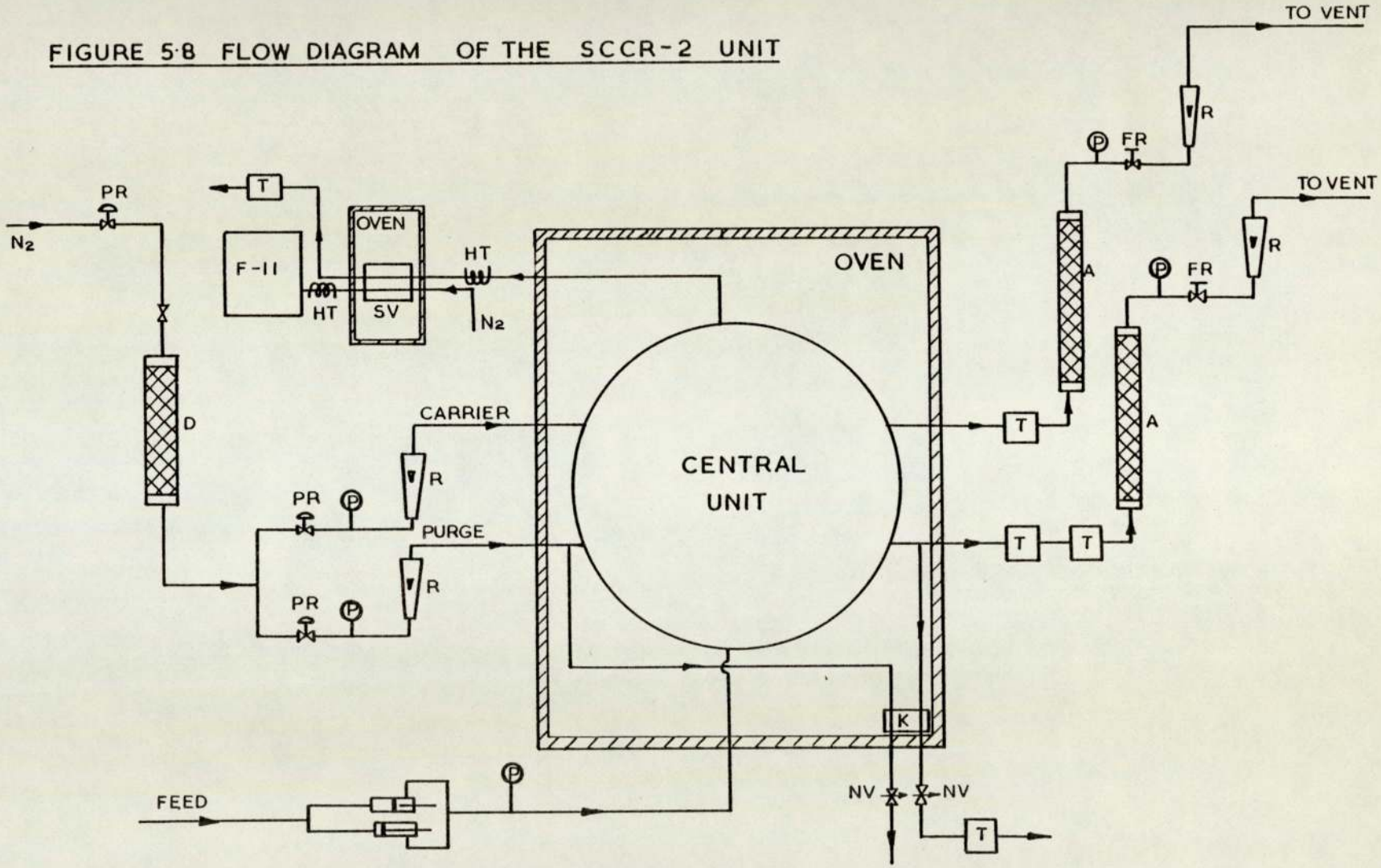
5.2.5 GAS PROCESS EQUIPMENT AND PIPEWORK

As shown in Fig. 5.8 the nitrogen, supplied in cylinders, is initially regulated to a pressure of 515 kN m^{-2} (60 psig) and then passes through a silica gel bed, 5.5 cm I.D. and 51 cm long for drying, before being split into the respective carrier and purge streams.

Both the carrier and purge streams are pressure regulated by two diaphragm type, "Norgren" regulators. The operating range of the regulators was 101-515 kN m^{-2} (0-60 psig) which matched the range of the "Norgren" pressure gauges employed. The individual gas flowrates were also monitored by two, type 1100, "Brooks" rotameters.

Copper, 0.64 cm O.D. tubing was used for the above mentioned gas inlet system, while all the fittings were in brass "1/4 in B.S.P."

FIGURE 5·8 FLOW DIAGRAM OF THE SCCR-2 UNIT



LEGEND

R = ROTAMETER	NV = NEEDVE VALVE	K = KATHAROMETER
P = PRESSURE GAUGE	A = CHARCOAL ADSORPTION BED	F-II = G.L.C. ANALYSIS UNIT
PR = PRESSURE REGULATOR	SV = SAMPLING VALVE	
FR = FLOW REGULATOR	T = TRAP	
D = SILICA GEL DRIER	HT = HEATING TAPE	

After leaving the rotameters, the nitrogen streams enter the SCCR-2 oven and passing through the respective preheating and distribution systems, enter the chromatographic columns through suitably opened diaphragm valves.

Product streams leaving the unit are collected by the appropriate distribution systems and then pass out of the oven, the solute vapours being condensed in a series of cold traps. Final clean-up of the outlet nitrogen streams was achieved by passing each stream through a charcoal adsorption bed, 2.5 cm in I.D. and 57 cm long.

The tubing employed for the outlet line circuit is from stainless steel, 0.64 cm O.D., also the fittings are in stainless steel, "1/4 in B.S.P."

The flowrates of both product streams are then regulated by "Brooks" regulators (of the type that control the downstream mass flowrate for varying upstream pressure) and finally measured by two, type 1100, "Brooks" rotameters before being vented to the atmosphere. In addition the outlet pressures were registered by two "Norgren" 101-308 kN m^{-2} (0-30 psig) pressure gauges.

A detailed description of the distribution and preheating systems, is given in the following sections.

5.2.5.1 THE CENTRAL DISTRIBUTION NETWORK

The basic element in the inlet/outlet gas line circuit to the 12 chromatographic columns was the central distribution system. This consisted of four distribution centres, one for each gas stream: carrier inlet, carrier outlet (Product I), purge inlet and purge outlet (Product II). The distribution centres were finally connected to the respective gas ports (valves) of the columns by 0.64 cm O.D. stainless steel tubing.

But the nature of the SCCR-2 operation required an even pressure drop across all the inlet/outlet gas lines to the chromatographic columns, therefore symmetry had to be obtained in the system. Consequently, the design and location of the distribution centres as well as the piping connection pattern from the columns to the distributors were dictated by the symmetry to be achieved.

However, the position of the four inlet/outlet gas ports successively alternated from the base of one column to the top of the next (Fig. 5.2). Thus, the use of two identical, linked together, distributors for each gas stream was necessary to accommodate the six connecting pipes (0.64 cm O.D. in stainless steel) for the top and bottom positioned gas ports, respectively.

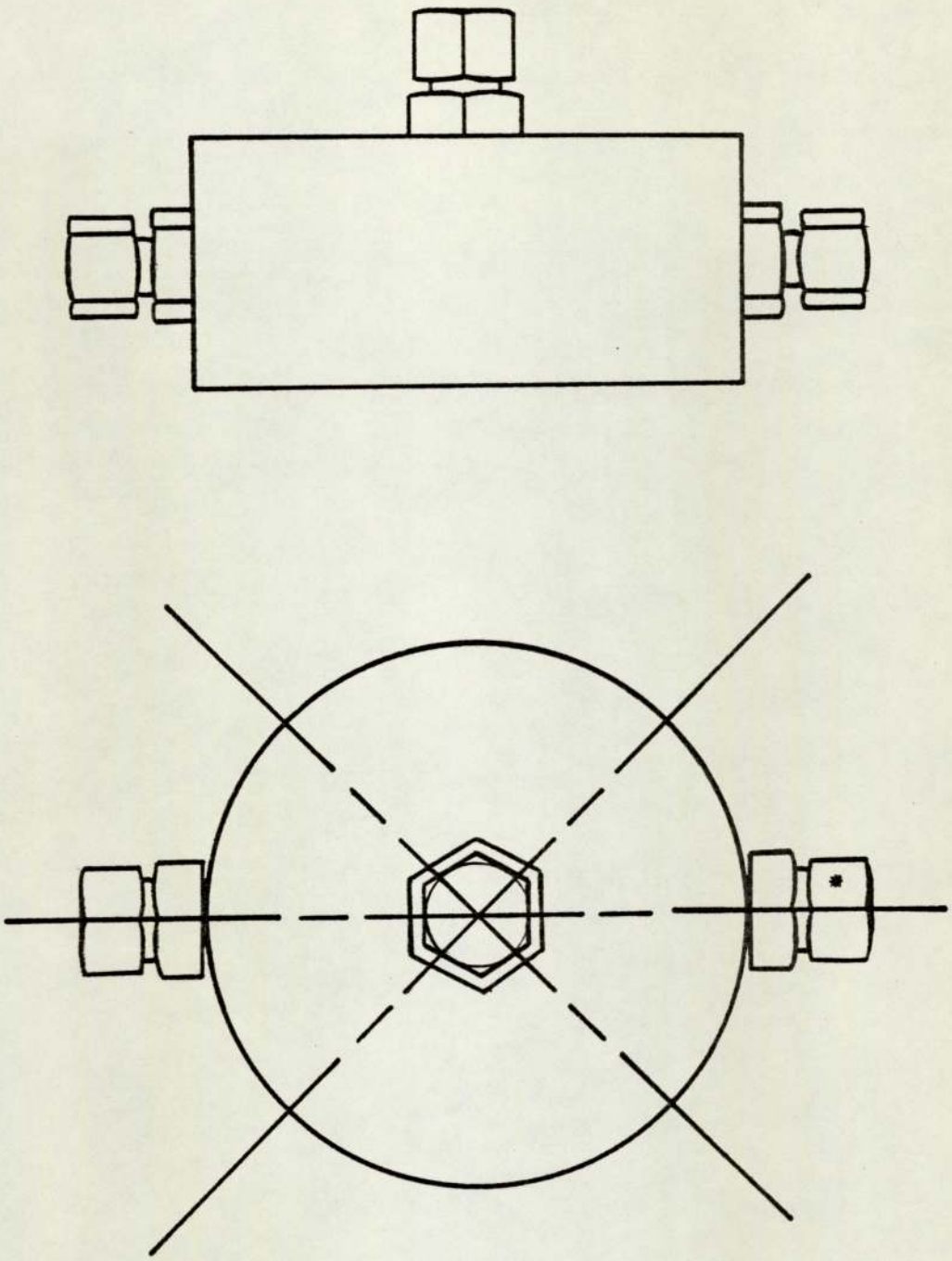
Each gas distributor was basically a stainless steel closed cylinder 3.5 cm in height and 7.7 cm in diameter with six "1/4 in B.S.P." parallel male stud stainless steel couplings silver soldered and evenly spaced on its cylindrical surface (Fig. 5.9). In addition a similar coupling was silver soldered onto the top plate of the cylinder, which was used to accommodate the 0.64 cm O.D. stainless steel tubing that links together the pair of like function distributors. This tube was then connected, by an equal tee coupling, to the respective inlet/outlet gas stream from/to the control and measuring devices.

Finally the eight gas distributors were set vertically on the axis of the "cylinder" formed by the 12 columns (Plate 5.6).

Also, the employed tubing pattern from the valves to the distributors (Plate 5.5), despite the space restrictions set by the size of the valves and the dimensions of the 12-columns ring, retained the symmetry.

FIGURE 5.9 THE GAS DISTRIBUTORS

(SCALE 1. 1)



* NOTE 6 STAINLESS STEEL PARALLEL MALE STUD COUPLINGS "1/4 IN B.S.P."

PLATE 5.5 THE CENTRAL DISTRIBUTION NETWORK

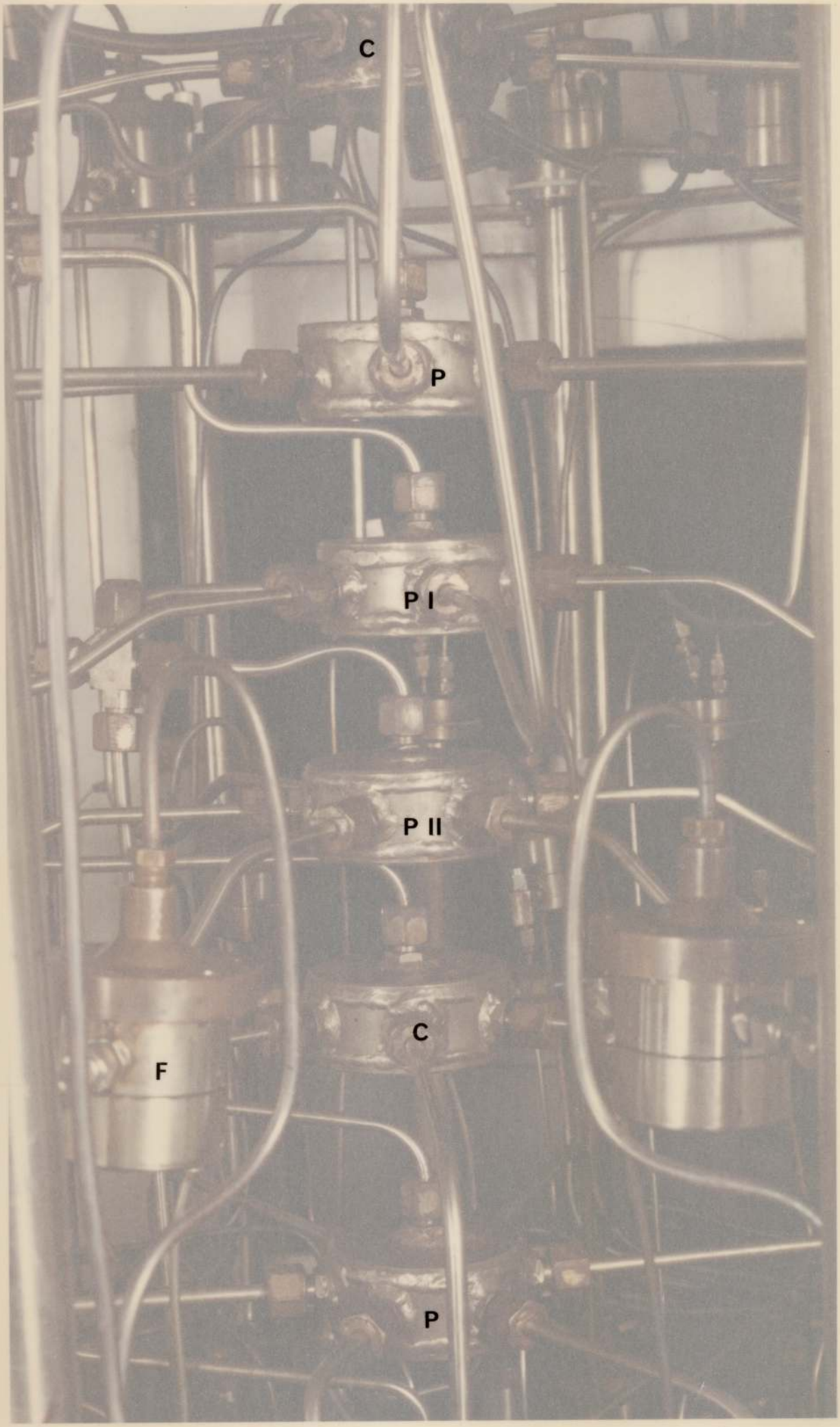
C = carrier gas inlet

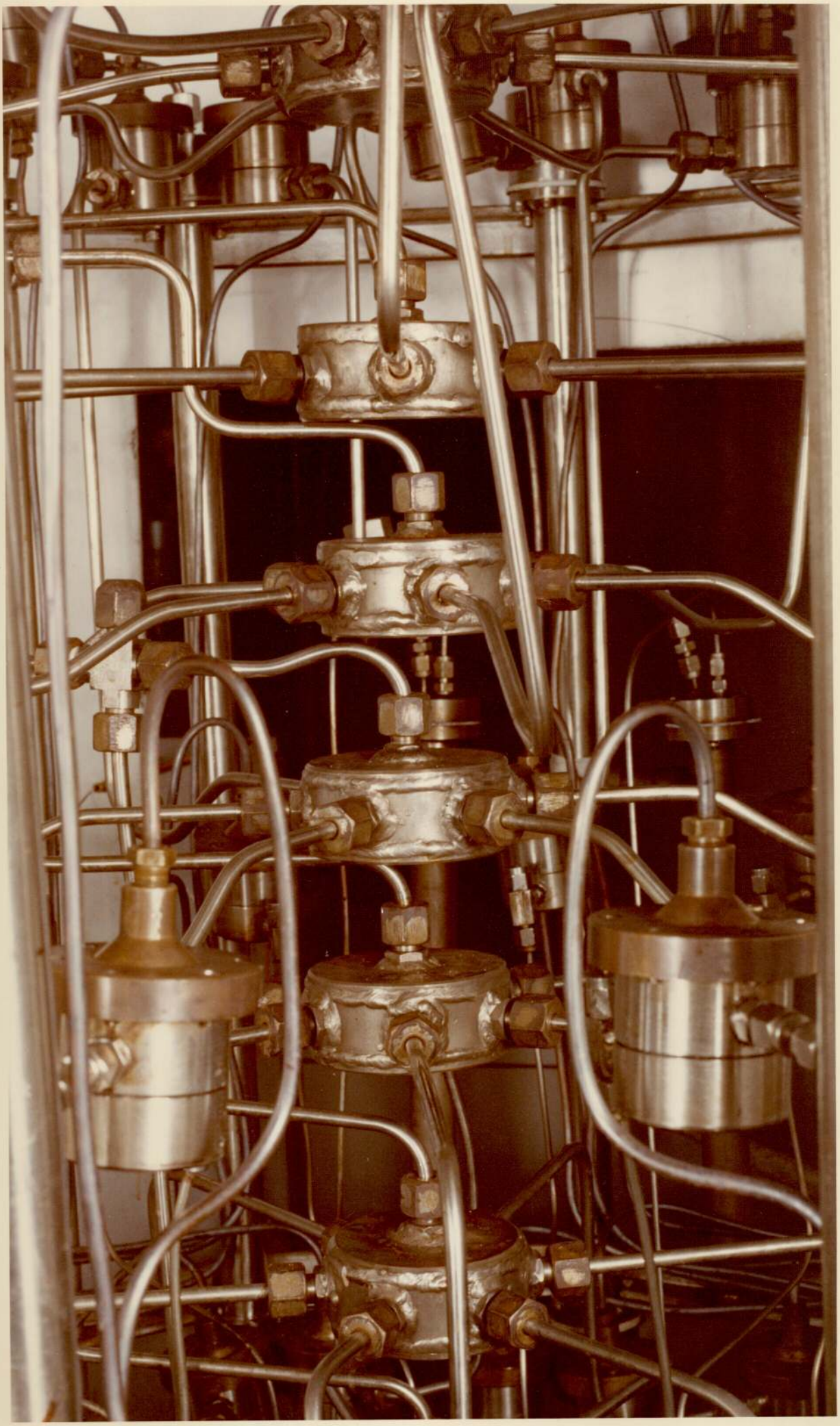
F = feed valve

P = purge gas inlet

PI = product I outlet

PII = product II outlet


C
P
P I
P II
C
F
P



5.2.5.2 PREHEATERS

Three main reasons have led to the development of the preheating system, as follows.

(1) To ensure the complete removal of the more soluble component from the purge section.

(2) To assist in the immediate vaporization of liquid feed mixture as it enters the chromatographic columns.

(3) To preheat carrier and purge gas streams to the temperature of the oven before entering the separation unit, thus avoiding thermal shocks in the extremely temperature sensitive chromatographic process.

Therefore, two identical preheaters were constructed for the purge and carrier nitrogen streams respectively, with a design based on shell and tube heat exchangers.

Each preheat chamber was made from a mild steel flanged tube, 35.6 cm long and 6.35 cm in I.D., with two mild steel pipes, 2 cm long and 0.64 cm O.D., silver soldered into its cylindrical surface to accept the inlet/outlet gas lines. Also a "1/4 in B.S.P" parallel male stud brass coupling was silver soldered near to the outlet port of the preheater to accommodate a "Pyrotenax" thermocouple. Inside the chamber ten mild steel baffles were set, each 0.32 cm thick and 6.3 cm in diameter with four 3.8 cm x 0.6 cm horizontal slots, arranged so as to be 2.5 cm apart and supported by three tie rods.

The heat was provided by three 300W steel jacketed heaters to replace the tube bundle normally employed in heat exchangers, while the energy flow to the heater was controlled by a variable resistor (variac). During operation, the gas to be preheated makes one pass over these heaters with the ten baffles diverting the flow across and back over the heaters. Also it was found experimentally that the

required heat energy to preheat the average employed nitrogen flowrate from 20°C to 200°C, was less than half the total capacity which the heaters can provide.

Since the preheaters were located in the hottest part of the SCCR-2 oven, besides its heating elements, the use of the electrical heaters was found unnecessary in some experimental runs.

5.2.6 FEED MIXTURE SUPPLY

The feed mixture was stored, prior to being pumped into the SCCR-2 unit, in a large glass cylindrical reservoir and also in a measuring burette attached to the reservoir. These vessels were connected at their lower ends to a three-way tap, which allowed a selection of either vessels for feeding the separation unit. During an experimental run, feed was normally taken from the large reservoir, switching occasionally to the burette to check the feedrate.

The outlet from the reservoirs was connected to the pump through a stainless steel gauze, of nominal aperture size 76 μm, filter unit for removing any particulate solid.

The pump used was a series 2, positive displacement metering micropump, supplied by Metering Pumps Ltd., in which one motor drives two independently adjustable pumpheads. All parts in contact with the working fluids, 18/8/3 grade stainless steel, ceramic and P.T.F.E., are resistant to most organic liquids. One of the operating requirements of the positive displacement type of pump is that there should be a positive pressure on the pump inlet side. Provision was made for this by placing the reservoirs 70 cm above the level of the pump. The two pump-heads were arranged for "180° out of phase" operation in order to rectify pulsation effects. In this manner consistent delivery was obtained. A nominal calibration chart for the pump is given in Appendix A.1.

From the pump the feed enters the oven and then the feed distributor which was located at the centre and near the base of the "cylinder" formed by the 12-chromatographic columns. A stainless steel/P.T.F.E., 101-515 kN m^{-2} pressure gauge supplied by Bristol Automation Ltd. was inserted in the feed line before entering the oven, to measure the feed pressure in the distributor.

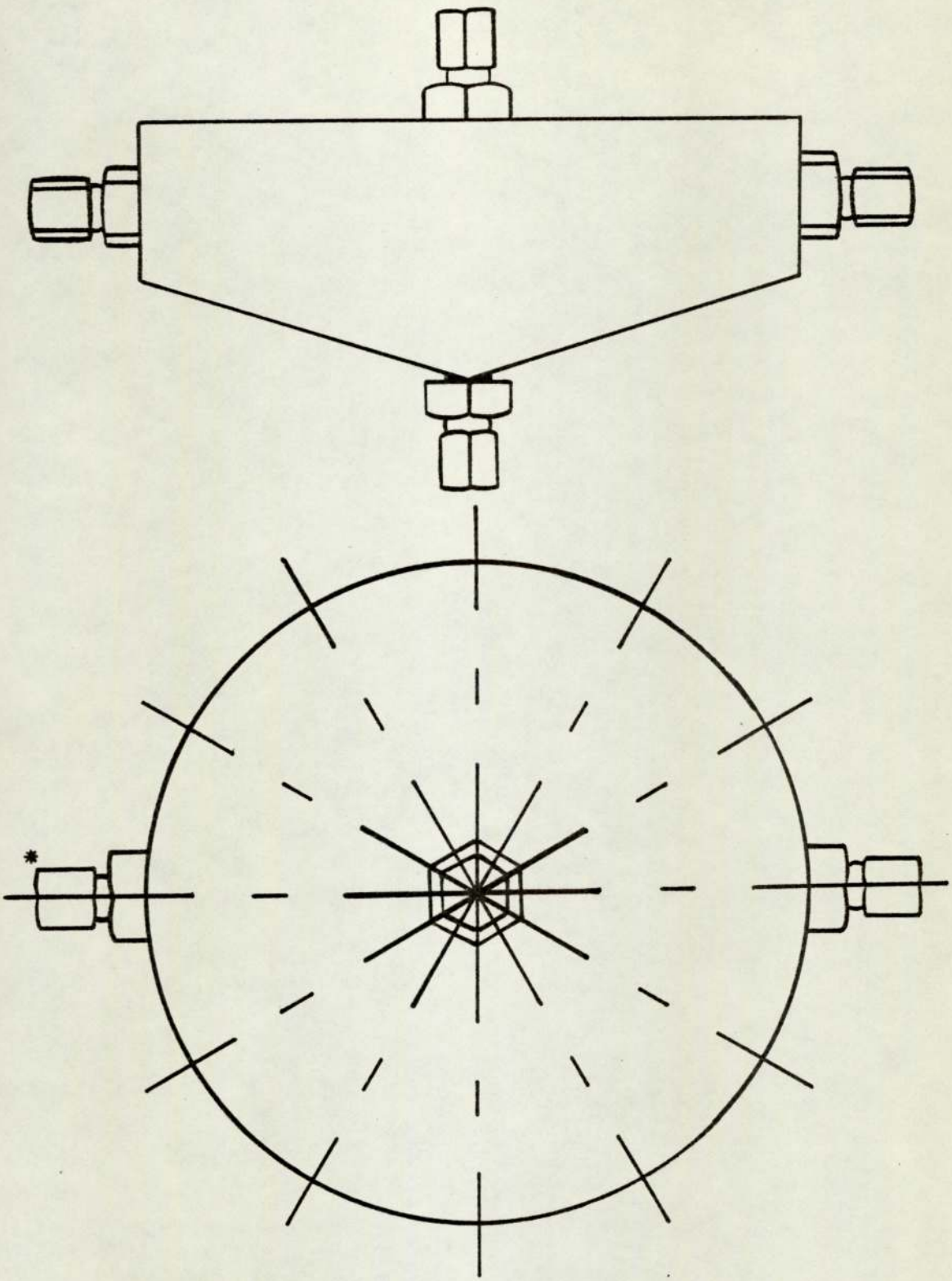
The liquid feed distributor was essentially a closed stainless steel cylinder of diameter 10.5 cm and height 2.5 cm with a shallow coned base (Fig. 5.10). This distributor was similar to the inlet gas and product stream distributors but with much smaller internal volume to facilitate the filling at start-up.

Twelve stainless steel parallel male stud couplings, "1/8 in B.S.P." were silver soldered into the circumference of the distributor at even spacing. These were used for connecting the distributor with the 12 feed diaphragm valves, located at the mid-height of the chromatographic columns. A similar coupling with a nut and septum was soldered into the centre of the top plate of the distributor, which was used to permit displacement of the air from the distributor during start-up. The same size coupling was also used in the centre of the base plate to accept the inlet feed line from the pump.

The tubing connecting the feed diaphragm valves to the feed distributor was of stainless steel, 0.32 cm O.D. A stainless steel "tee" fitting was placed in the line immediately proceeding the valve to enable all air to be displaced from the feed lines before start-up. The vertical stem of the "tee" was capped with a nut and a silicone rubber septum.

FIGURE 5.10 THE FEED DISTRIBUTOR

(SCALE 1:1)



* NOTE 12 STAINLESS STEEL PARALLEL MALE STUD COUPLINGS "1/8 IN B.S.P."

From the distributor, feed passes through the energized feed diaphragm valve and via a stainless steel capillary tube entering the chromatographic columns as a point source. The capillary tubing, 5.08 cm long and 0.05 cm in O.D. was used to reduce the feed hold-up in the line between feed valve and column. A large volume of liquid feed in this line after the feed valve was closed would slowly vaporize, resulting in contamination of resolved products during operation.

In general the design and location of feed distributor as well as the tubing pattern from the valves to the distributor was mainly dictated by the order of symmetry to be maintained, therefore allowing uniform "feeding" around the 12-chromatographic columns system to be achieved.

5.2.7 PRODUCT COLLECTION

The products of separation leaving the chromatographic columns were collected in a series of cooling traps. These were made from stainless steel to withstand the pressure of operation and were connected to the product offtake lines of the SCCR-2 unit, as shown in Fig. 5.8. The cooling mixture used was ice-water, kept in Dewar flasks.

As the products recovery were not considered to be of crucial importance in this experimental work, simplicity and economics dictated the design of traps. However, collection efficiencies of at least 75% were obtained for both product streams.

The condensing trap was essentially a closed rectangular stainless steel box 12 cm in height, 4.9 cm wide and 4.9 cm long with a sloping base plate. A helical stainless steel tube 0.64 cm O.D., 2.6 cm long with 3 coils, 7 cm in diameter, was connected to the box by a parallel male stud coupling, "1/4 in B.S.P.", silver soldered into

the top plate of the box. Also a same sized stainless steel coupling was soldered into the top plate to accept the outlet line of the trap.

Samples of the condensing products were taken, during a run and without disturbing the operating conditions, from a sample point set near the base of the rectangular box, by a liquid syringe.

The use of two of these traps in series, was found to give a satisfactory degree of solute recovery for the purge outlet stream, while for the carrier outlet stream, where the gas flowrate is normally less, one trap was found to be sufficient.

5.2.8 SAFETY

Safety precautions were taken because of the highly toxic, flammable and explosive chemicals which could be used in the SCCR-2 unit, thus increasing the range of possible separations being tackled by the sequential unit.

Consequently, the oven was provided with an explosion relief door having an adjustable release device. Also an adjustable exhaust vent was fitted in the oven to allow continuous purge of the air within the oven to the extractor fan near the roof of the laboratory.

The feed reservoirs were sealed from the laboratory atmosphere by rubber bungs. A glass tube filled with charcoal was passing through each bung to adsorb the feed mixture vapours.

In addition the outlet (product) gas lines were connected after the rotameters, into the main line running to the extractor fan. The solute gas streams from the Katharometer and sampling valve were also led to the extractor fan, after being passed through the ice-traps.

Safety precautions were finally taken against overheating or overpressurising the SCCR-2 unit. Thus, a temperature safety cut-out

was set in the oven to prevent the heaters remaining energized excessively, giving possible damage to the diaphragm valves or packing material of the sequential unit, while the glass adsorption beds and rotameters were enclosed in thick perspex boxes.

5.3 AUXILLIARY EQUIPMENT

5.3.1 INSTALLATION OF SAMPLING VALVE

Preliminary experimental work has shown that a gas tight syringe is not satisfactory for drawing samples from the SCCR-2 unit, because of the problem of condensation that occurs with high boiling point solutes.

Therefore, a sampling valve supplied by Pye Unicam was employed. This was made from stainless steel and P.T.F.E. with a maximum operating temperature 200°C. The timing of the actuation was done automatically by an electronic timer, connecting to the sampling valve via a solenoid valve, which could repeat the operation at preset time intervals. The sampling valve itself, was housed in an oven capable of maintaining the valve at temperatures up to 200°C with an accuracy of 1°C. Inlet and outlet lines of the valve were heated by heating tape connected to a variac.

The principle of operation of such a valve and the overall description of the one employed in this work, is given in Section 3.5.

During operation, at predetermined time intervals, samples of a given size were taken from a sample point of the SCCR-2 unit via a capillary tubing into the F-11 chromatograph, on actuation of the sampling valve, for quantitative analysis.

The installation of the sampling valve in the SCCR-2 machine is shown diagrammatically in Fig. 5.8 and the required circuit for its operation is presented in Fig. 3.2.

5.3.2 MONITORING OF PRODUCT STREAMS WITH A KATHAROMETER

In a sequential unit a stable state is eventually reached which is not a true steady state condition, because of the semi-continuous mode of operation.

This pseudo-steady condition was determined in the SCCR-2 unit, by monitoring one product stream (usually, product II) with a Katharometer. Therefore, the product concentration level has been continuously observed by the Katharometer traces, which become reasonably consistent when the stable state condition is established in the system, usually after 2 cycles.

A Gow-Mak model 10-454 Katharometer, most suitable for preparative chromatography, was employed. This is described in Section 3.3. The Katharometer was installed in the SCCR-2 oven, inside a mild-steel box filled by fibre-glass to accept the temperature fluctuations of the oven (as is shown in Fig. 5.8).

The Katharometer traces give no indication of the composition of the exit streams, but they assist in observing the removal of product II from the purge section as well as to estimate the time to the pseudo-steady state condition.

5.3.3 TEMPERATURE MEASUREMENTS

The significant effect of temperature on the gas chromatographic process is well documented in the literature. This has been also experimentally demonstrated in Section 4.1 by measuring the partition coefficients of various solutes over a wide range of temperatures.

In large-scale G.L. chromatography the heat of absorption, desorption and vaporization seem to cause significant temperature

fluctuations within the column, which seriously affect the separation process, current research by M. Bell (12) with a 7.6 cm diameter 12 columns sequential unit (SCCR-1) particularly demonstrating this. With such considerations in mind, the necessity of measuring the operating temperature and temperature distribution throughout the SCCR-2 unit was of prime importance.

Consequently, 6 thermocouples supplied by Pyrotenax Ltd. were arranged around the SCCR-2 unit to measure the following temperatures.

(1) The temperature of the carrier inlet stream after the preheater.

(2) The temperature of the purge inlet stream after preheating.

(3) The oven temperature.

(4) The temperature distribution throughout the separation unit. This was achieved by inserting 3 thermocouples into the chromatographic columns, arranged at even spacing.

The thermocouples were finally connected via a selector switch to an Ether compensated temperature indicator.

CHAPTER 6

Selection of Chemical Systems for Separation Studies

The chemicals chosen for separation study on the SCCR-2 machine had to fulfil the following requirements.

1) To be available in bulk in reasonable purity.

2) To be relatively cheap.

3) To have relatively low toxic properties and flammability.

4) To exhibit high volatility at the required equipment temperature for separation.

5) Preferable to be members or derivatives of fatty acids.

In addition, the partition coefficient values (K) of the selected chemicals had to be relatively low on F.F.A.P. phase in order to reduce the required carrier gas flowrate, when operating the SCCR-2 unit at a given sequencing rate and temperature (Section 7.1), thereby keeping the pressure drop and nitrogen cost down.

Thermodynamic measurements of various solutes on F.F.A.P. columns (see Section 4.1) had indicated the following chemicals favourable for separation study. "Arklone" P, "Genklene" P, acetic acid, propionic acid, methyl chloroacetate, ethyl chloroacetate and ethyl lactate. The relevant physical properties of those chemicals are given in Table 6.1.

The selected organic compounds provide a combination of chemical mixtures of varying separation difficulty and volatility (Table 6.2). Hence, a systematic study of the sequential unit performance at various temperatures and with varying separation difficulty could be achieved.

Finally, the recovery of γ-linolenic acid from "fungal oil", an application of interest to pharmaceutical companies, was investigated. The hydrolysed and methylated "fungal oil" provided a multicomponent mixture of methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl γ-linolenate.

The relatively high K values of the above mentioned components on F.F.A.P. phase as well as their likely decomposition at the required sequential unit temperature for fractionation, have led to the necessity of replacing the initial packing for a more suitable one. The selection of a new solvent phase was made from consideration of the partition coefficients on three recommended phases (Section 4.1). OV-275 (a cyanosilicone) was chosen because it gave comparatively low values for the respective partition coefficients and has high thermal stability.

TABLE 6.1 PROPERTIES OF SELECTED CHEMICALS (158,175,176)

NAME	SYNONYM AND FORMULA	DENSITY **	BOILING POINT *	MOLECULAR WEIGHT	SUPPLIER	PURITY	RELATIVE COST PER 1 Kg	TOXICITY
		$g\ cm^{-3}$	°C			%		
"Arklone" P (trade name)	1,1,2-trichloro-1,2,2-trifluoro-ethane $Cl_2CFCClF_2$	1.5635_4^{25}	47.7^{760}	187.4	I.C.I.Ltd.	99	1.1	Dangerous when heated to decomposition or on contact with acids as it evolves highly toxic fumes
"Genklene" P (trade name)	1,1,1-trichloro-ethane or methylchloroform CH_3CCl_3	1.3492_4^{29}	74.0^{760}	133.4	I.C.I.Ltd.	99	1.0	Narcotic in high concentrations. Dangerous when heated to decomposition or on contact with acids as it emits highly toxic chloride fumes.
Acetic acid	ethanoic acid, or vinegar acid CH_3CO_2H	1.0491_4^{20}	118.5^{760}	60.05	Ralph N Emanuel Ltd.	99.8	1.1	Caustic, irritating, can cause burns, lachrymation and conjunctivities. It attacks the skin easily and can cause dermatitis and ulcers. Inhalation causes irritation of mucous membranes. It is a general purpose food additive.
Propionic acid	propanoic acid $CH_3CH_2CO_2H$	0.992_4^{20}	141.1^{760}	74.08	Ralph N. Emanuel Ltd.	99	2.9	Data based on animal experiments show low toxicity. A chemical preservative food additive
Methyl chloroacetate	acetic acid, chloro-methyl ester $Cl\ CH_2CO_2CH_3$	1.2358_4^{20}	131.5^{760}	108.53	Ralph N. Emanuel Ltd.	99	5.8	Details of toxicity unknown. However, it must be considered highly toxic. An irritant.
Ethyl chloroacetate	acetic acid, chloro-,ethyl ester $ClCH_2CO_2C_2H_5$	1.159_4^{20}	144^{740}	122.55	Ralph N. Emanuel Ltd.	99	7.4	Moderate toxicity not severe enough to cause death or permanent injury. Dangerous when heated to decomposition as emits highly toxic fumes of chlorides.
Ethyl lactate (L)	propanoic acid, 2-hydroxy-, ethyl ester $CH_3CHOHCO_2C_2H_5$	$1.0324_4^{20.4}$	155^{760}	118.13	Ralph N. Emanuel Ltd.	98	4.4	Details unknown. It is expected to have moderate toxicity not severe enough to cause death or permanent injury. (***)

TABLE 6.1 CONTINUED

NAME	SYNONYM AND FORMULA	DENSITY ** g cm^{-3}	BOILING POINT * °C	MOLECULAR WEIGHT	SUPPLIER PURITY RELATIVE COST PER 100 gms	TOXICITY
Methyl palmitate	hexadecanoic acid methyl ester $CH_3(CH_2)_{14}CO_2CH_3$	-	$415\text{-}8^{747}$	270.46	Methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl γ-linolenate are the main constituents of the hydrolysed and methylated "fungal oil". This multicomponent fatty acid esters mixture was prepared and supplied free by Iveresk Research International in order the recovery of γ-linolenic acid ester to be investigated on the SCCR-2 machine.	Unknown
Methyl stearate	Octadecanoic acid methyl ester $CH_3(CH_2)_{16}CO_2CH_3$	-	215^{15}	298.51		Unknown
Methyl oleate	9, octadecenoic acid methyl ester (cis) $CH_3(CH_2)_7CH{:}CH(CH_2)_7CO_2CH_3$	0.879^{18}	$216\text{-}7^{20}$	296.50		Unknown
Methyl linoleate	9,12,Octadecadienoic acid methyl ester $CH_3(CH_2)_4CH{:}CHCH_2CH{:}CH(CH_2)_7CO_2CH_3$	0.8886_4^{18}	$211\text{-}2^{16}$	294.48		Unknown
Methyl γ-linolenate	9,12,15 octadecatrienoic methyl ester $CH_3[CH_2CH{:}CH]_3(CH_2)_7CO_2CH_3$	-	-	-		Unknown

NOTES * The pressure at which the boiling point is determined appears as a superscript.

** Density is relative to water. A superscript indicates the temperature of the liquid and a subscript indicates the temperature of water to which the density is referred.

*** A rough guide to the toxicity of a given ester may be the sum of the toxicities of the products of hydrolysis.

TABLE 6.2 CHEMICAL MIXTURES FOR SEPARATION STUDY ON THE SCCR-2 MACHINE

MIXTURE	COMMENTS	LIQUID PHASE USED	PARTITION COEFFICIENT OF SOLUTES		SEPARATION FACTOR	REQUIRED OPERATING TEMPERATURE RANGE FOR SEPARATION
			K_1^∞	K_2^∞		
"Arklone" P - "Genklene" P	An artificially made equivolume binary mixture.	F.F.A.P. (free fatty acid phase)	$K^\infty_{\text{"A"P}} = 35$ at 55°C	$K^\infty_{\text{"G"P}} = 202$ at 55°C	5.77 at 55°C	55 - 65°C
Acetic acid - Propionic acid	"	F.F.A.P.	$K^\infty_{\text{Ac.}} = 329$ at 130.5°C	$K^\infty_{\text{Pr.}} = 482$ at 130.5°C	1.47 at 130.5°C	120-135°C
Methyl chloroacetate Ethyl lactate	"	F.F.A.P.	$K^\infty_{\text{M.Chl.}} = 184$ at 120°C	$K^\infty_{\text{E.lact.}} = 276$ at 120°C	1.50 at 120°C	105 - 130°C
Ethyl chloroacetate Ethyl lactate	"	F.F.A.P.	$K^\infty_{\text{E.Chl.}} = 145$ at 135°C	$K^\infty_{\text{E.lact.}} = 170$ at 135°C	1.17 at 135°C	105 - 140°C
Methyl palmitate - Methyl stearate - Methyl oleate- Methyl linoleate - Methyl γ-linolenate	Multicomponent mixture produced by hydrolysing and methylating "fungal oil", from which the recovery of methyl γ-linolenate was studied on the SCCR-2 unit. The methyl γ-linolenate is the heaviest component in the mixture (the most soluble in the liquid phase) while the nearest lighter component is the methyl linoleate.	F.F.A.P.	$K^\infty_{\text{M.linoleate}} = 748$ at 216°C	$K^\infty_{\text{M-}\gamma\text{-linolenate}} = 881$ at 216°C	1.18 at 216°C	200-230°C
" "		OV-275	$K^\infty_{\text{M.Linoleate}} = 144$ at 203°C	$K^\infty_{\text{H.}\gamma\text{-linolenate}} = 172$ at 203°C	1.19 at 203°C	170-210°C

CHAPTER 7

Experimental Procedure for the Operation of the SCCR-2 Unit

7.1 SELECTION OF EXPERIMENTAL OPERATING CONDITIONS

The selection of operating conditions for the separation of a binary feed mixture with the SCCR-2 machine, was based on the theory outlined by Barker and Lloyd (16,45) for counter-current chromatographic systems.

In the counter-current mode the mobile phase flow, G, moves in the opposite direction to the stationary phase flow, L. In order for a binary feed mixture to be separated under these conditions the mobile and stationary phase flows must be adjusted so that the less soluble component I travels with the mobile phase, while the more soluble component II is held preferentially on the stationary phase.

The condition for preferential movement of component I in the mobile phase is,

$$G.c_I > L.q_I \tag{7.1}$$

where, c_I and q_I are the concentrations of component I in the gas and liquid phase respectively.

By definition, the partition coefficient is given as

$$K = \frac{q}{c} \tag{7.2}$$

Therefore, equation (7.1) becomes

$$\frac{G}{L} > K_I \tag{7.3}$$

Similarly, component II is preferentially moving with the stationary phase if

$$\frac{G}{L} < K_{II} \tag{7.4}$$

Hence separation of a binary feed mixture under counter-current conditions occurs if the ratio of mobile to stationary phase flow is between the partition coefficient of the solutes of the mixture.

$$K_I < \frac{G}{L} < K_{II} \tag{7.5}$$

In the SCCR-2 unit, where the counter-current movement between the carrier gas and column packing is simulated by a valve sequencing action (see Section 5.1.1), the equation (7.5) is again true. In addition it may be explained in the same way that component II is completely purged from the isolated section (see Fig. 5.1) if

$$\frac{S}{L} > K_{II} \tag{7.6}$$

where, S is the gas flowrate in the purge section of the SCCR-2 unit.

The preceding relations are true only at infinite solute concentrations, for an infinite number of plates in the packed section, for negligible pressure drop across the columns and when the sequential nature of the SCCR-2 operation is ignored. As none of these conditions are realized in practice, the real operating conditions are slightly different. Barker and Deeble (19) have shown that the actual conditions for the separation of a binary mixture by a sequential type of chromatograph are as follows

$$(K_I^{\infty} + \Delta K_I + \delta_I + \delta_I' + s_I) < \frac{G_{min}}{L'} < \frac{G_{max}}{L'} \quad (K_{II}^{\infty} + \Delta K_{II} - \delta_{II} - \delta_{II}' - s_{II})$$

$$\frac{S}{L} > (K_{II}^{\infty} + \Delta K_{II} + \delta_{II} + \delta_{II}' + s_{II}) \qquad (7.7)$$

where, $L' = \frac{\text{total volume of liquid phase in columns}}{\text{cycle time}}$, the apparent stationary phase volumetric flowrate in the sequential unit

G_{min}, G_{max}: the volumetric mobile phase flowrates at the column inlet and outlet respectively

K_I^{∞} : the partition coefficient of less soluble component at infinite dilution

K_{II}^{∞} : the partition coefficient of more soluble component at infinite dilution

ΔK_I, ΔK_{II} : factors accounting for the effect of finite concentrations on the partition coefficient

δ, δ' : factors to correct the operating range for successful separation on the sequential unit attributable to the finite column length and solute zone broadening respectively

s_I, s_{II} : factors to correct the operating range for successful separation on the sequential unit attributable to the sequential nature of operation.

Concluding, the effect of finite column length, sequential mode of operation, pressure drop across the columns and finite solute concentrations, narrow the operating range of conditions required for a successful separation on the SCCR-2 unit. A comprehensive theoretical study of the above factors and of their effects on the performance of the SCCR-2 unit is given in Section 9.

Unfortunately use of the inequalities (7.7) would require detailed knowledge of the parameters involved, which in turn would necessitate an extensive experimental and theoretical study. Thus, in practice the following approximate relations were used as a guide to the selection of experimental settings for the operation of the SCCR-2 unit:

$$\left.\begin{aligned} K_I^{\infty} < \frac{G_{mc}}{L'} < K_{II}^{\infty} \\ \frac{S_{mc}}{L'} > K_{II}^{\infty} \end{aligned}\right\} \qquad (7.8)$$

where,

$$\left.\begin{aligned} G_{mc} &= G_a \times \frac{T_{mc}}{T_a} \times \frac{P_a}{P_{co}} \times J_3^2 \\ S_{mc} &= S_a \times \frac{T_{ms}}{T_a} \times \frac{P_a}{P_{so}} \times J_3^2 \\ L' &= \frac{W_L}{12.\rho_L.I_s} \end{aligned}\right\} \qquad (7.9)$$

and

G_{mc}, S_{mc} : the mean carrier and purge gas volumetric flowrate, respectively.

G_a, S_a : volumetric carrier gas and purge gas flowrate, respectively, measured at ambient conditions

P_a : ambient pressure

T_a : ambient temperature

P_{co} : carrier gas outlet pressure

P_{so} : purge gas outlet pressure

T_{mc} : SCCR-2 operating temperature (mean column temperature in the separating section)

T_{ms} : mean column temperature in the purge section

J_3^2 : the gas phase compressibility factor

W_L : weight of liquid phase in the SCCR-2 system

ρ_L : density of liquid phase

I_s : time for a sequencing interval

Thus, for a specific separation study on the SCCR-2 unit, values for L', G_{mc} and S_{mc} were selected according to the inequalities (7.8). From a selected L' value the sequencing time interval, I_s, was determined and the digital timer of the pneumatic control was adjusted accordingly. Also from the selected G_{mc}, S_{mc} values, the carrier and purge gas outlet flowrates (G_a,S_a) were determined, through the equations (7.9), which finally specified the product streams rotameter settings required for the separation.

7.2 START-UP PROCEDURE

The start-up procedure involved the following routine.

1. General check and servicing of the various functions of the SCCR-2 unit.

Before starting any experimental run, the condensing products cooling traps were thoroughly cleaned with a solvent, i.e. acetone and the silica-gel or charcoal adsorption beds were recharged if needed. Also the silicone rubber septums throughout the unit were checked and replaced as necessary.

Then the SCCR-2 unit was tested for leaks at the normally employed range of pressures, with the leaks being traced by a soap solution.

For testing the diaphragm valves, nitrogen pressure was only applied to the purge section, the carrier inlet gas pressure regulator being fully closed. Under these conditions the presence of gas in the separating section or in the feed distributor indicated leakage across a closed diaphragm valve. The location of this faulty operated valve could be found by "skipping" the isolated section round the cycle, depressurising the separating section between each sequencing step, and observing the effect on the leak rate.

Appropriate action was taken to eliminate any detected leakage in columns, pipe work or diaphragm valves, before continuing.

2. Start heating the system.

The oven usually required two extra hours of operation before the start of a run in order for a steady temperature to be established around the 12-columns system. During that period nitrogen was flowing through the separating and purge section of the SCCR-2 unit to purge

out any chemicals present from previous experiments and to avoid possible contamination of packing material at high temperatures under non-inert conditions (177).

3. Introduction of feed mixture and the setting of the gas flowrates.

The solute mixture was pumped into the system until the feed distributor was filled-up. Air was completely displaced from each feed line via the open vertical arm of the tee-connection immediately proceeding the closed diaphragm valve. Thus, when liquid issued from the "tee", it was firmly capped with a nut and septum.

The gas flowrates and pressures in purge and separating section were adjusted to the values selected according to the procedure in Section 7.1. Meanwhile, the feed diaphragm valves were kept closed by disconnecting the appropriate air lines from the pneumatic control box, until with continued pumping the liquid feed pressure becomes approximately equal to the mid-pressure of the separating section. This precaution was taken to avoid surging from, or "blow-back" into, the feed distributor network.

Finally the digital timer in the control box was adjusted to the selected sequencing time interval and a fine adjustment of the feed throughput was made by the pumps micrometer settings. Also the time and point of start-up was recorded.

7.3 DATA RECORDED DURING A RUN

7.3.1 AVERAGE EXPERIMENTAL SETTINGS

During operation the flow of nitrogen in the off-take lines together with the temperature and pressure readings were recorded and subsequently checked at frequent intervals. The off-take flowrates as well as the inlet/outlet pressure readings were usually found very steady during a run. In contrast, fluctuations in the oven temperature as high as ± 4°C were often registered. However, because of the appreciable mass of the columns and the low thermal conductivity of packing material, the temperature fluctuations inside the columns found a lot smaller, ± 2°C about the mean.

It should be noted that gas flowrate readings were made from the rotameter floats settings by reference to the calibration charts (Appendix A.1), while the temperature around the SCCR-2 unit was directly read on an Ether compensated indicator via a series of thermocouples.

In addition the feedrate, initially adjusted by the pumps micrometer settings with reference to the calibration chart (see Appendix A.1), was often checked during a run by timing the discharge rate from the burette attached to the feed reservoir. Usually the feedrate was found to remain constant throughout the run, except when very low feed throughputs were used, i.e. feed rates less than 10 $cm^3\ h^{-1}$ or when air was present in the feed lines.

From the recorded data, the average experimental settings of the run could be obtained which were tabulated as shown in Table 7.1. The calculated ratio of mobile to stationary phase (see Equations 7.9) was also included in the Table. Finally the ambient conditions of temperature and pressure as well as the operating conditions of the analysis units were noted, as shown in Table 7.1.

7.3.2 TIME TO PSEUDO-STEADY STATE CONDITION

In the SCCR-2 unit during an experimental run a reproducible state condition was eventually reached. This was not a true steady state condition due to the sequential nature of operation, the separation being in fact semi-continuous. However, the reproducible state condition was generally established in the system usually after two sequencing cycles whereby, although the solute concentration profiles within the columns and outlets changed with time during a sequencing interval, the concentration profiles were reproduced from one cycle to the next.

The approach to this pseudo-steady state condition was determined during the run by monitoring one product stream of the SCCR-2 unit (usually product II) with a Katharometer. Consequently, the product concentration level could be continuously observed by the Katharometer traces, which become reasonably consistent once the pseudo-steady condition is established in the unit, as shown in the example given in Fig. 7.1.

The time to this pseudo-steady state condition was recorded and the sampling period for the determination of column to column concentration profile and products purities was begun.

7.3.3 COLUMN TO COLUMN CONCENTRATION PROFILE

Once the pseudo-steady condition was achieved, the symmetry of the sequential unit permitted determination of the column to column concentration profile and the main record of performance of the SCCR-2 unit under varying operating conditions was this solute concentration profile around the 12-columns. A column to column concentration profile was obtained experimentally by analysing gas samples taken from a fixed

sample point in the 12-column arrangement during a complete sequencing cycle, at a constant time after each sequencing action of the valves.

The basis of the column to column concentration profile analysis is that the sample point although in a fixed position in one column, essentially changes its position relative to the input and output functions as the unit sequences around the closed cycle. Therefore, the resultant profile is equivalent to sampling all twelve columns at a constant time after the sequencing of valves.

Gas samples were automatically withdrawn from the sample point by using a sampling valve, connected to a timer and housed in an oven (see Section 5.3.1). On actuation of this sampling valve, samples were taken from the sequential unit into the Perkin-Elmer F-11 chromatograph for quantitative analysis. Meanwhile, the sample volume was such as to give a response within the linear range of the F-11 detector and to permit thus direct quantitative analysis through the calibration charts of the F.I.D. (see Section 3.6). This could be achieved by adjusting the sample loop volume of the sampling valve to the required value.

The analysis results, made for a set of gas samples of given volume, taken from a fixed sample point, at a constant time after the sequencing action of a valve and for a complete cycle, were recorded (see Table 7.1). From the above records the mass of each sample was determined using the F-11 detector calibration. Dividing the analysed mass by the sample volume corrected to normal temperature conditions (20°C), the standar ised concentration for each solute in a specific gas sample was obtained, and recorded as shown in Table 7.1. However, no correction to the sample volume was made for pressure as the analysed samples were always at ambient pressure conditions.

From the recorded analysis data (see Table 7.1), the column to column concentration profile was plotted as is shown in the example given in Fig. 7.2. To plot the concentration profile the distance of the sample point from the carrier gas outlet after each sequencing action was required. This was determined by ignoring the column to column transfer line length and considering each column length equal to 61 cm.

An experimental study for testing the reproducibility of the concentration profiles obtained from different sequencing cycles or from differing sample points was made using a mixture of "Arklone" P/"Genklene" P, and the derived results are recorded in Section 8.1.1.

7.3.4 PRODUCTS PURITIES

From the recorded column to column concentration profiles during a run a products purity level could be determined. In addition when volatile feed mixtures were involved for separation, i.e. "Genklene" P/"Arklone" P, gas samples were withdrawn from the product outlet lines by a gas tight syringe to determine their purity. However, for less volatile components liquid samples were collected from the condensing traps into marked sample bottles which were usually analysed at the end of the run.

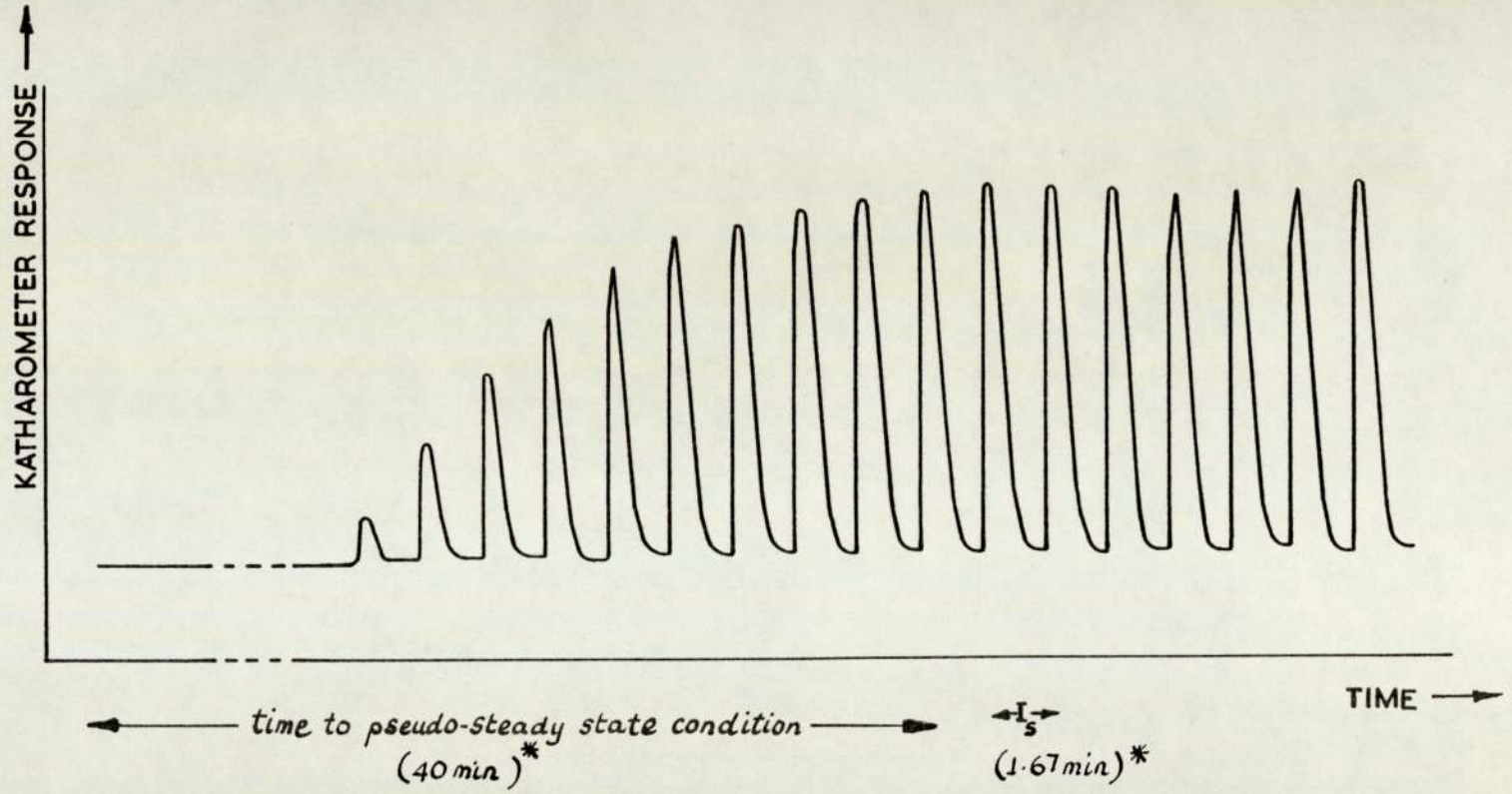


FIGURE 7.1 TYPICAL EXAMPLE OF THE RECORDED SOLUTE CONCENTRATION PROFILES OBTAINED DURING A RUN BY MONITORING THE PRODUCT II OUTLET STREAM WITH A KATHAROMETER

*NOTE: VALUES OBTAINED FROM THE EXPERIMENTAL RUN DESCRIBED IN TABLE 7.1.

TABLE 7.1 EXAMPLE OF RECORDED DATA FOR AN EXPERIMENTAL RUN

RUN DESCRIPTION		
System:	50/50 V/V-"Arklone" P/ "Genklene" P	
Temper.	Oven	: 55°C
	Purge in	: 80°C
	Carrier in	: 58°C
Ambient conditions	Pressure	: 101 kNm^{-2}
	Temper.	: 21°C
Gmc/L′		: 43.1
Switching rate		: 100 s
Feedrate		: 21 $cm^3 h^{-1}$
Separating section	Pin	: 198 $kN\ m^{-2}$
	Pout	: 177 $kN\ m^{-2}$
	Ga	: 7.9 $cm^3 s^{-1}$
Purge section	Pin	: 184 $kN\ m^{-2}$
	Pout	: 157 $kN\ m^{-2}$
	Sa	: 188 $cm^3 s^{-1}$

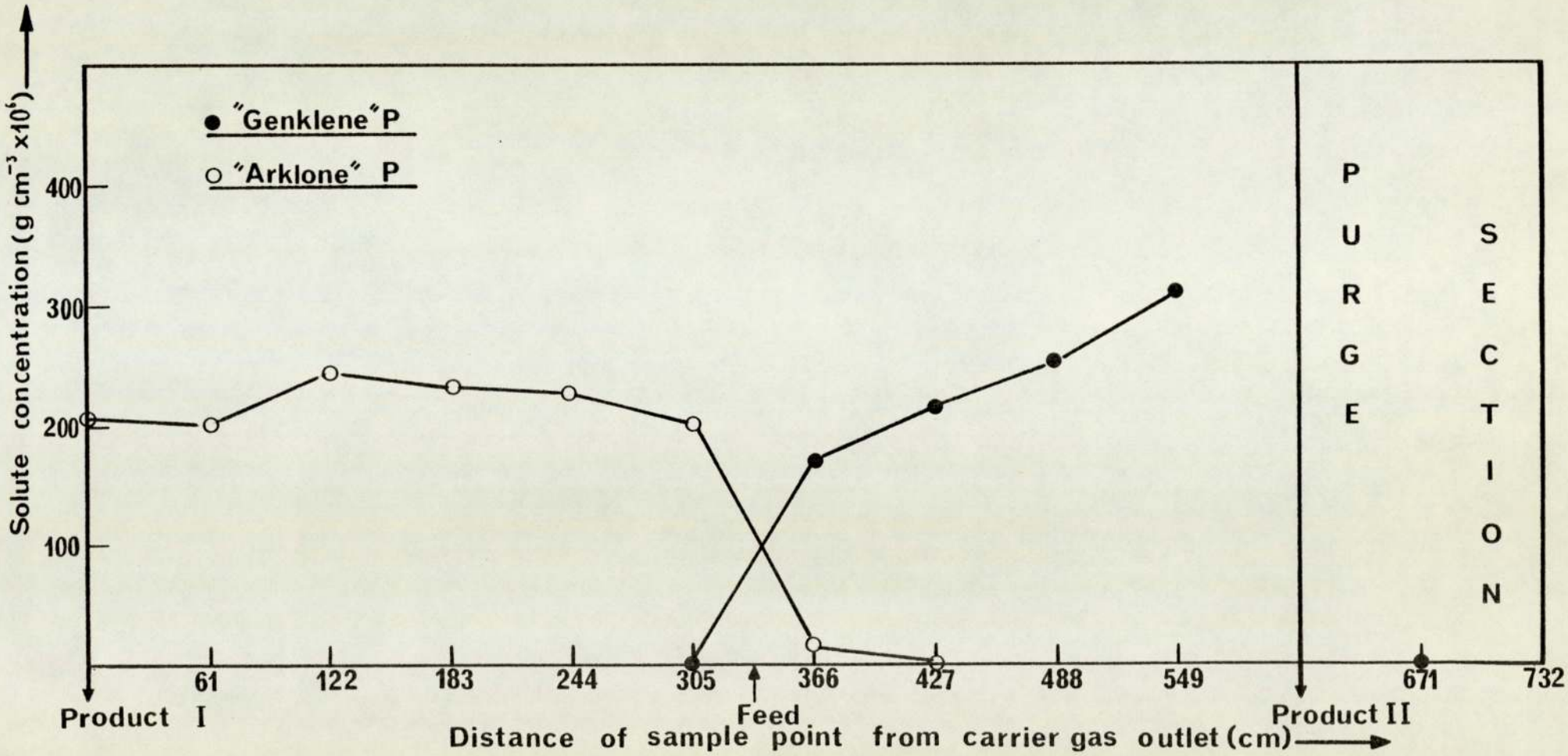
ANALYSIS DESCRIPTION	
Katharometer	
Gas flow	: 3.1 $cm^3\ s^{-1}$
Bridge current	: 115 mA
Bridge voltage	: 18 V
Sensitivity	: 9.7
Sampling valve	
Temperature	: ambient
Pressure in Sample loop	: ambient
Sample volume (corrected to N.T.P.)	: 0.26 cm^3
F-11	
Pressure H_2	: 236 $kN\ m^{-2}$
Pressure O_2	: 270 $kN\ m^{-2}$
Flow N_2	: 0.42 $cm^3 s^{-1}$
Sensitivity	: 1×10^4
Column temper.	: 55°C
Chromat. Column Specific.	121.9 cm long and 0.3 cm in O.D. stainless steel column with 1.0625 g packing material, 16.67% of F.F.A.P. on 500-353 µm chromosorb W, AW-DMCS

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 70 sec after sequencing action, on the 6th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I $\times 10^3 g\ cm^{-3}$	Product II $\times 10^3 g\ cm^{-3}$
5,6	366	581	8461	15.4	169.2
6,7	427	<40	10440	<1.0	207.7
7,8	488	<40	12460	<1.0	251.9
8,9	549	<40	15500	<1.0	311.5
9,10	610	<40	<20	<1.0	<0.4
10,11	671	<40	<20	<1.0	<0.4
11,12	0	8437	<20	207.7	<0.4
12,1	61	8097	<20	200.0	<0.4
1,2	122	9915	<20	244.2	<0.4
2,3	183	9332	<20	230.8	<0.4
3,4	244	9170	<20	226.9	<0.4
4,5	305	8322	<20	203.8	<0.4

FIGURE 7.2 Column to column concentration profile plotted for the run described in table 7. 1



7.4 ESTIMATION OF EXPERIMENTAL ERRORS

The experimental errors involved in the operation of the SCCR-2 unit were estimated to indicate the accuracy of the results obtained from the separation studies.

As was mentioned earlier during an experimental run the carrier outlet and purge outlet gas flowrates were measured at frequent intervals (at least once per sequencing interval) and the average values were recorded. These off-take flowrates were accurately measured by carefully calibrated rotameters.

In addition the inlet/outlet pressures in the separating and purge section were frequently measured by pressure gauges, and the average values were again recorded. The accuracy of these pressure measurements was often checked by a "dead weight" pressure tester.

Flow or pressure fluctuations in the separating section mainly occurred from one sequencing interval to the next, due to the variation in flow resistance from the differing configuration of the ten packed beds. However, the carrier inlet pressure and carrier gas outlet flowrates were accurately controlled at constant values by a pressure and flow regulator respectively. Consequently, the only fluctuation occurring from one sequencing action to the next was in the measured carrier gas outlet pressure. An extreme fluctuation of $\pm$ 4 kN m^{-2} in the value of carrier gas outlet pressure could introduce a possible error into G_{mc} of $\pm$ 2%.

An error was estimated in S_{mc} of about $\pm$ 1% due to the extreme outlet pressure fluctuations in the purge section.

However, if the column temperature fluctuations are also to be taken into account, which are usually less than $\pm$ 2°C, an additional error of less than $\pm$ 1% must be considered in the G_{mc} and S_{mc} calculations.

The possible error in the calculated value of the apparent liquid rate, L', may be considered negligible as the sequencing rate, weight of packing and liquid phase loading were very accurately determined.

For the quantitative analysis required for the determination of column to column concentration profile and products purities, the main error involved is due to the calibration of the flame ionization detector (F.I.D.). This error was estimated in Section 3.6 as being generally within ± 2%.

Finally, the assumption of perfectly matched columns, which forms the basis of the concentration profile technique, is idealistic. In fact it was found that there was a significant variation in efficiency between the individual columns (see Section 8.1.5). However, the column to column variation in packing bed characteristics were found to be less important than was first thought since when concentration profile analyses from differing sampling points were compared, reproducible profiles were obtained (see Section 8.1.1).

CHAPTER 8

Separation Studies on the SCCR-2 Unit

Several separations were performed on the SCCR-2 unit. The objectives of these experimental studies were to determine the separating capabilities of the unit and its separating limits.

For this reason the separation of chemical mixtures which had varying separation difficulty and volatility was studied on the SCCR-2 equipment. The systems selected had separation factors in the range of 1.1-5.8 and required equipment operation in the range of 55-200°C.

Initially the simple separation of the equivolume mixture of "Arklone" P and "Genklene" P was attempted, which was followed by increasingly more difficult separations such as that of ethyl chloroacetate from ethyl lactate and the recovery of γ-linolenic acid from "fungal oil". From the above studies the performance of the SCCR-2 equipment, recorded as column to column concentration profile or product purities, was able to be qualitatively related to the volatility and the separation difficulty of the chemical systems used.

In addition the effect of the operating variables such as feed throughput, temperature, ratio of the mean gas flowrate to the liquid rate, and sequencing rate, on the SCCR-2 performance was extensively studied.

8.1 THE SEPARATION OF "ARKLONE" P AND "GENKLENE" P

Although the SCCR-2 equipment was constructed for high temperature separations and was mainly intended for the separation of fatty acids or other related compounds, separation studies were initially attempted using an equivolume binary halocarbon mixture ("Arklone" P - "Genklene" P) to test the performance of the unit at temperatures near ambient. In general high purity products were obtained for both product streams under various operating conditions, at feedrates of about 21 $cm^3\ h^{-1}$. Throughputs could have been increased to over 100 $cm^3\ h^{-1}$ but it was decided to keep throughputs low so as not to strip any liquid phase from the packing at this stage of the experiments.

In the following Sections details of nine experimental runs with the "Arklone" P/"Genklene" P system are given which record the effect of three significant variables (T, $\frac{Gmc}{L}$, I_s) on the performance of the sequential unit and demonstrate the reproducibility of the concentration profile analysis. In addition the efficiency of the sequential unit in terms of the number of theoretical plates was experimentally determined for the "Genklene" P solute, using the procedure described in Section 8.1.5.

8.1.1 TEST OF REPRODUCIBILITY OF CONCENTRATION PROFILE ANALYSIS

As was mentioned earlier the column to column concentration profile was the main record of performance of the sequential unit during an experimental run. This concentration profile was experimentally determined by the method described in Section 7.3.3. The reproducibility of this concentration profile analysis technique was tested by comparing profiles obtained during two different sequencing cycles from a fixed sample point (see Fig. 8.1) as well as by comparing profiles obtained during two different sequencing cycles, from differing samples points (see Fig. 8.2).

FIGURE 8.1 Experimental test of the reproducibility of the concentration profiles by comparing profiles obtained during two different sequencing cycles from the same sample point

The samples were taken from column 10, 100 sec after sequencing action ——on the 4th cycle - - -on the 7th cycle

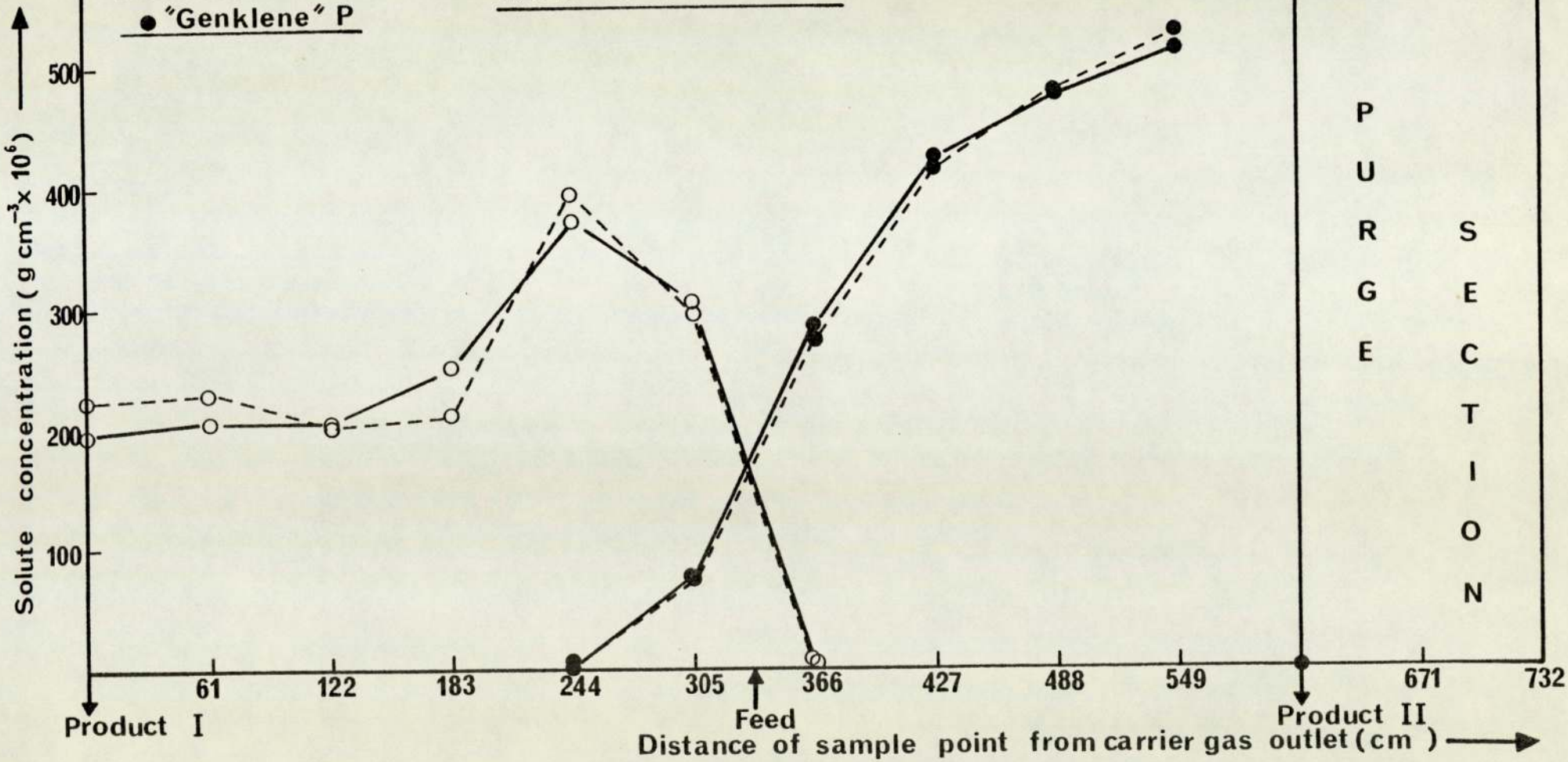


FIGURE 8.2 Experimental test of the reproducibility of the concentration profiles by comparing profiles obtained at different sequencing cycles from differing sample points

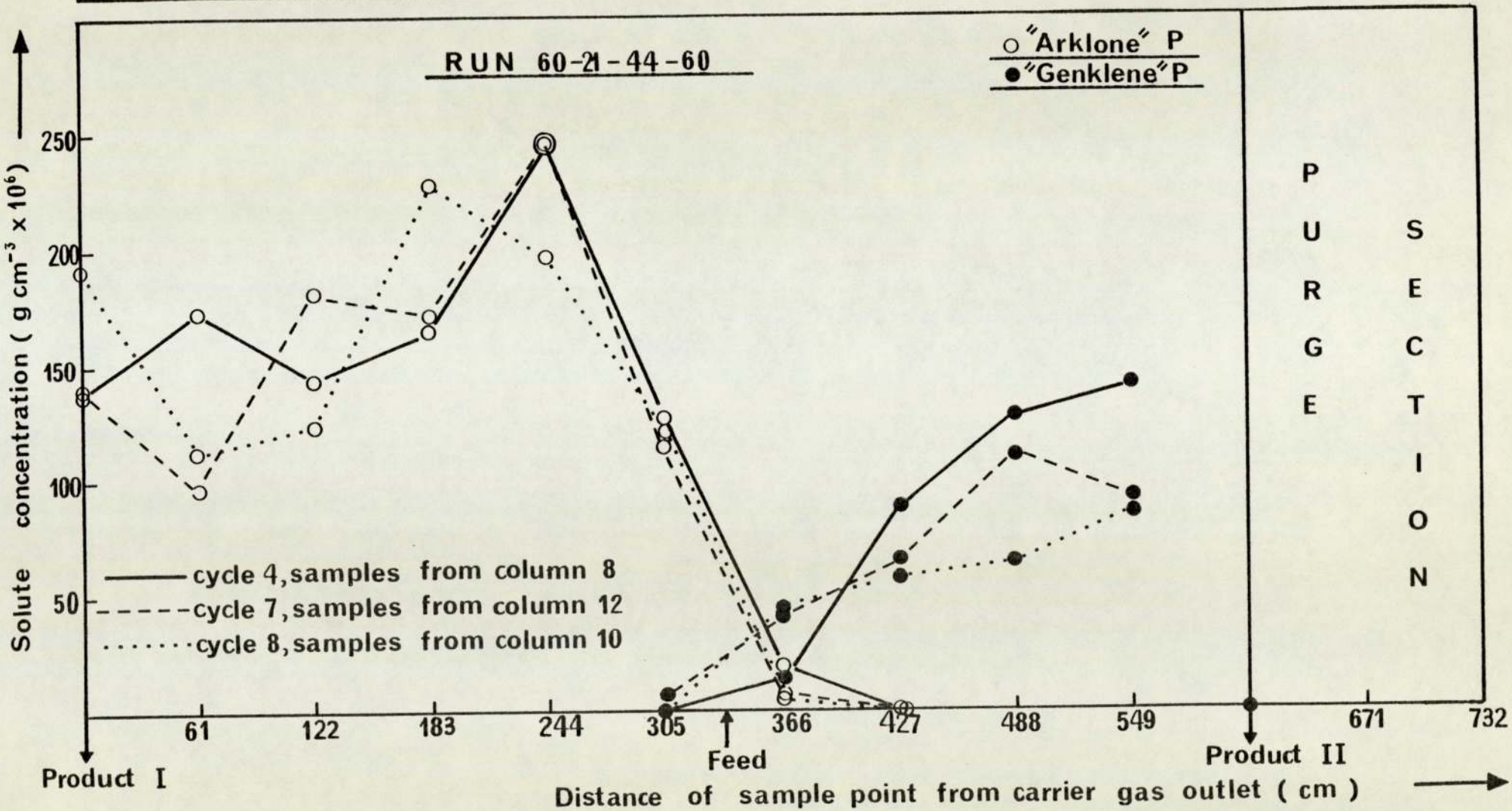


Fig. 8.1 shows that the profiles determined from the same sample point are quite reproducible. This establishes the fact that a pseudo-steady state condition is achieved in the sequential unit. However, one should bear in mind that this column to column concentration profile changes with time during a sequencing interval, due to the semi-continuous nature of operation; although these concentration profile changes are well reproduced from one cycle to the next.

Reasonably reproducible profiles were also obtained from differing sample points (see Fig. 8.2), which suggests well-matched chromatographic columns in the sequential unit. However, it is expected, owing to the column to column variations in bed packing characteristics, that when the unit is operated at conditions close to its separating limits the concentration profiles obtained from differing sample points would be less reproducible.

8.1.2 THE EFFECT OF THE "APPARENT GAS TO LIQUID RATE RATIO" ON THE SEPARATION

8.1.2.1 RESULTS

Description of four experimental runs which record the effect of the apparent gas to liquid rate ratio, $\frac{Gmc}{L'}$, on the performance of the sequential unit are presented in Table 8.1. Further details for the runs and a complete record of the concentration profile analysis are given in Appendix A.3.1.

Each experimental run is denoted by a combination of the four main operating variables; the operating temperature (°C), the feedrate ($cm^3\ h^{-1}$), the ratio of the mean column gas flowrate to the apparent liquid rate, and the sequencing rate (s). Thus, in the present study the runs 60-21-29-130, 60-21-38-130, 60-21-43-130 and 60-21-58-130 show

the effect of increasing the apparent gas to liquid rate ratio, $\frac{Gmc}{L'}$, while maintaining constant the operating temperature, feedrate and sequencing rate. This was achieved by increasing the carrier gas outlet flowrate, Ga, from 4.2 $cm^3\ s^{-1}$ to 8.3 $cm^3\ s^{-1}$.

The mean column purge gas rate, Smc, was always set such that $\frac{Smc}{L'}$ was substantially in excess of the partition coefficient of "Genklene" P at infinite dilution. In addition the purge nitrogen stream was preheated before entering the chromatographic columns to temperatures up to 80°C with the preheating system described in Section 5.2.5.2. These precautions were taken so that the complete removal of "Genklene" P from the purge section at the end of each sequencing interval was ensured.

Table 8.1 also includes the values of the respective partition coefficients at infinite dilution, K^{∞}, determined experimentally as shown in Section 4.1. Also from the average gas flowrates and inlet and outlet pressures for both the separating and purge section, G_{min}/L', G_{max}/L' and S_{min}/L' have been calculated and recorded in the same Table. For each experimental run, the total time of operation, the time to pseudo-steady state condition, the time to quantitative analysis and the determined product purities were also recorded (see Table 8.1).

From the recorded analysis data of the respective experimental runs (see Appendix A.3.1), the column to column concentration profiles were plotted as shown in Figures 8.3.1-8.3.4. It should be noted that solute concentrations which were less than 5×10^{-6} g cm^{-3} have not been included on the concentration profile plots.

TABLE 8.1 : THE STUDY OF G_{mc}/L'
SUMMARY OF OPERATING CONDITIONS

Run title	Temperature			Ambient conditions		Solute mixture feedrate	I_s	L'	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L'	Sa	Pin	Pout	J	Smc/L'
Θ-f-Gmc/L'-I_s	°C	°C	°C	°C	kNm^{-2}	$cm^3 h^{-1}$	s	$cm^3 s^{-1}$	$cm^3 s^{-1}$	kNm^{-2}	kNm^{-2}	—	—	$cm^3 s^{-1}$	kNm^{-2}	kNm^{-2}	—	—
60-21-29-130	60	61	80	20	101	21	130	0.087	4.2	198	184	0.96	28.9	188	184	158	0.93	1460
60-21-38-130	60	63	80	20	100	21	130	0.087	5.5	198	179	0.95	38.1	188	184	156	0.92	1448
60-21-43-130	60	62	80	21	102	21	130	0.087	6.2	198	181	0.95	43.1	212	184	153	0.91	1674
60-21-58-130	60	62	80	19	101	21	130	0.087	8.3	198	177	0.94	58.4	212	184	153	0.91	1670

SUMMARY OF RESULTS

Run title	K^∞		Separating section		Purge section	Total time of run	Total no. of cycles	Time to pseudo steady state	Concentration profile analysis				
	A.P	G.P	Gmin/L'	Gmax/L'	Smin/L'				Time to analysis	Table	Figure	Product Purities	
Θ-f-Gmc/L'-I_s						h		m	m			% A.P	% G.P
60-21-29-130	30	174	28.0	30.1	1348	3.03	7	52.0	58.0	A.3.1.1	8.3.1	>99.9	>99.6
60-21-38-130	30	174	36.3	40.1	1335	3.03	7	52.0	130.0	A.3.1.2	8.3.2	>99.9	>99.8
60-21-43-130	30	174	41.6	45.5	1530	2.60	6	52.0	104.0	A.3.1.3	8.3.3	>99.9	>99.8
60-21-58-130	30	174	55.1	52.1	1525	7.37	17	52.0	104.0	A.3.1.4	8.3.4	>99.9	>99.9

FIGURE 8.3.1 CONCENTRATION PROFILE FOR RUN 60 - 21 - 29 -130

The samples were taken from column 4 —— 80 sec after sequencing action on the 3rd cycle
- - - - 120 sec after sequencing action on the 4th cycle

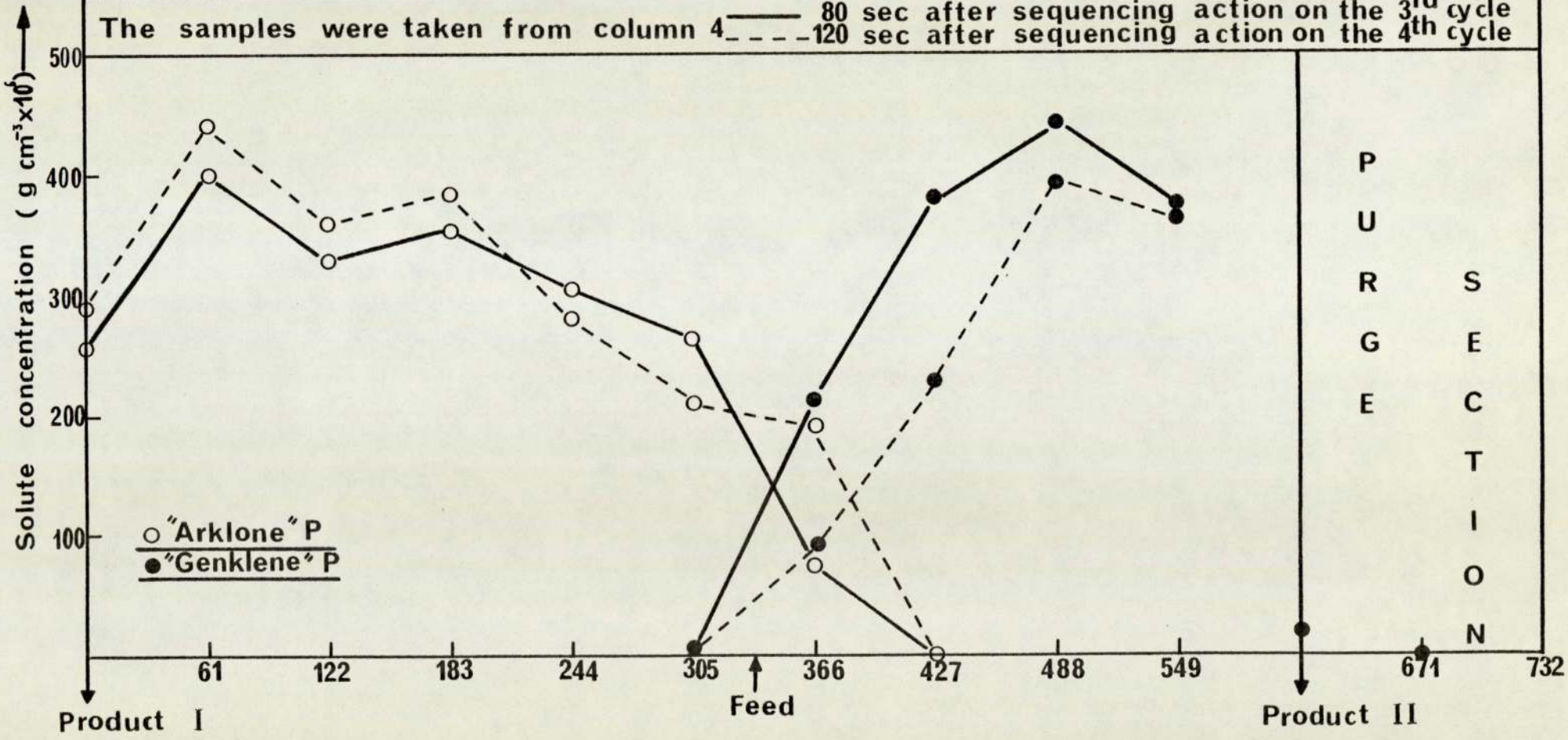
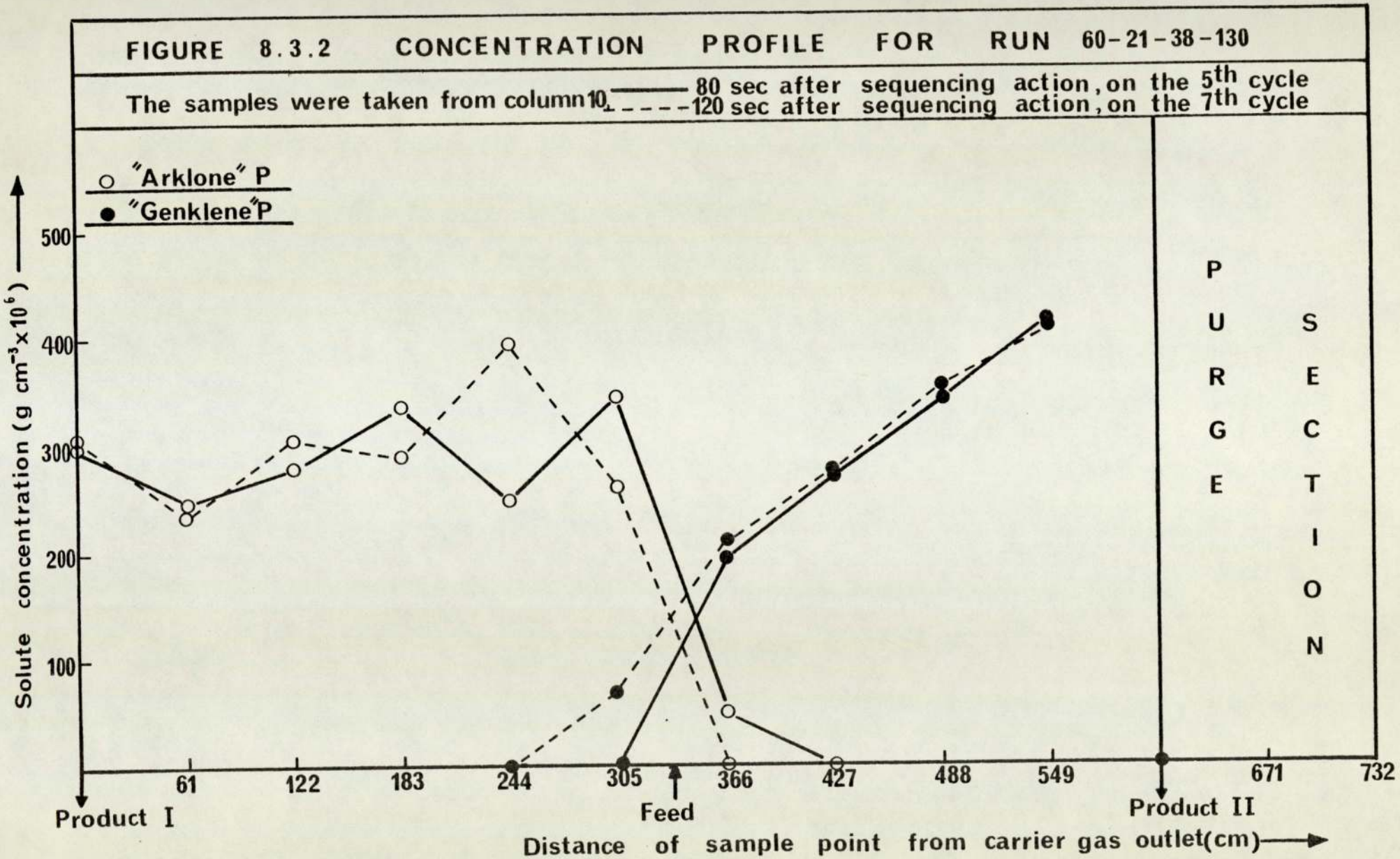


FIGURE 8.3.2 CONCENTRATION PROFILE FOR RUN 60-21-38-130

The samples were taken from column 10, ——— 80 sec after sequencing action, on the 5th cycle
- - - - 120 sec after sequencing action, on the 7th cycle



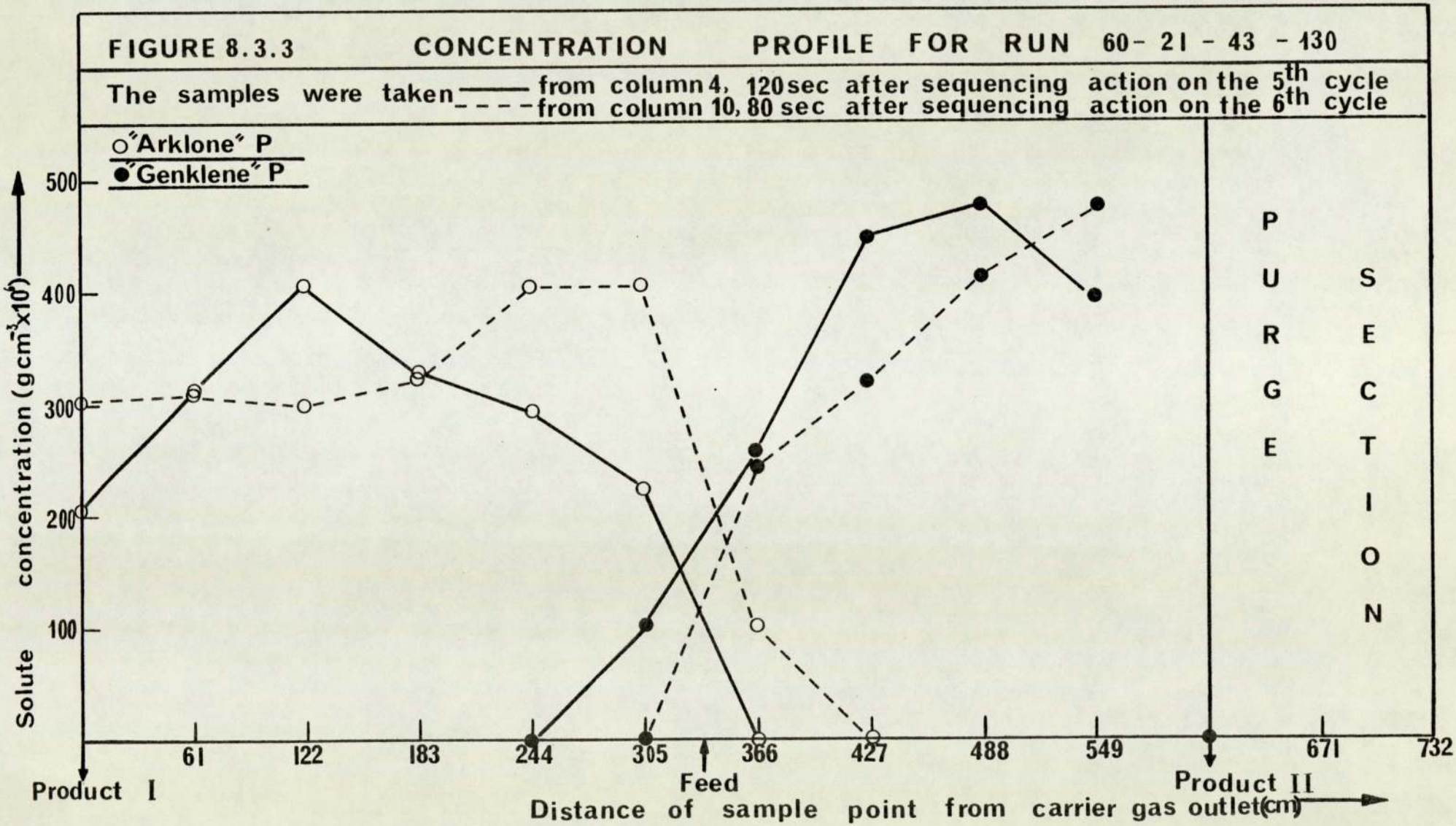


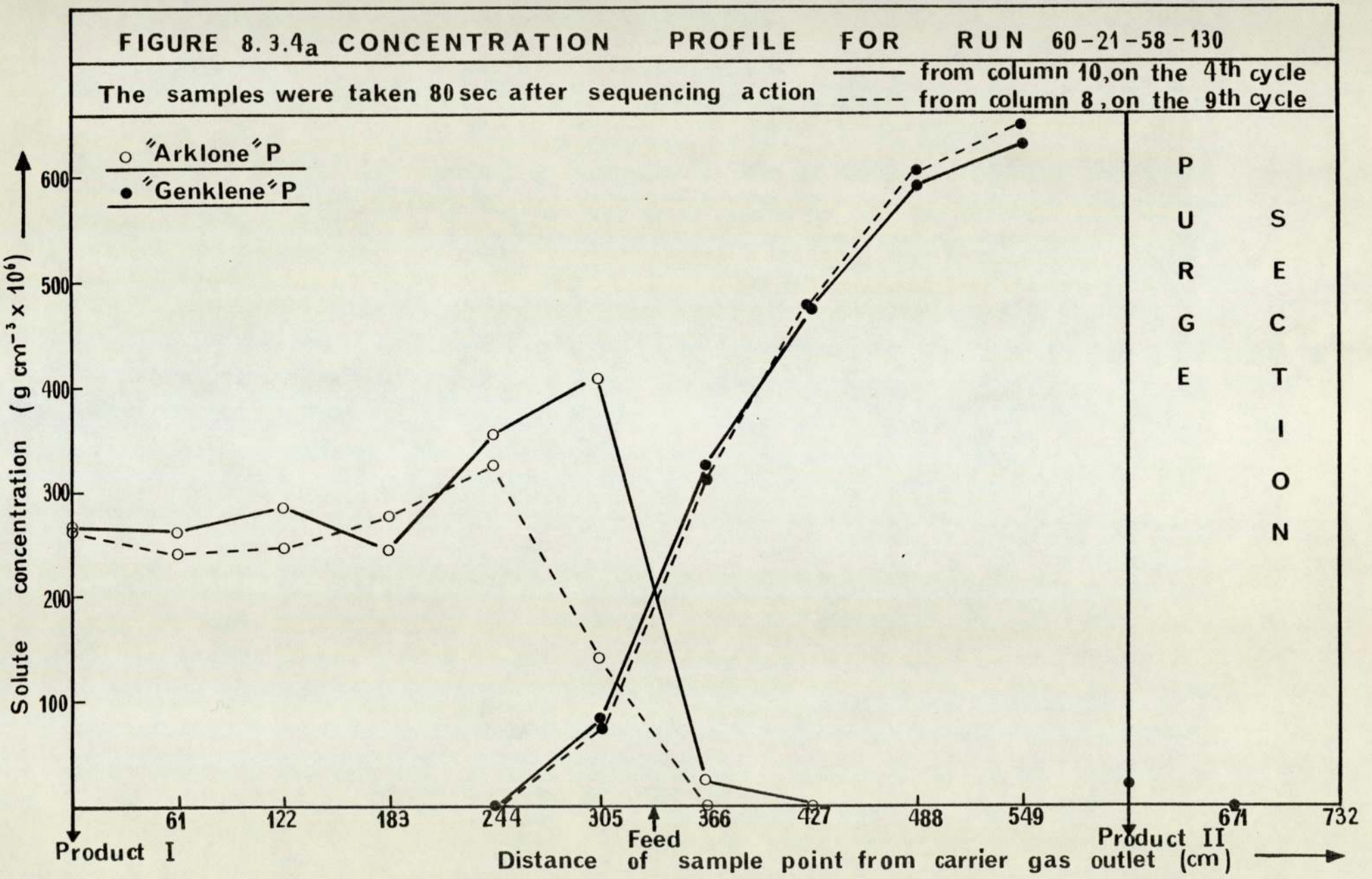
FIGURE 8.3.3 CONCENTRATION PROFILE FOR RUN 60-21-43-130
The samples were taken —— from column 4, 120 sec after sequencing action on the 5th cycle
- - - - from column 10, 80 sec after sequencing action on the 6th cycle
○ "Arklone" P
● "Genklene" P
Solute concentration (gcm⁻³x10⁶)
500
400
300
200
100
61
122
183
244
305
366
427
488
549
671
732
PURGE SECTION
Product I
Feed
Product II
Distance of sample point from carrier gas outlet (cm)

FIGURE 8.3.4a CONCENTRATION PROFILE FOR RUN 60-21-58-130

The samples were taken 80 sec after sequencing action

—— from column 10, on the 4th cycle

---- from column 8, on the 9th cycle



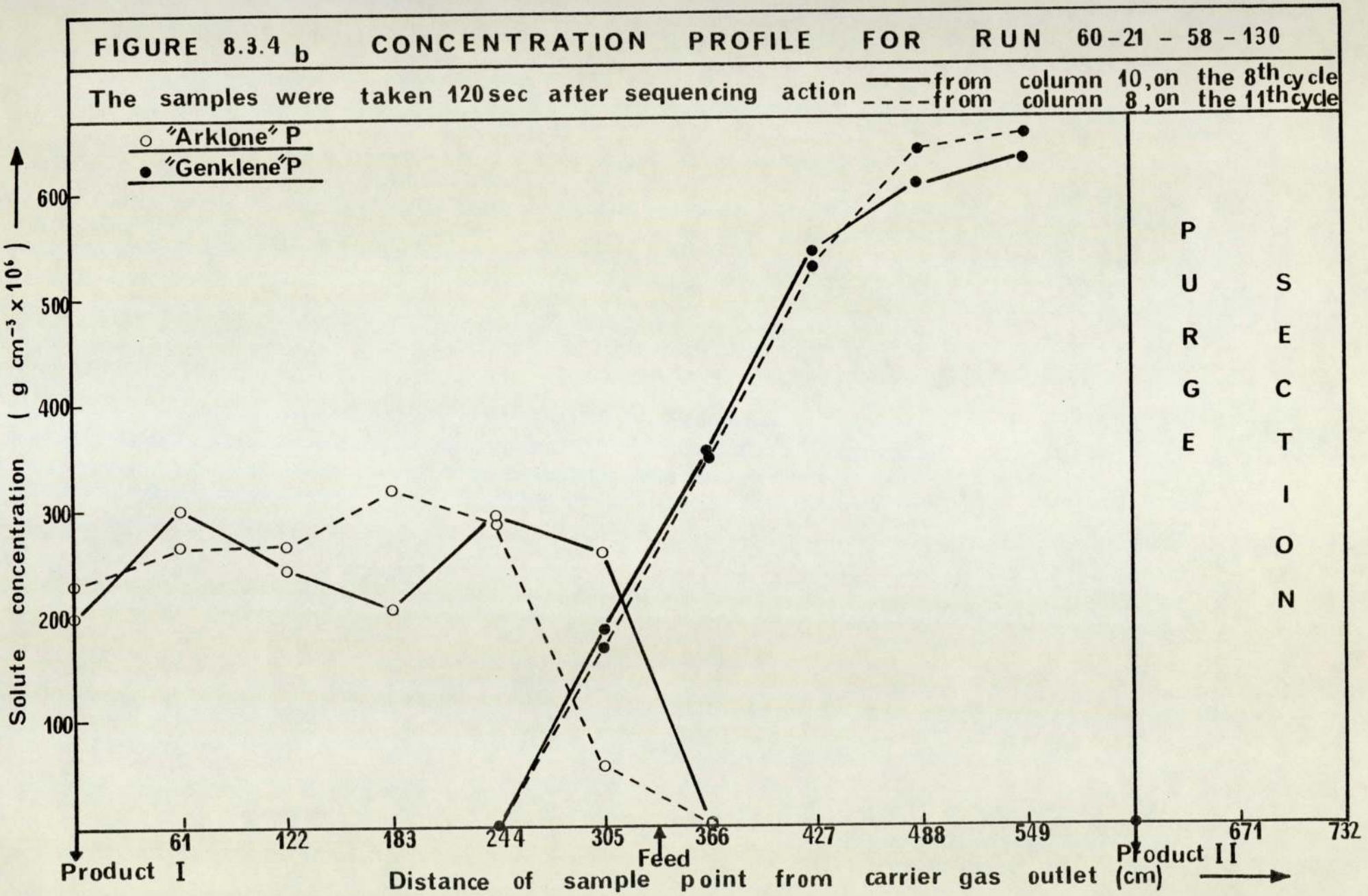


FIGURE 8.3.4 b CONCENTRATION PROFILE FOR RUN 60-21 - 58 - 130
The samples were taken 120 sec after sequencing action ——— from column 10, on the 8th cycle
- - - - from column 8, on the 11th cycle
○ "Arklone" P
● "Genklene" P
Solute concentration (g cm⁻³ x 10⁶)
600
500
400
300
200
100
PURGE SECTION
61
122
183
244
305
366
427
488
549
671
732
Product I
Feed
Product II
Distance of sample point from carrier gas outlet (cm)

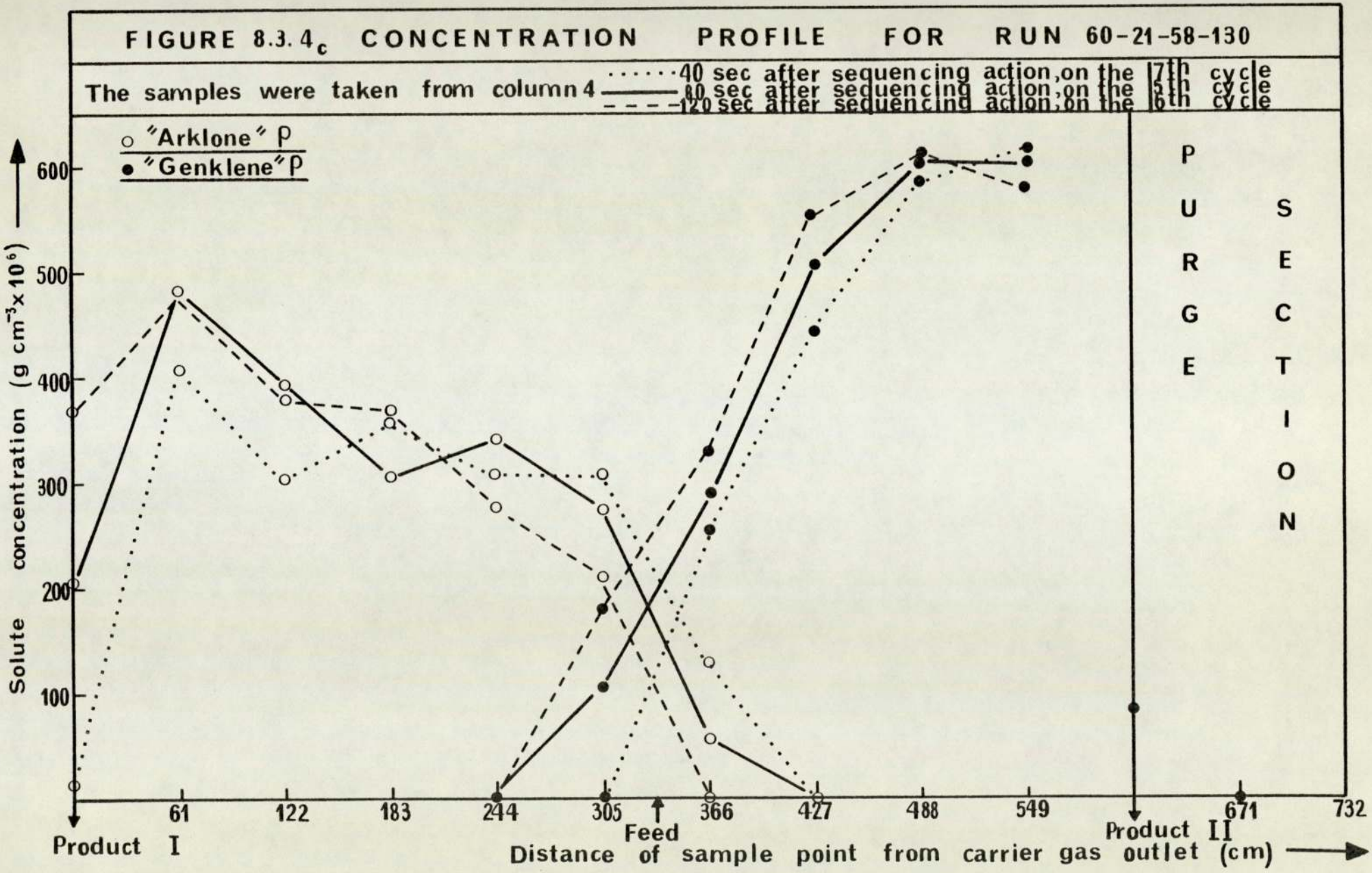


FIGURE 8.3.4c CONCENTRATION PROFILE FOR RUN 60-21-58-130
The samples were taken from column 4
40 sec after sequencing action, on the 7th cycle
80 sec after sequencing action, on the 5th cycle
120 sec after sequencing action, on the 6th cycle
○ "Arklone" ρ
● "Genklene" ρ
Solute concentration (g cm⁻³ x 10⁶)
600
500
400
300
200
100
61
122
183
244
305
366
427
488
549
671
732
Product I
Feed
Product II
PURGE SECTION
Distance of sample point from carrier gas outlet (cm)

8.1.2.2 DISCUSSION

A successful separation was defined as one having product purities in excess of 99.7%.

Considering the results obtained for the experimental runs 60-21-29-130, 60-21-38-130, 60-21-43-130 and 60-21-58-130 conducted at constant temperature, feedrate and sequencing rate, the effect of doubling the $\frac{Gmc}{L'}$ ratio on the successful separation of the "Arklone" P/ "Genklene" P mixture is shown. In selecting the $\frac{Gmc}{L'}$ values, the procedure described in Section 7.1 was adopted, so that the $\frac{Gmc}{L'}$ values were approximately between the partition coefficients of "Arklone" P and "Genklene" P, measured at infinite dilution and the respective operating temperature, 60°C.

The performance of the sequential unit in these experimental runs has shown very little sensitivity to changes in $\frac{Gmc}{L'}$, as is shown in the concentration profiles plotted in Figures 8.3.1-8.3.4. This was expected because of the large differences between the partition coefficients of the feed components (separation factor 5.8 at 60°C) and therefore the wide range of $\frac{Gmc}{L'}$ values for which the successful separation is effected. The ease of separation of the "Arklone" P/ "Genklene" P system is also indicated from the shape of the solute concentration profiles, which have sharp leading and trailing edges (see Figures 8.3.1-8.3.4).

As is shown in the column to column concentration profile plots, only two to three chromatographic columns were used for this separation, the remaining being partially served to improve the purity of both products. This resulted in high product purities (see Table 8.1).

Run 60-21-29-130 produced a product I purity of 99.9% and Product II purity of 99.6%. Increasing the value of $\frac{Gmc}{L'}$ by holding constant L', the mean column carrier gas flowrate Gmc increases, which leads to the two feed components exhibiting a greater preference to move in the direction of the flowing carrier gas stream towards the product I exit port. Thus, as the experimental run 60-21-58-130 demonstrates, the expected increase in product II purity occurs (99.9%) without any loss of product I purity. In addition as the $\frac{Gmc}{L'}$ ratio was increased, with the corresponding increase in the mean column carrier gas flowrate, a general reduction in the "hold-up" of "Arklone" P occurred, while that for "Genklene" P increased (see Figures 8.3.1-8.3.4).

Further increase in the value of $\frac{Gmc}{L'}$ is expected to lead to some loss of product I purity. As the carrier gas flowrate is increased more "Genklene" P molecules will move preferentially in the direction of carrier gas stream towards the product I exit port thus contaminating the product I ("Arklone" P) gas stream. The above effect is demonstrated experimentally for the methyl chloroacetate/ethyl lactate system in Section 8.2.1.

For each experimental run, several concentration profiles have been plotted to show the reproducibility of the separation (see Figures 8.3.1-8.3.4). Thus, column to column concentration profiles at different sequencing cycles, from varying sample points and at different time after the sequencing action, were recorded. In particular, for the experimental run 60-21-58-130, seven concentration profiles were plotted as shown in Figures 8.3.4a-8.3.4c. Despite the sequential nature of operation, the levels of concentration and purities were satisfactorily retained during an experimental run.

8.1.3 THE EFFECT OF "SEQUENCING RATE" ON THE SEPARATION

8.1.3.1 RESULTS

Further experimental runs were performed to show the effect of sequencing rate, Is, on the performance of the sequential unit.

Table 8.2 summarizes the operating conditions employed, and the results obtained for each experimental run. The full details of the runs and a complete record of their concentration profile analyses are included in Appendix A.3.1. Figures 8.4.1-8.4.4 illustrate the column to column concentration profiles, plotted for each run.

In the above separation studies the $\frac{Gmc}{L}$, value was held constant within 43 ± 1, while the sequencing interval, Is, was increased from 60 to 130 seconds. Feedrate and temperature were maintained at constant values of 21 cm^3h^{-1} and 60°C respectively, throughout this set of runs.

8.1.3.2 DISCUSSION

The experimental runs 60-21-44-60, 60-21-43-80, 60-21-42-100 and 60-21-43-130 conducted in this study show the effect of increasing the sequencing rate, while maintaining the value of $\frac{Gmc}{L}$ approximately constant by proportionately reducing the carrier gas flowrate. As the sequencing interval was extended from 60 to 130 seconds, with a corresponding reduction in the carrier gas flowrate, Ga, from 13.3 to 6.2 cm^3s^{-1}, the concentration of "Arklone" P and "Genklene" P more than doubled (see Figures 8.4.1-8.4.4). However, these solute concentration changes were not severe enough to affect the performance of the sequential unit. Thus, the shape of the concentration profiles remained the same throughout these runs, with sharp leading and trailing edges, while the degree of overlap of the two solute profiles was always retained within two to three column-lengths around the feed point.

On increasing the sequencing rate up to 160 seconds no significant change in the present pattern of concentration profiles were observed. However, these runs were performed at slightly different temperatures and are summarized in Section 8.1.4. Further increase of sequencing rate was limited because of the difficulty in controlling very low carrier gas flowrates.

The above studies as well as the ones demonstrated in Section 8.1.2 show that the "Arklone" P/"Genklene" P separation is insensitive to concentration changes. This is typical of the ease of separation of the "Arklone" P/ "Genklene" P system. It is expected that as the difficulty of separation increases, the effect of solute concentration on the successful separation would be more important.

It should also be emphasized that at high feedrates, near the throughput limits of the sequential unit, the degree of overlap of the two solute profiles will be increased and concentration changes will severely effect the separation. However throughputs were kept low at 21 cm^3h^{-1} throughout these experimental runs, so as not to strip the liquid phase from the packing.

As is shown in Table 8.2 increasing the sequencing time interval results in relatively better separations with higher separating product purities. This is probably due to the sequential nature of operation, in which the counter-current movement of the liquid phase relative to the gas phase is imposed by the discontinuous stepping of the port functions around the twelve columns, and the degree to which this discontinuity affects the separation as the sequencing rate increases.

Several concentration profiles have been plotted for each experimental run to show the reproducibility of separation (see Figures 8.4.1-8.4.4). The concentration profiles and product purities were found satisfactorily reproducible within a run.

TABLE 8.2 : The study of Is
SUMMARY OF OPERATING CONDITIONS

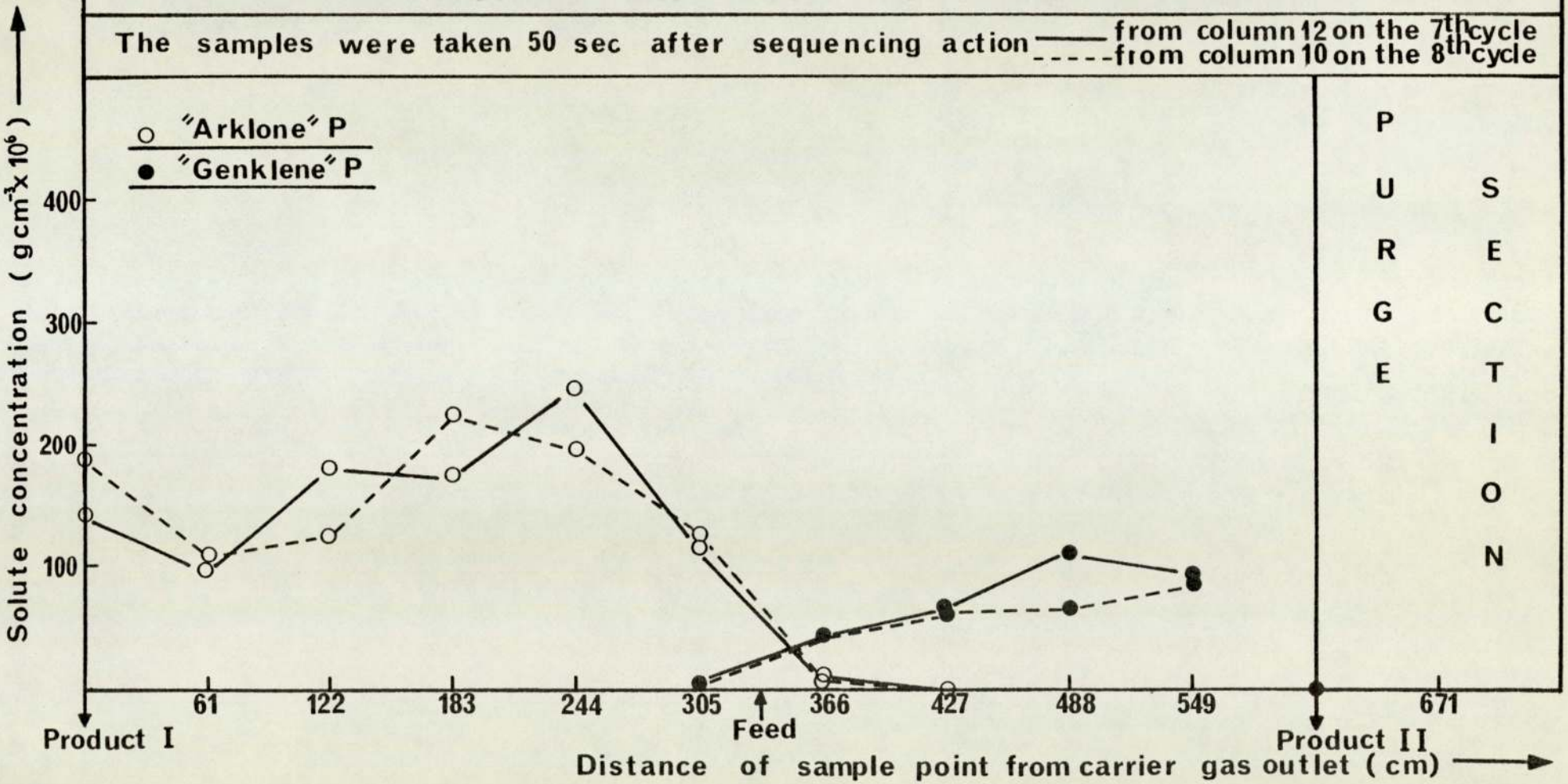
Run title	Temperature			Ambient conditions		Solute mixture feedrate	I_s	L′	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L′	Sa	Pin	Pout	J	Smc/L′
Θ-f-Gmc/L′-I_s	°C	°C	°C	°C	kNm^{-2}	$cm^3\ h^{-1}$	s	$cm^3\ s^{-1}$	$cm^3\ s^{-1}$	kNm^{-2}	kNm^{-2}	—	—	$cm^3\ s^{-1}$	kNm^{-2}	kNm^{-2}	—	—
60-21-44-60	60	62	80	21	101	21	60	0.189	13.3	198	167	0.91	43.8	188	184	158	0.92	662
60-21-43-80	60	63	80	20	100	21	80	0.142	10.0	198	172	0.93	43.3	190	184	159	0.93	889
60-21-42-100	60	63	80	21	101	21	100	0.114	7.9	198	177	0.94	42.1	188	184	157	0.92	1105
60-21-43-130	60	62	80	21	102	21	130	0.087	6.2	198	181	0.95	43.1	212	184	153	0.91	1674

SUMMARY OF RESULTS

Run title	K^∞		Separating section		Purge section	Total time of run	Total no. of cycles	Time to pseudo steady state	Concentration profile analysis				
	A.P	G.P	Gmin/L′	Gmax/L′	Smin/L′				Time to analysis	Table	Figure	Product Purities	
Θ-f-Gmc/L′-I_s						h		m	m			% A.P	% A.P
60-21-44-60	30	174	40.6	48.2	618	1.60	8	24	48	A.3.1.5	8.4.1	>99.6	>99
60-21-43-80	30	174	40.4	46.5	826	3.20	12	32	64	A.3.1.6	8.4.2	>99.8	>99.2
60-21-42-100	30	174	40.0	44.8	1025	4.00	12	40	80	A.3.1.7	8.4.3	>99.8	>99.6
61-21-43-130	30	174	41.6	45.5	1530	2.60	6	52	104	A.3.1.3	8.4.4	>99.9	>99.8

FIGURE 8.4.1 CONCENTRATION PROFILE FOR RUN 60-21-44-60

The samples were taken 50 sec after sequencing action —— from column 12 on the 7th cycle
----- from column 10 on the 8th cycle



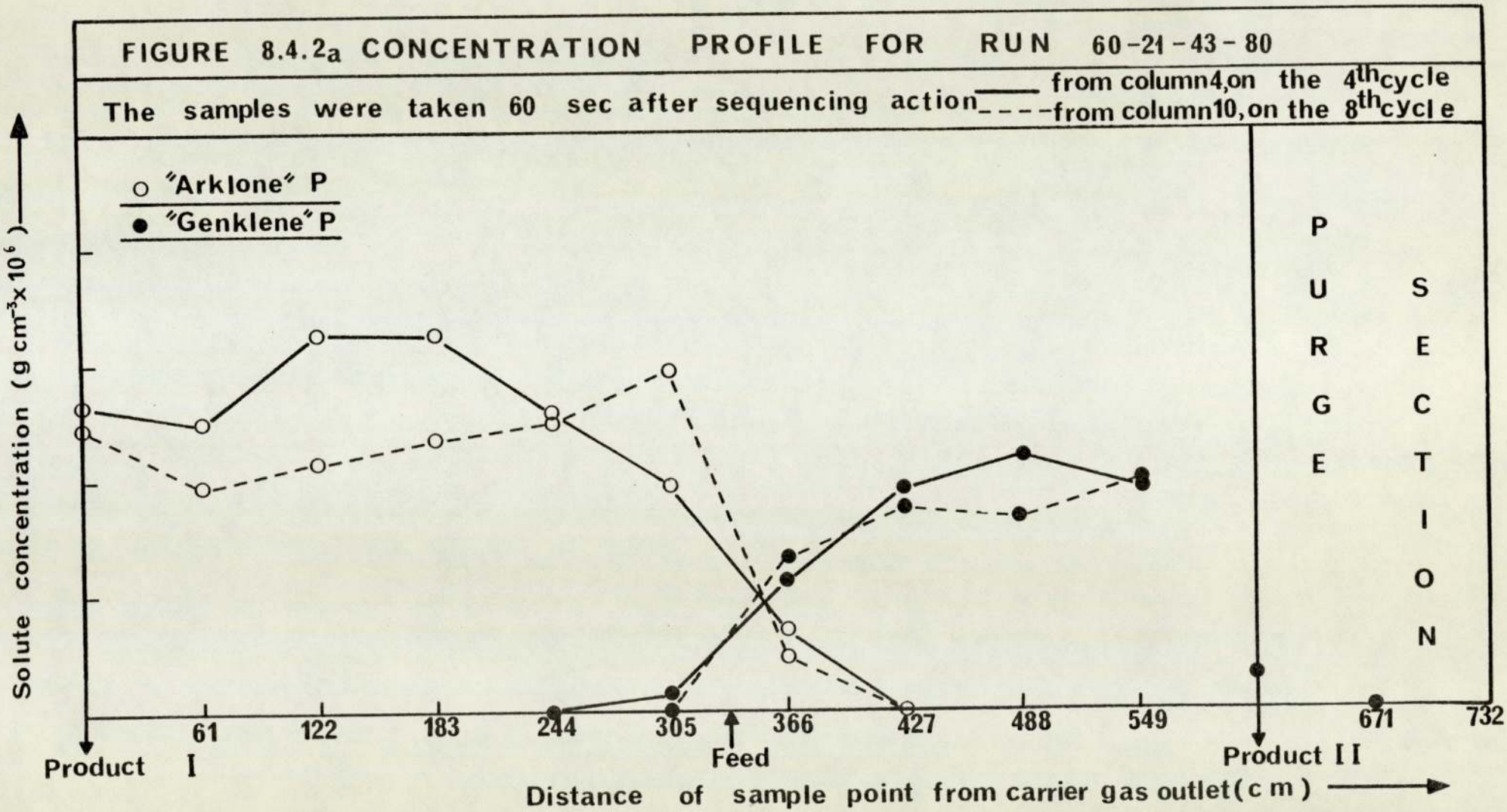
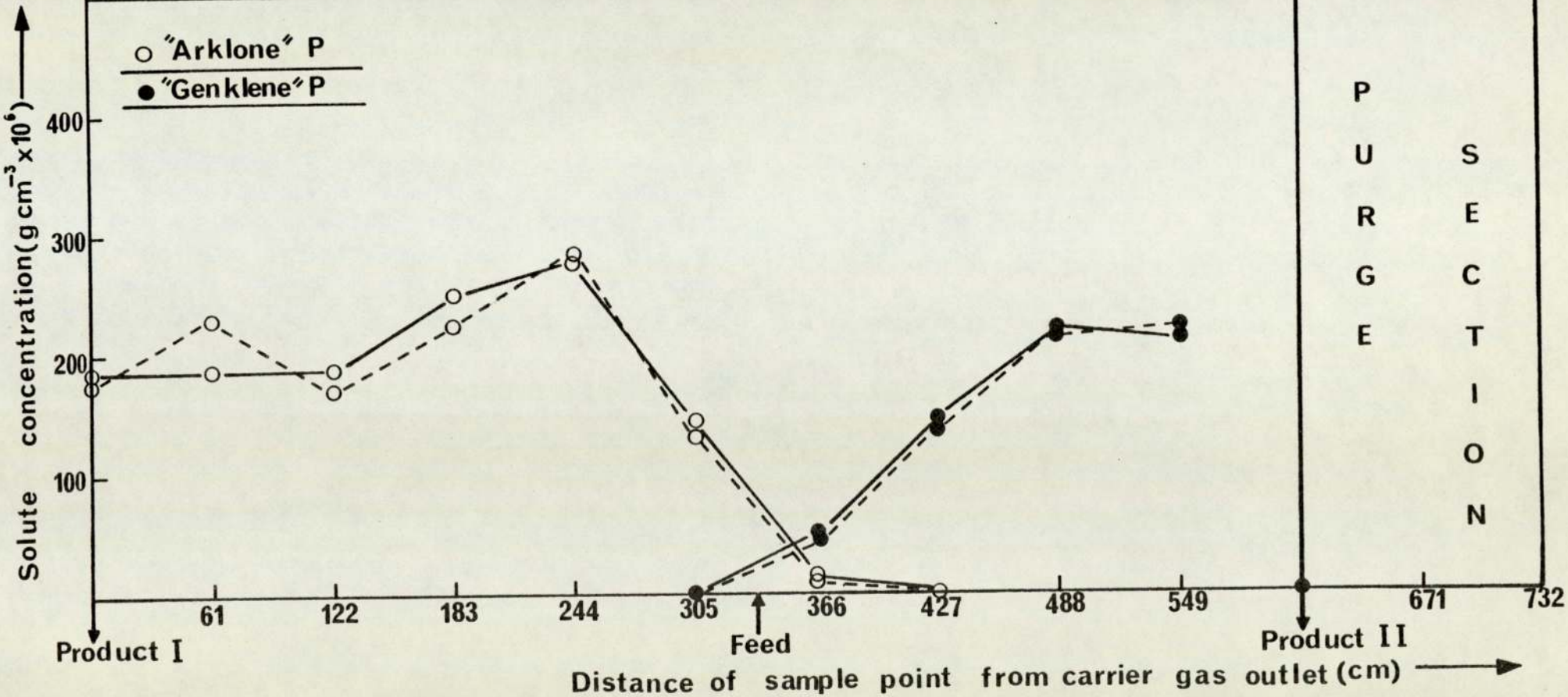


FIGURE 8.4.2a CONCENTRATION PROFILE FOR RUN 60-21-43-80
The samples were taken 60 sec after sequencing action
from column4,on the 4thcycle
from column10,on the 8thcycle
"Arklone" P
"Genklene" P
Solute concentration (g cm⁻³x 10⁶)
PURGE SECTION
61
122
183
244
305
366
427
488
549
671
732
Product I
Feed
Product II
Distance of sample point from carrier gas outlet(cm)

FIGURE 8.4.2b CONCENTRATION ROFILE FOR RUN 60 - 21 - 43 - 80

The samples were taken from column 8,60sec after sequencing action —— on the 10th cycle ---- on the 11th cycle



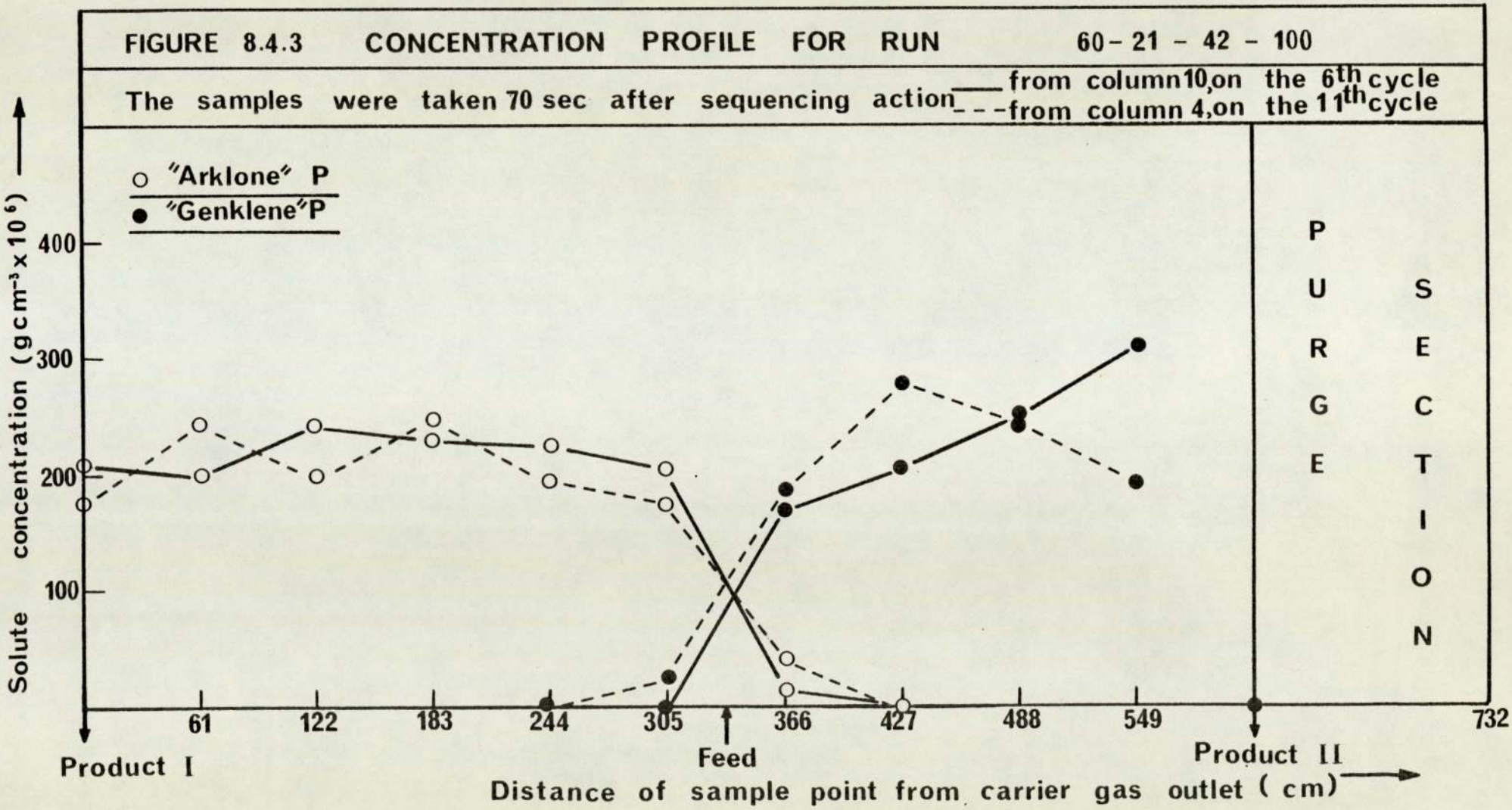
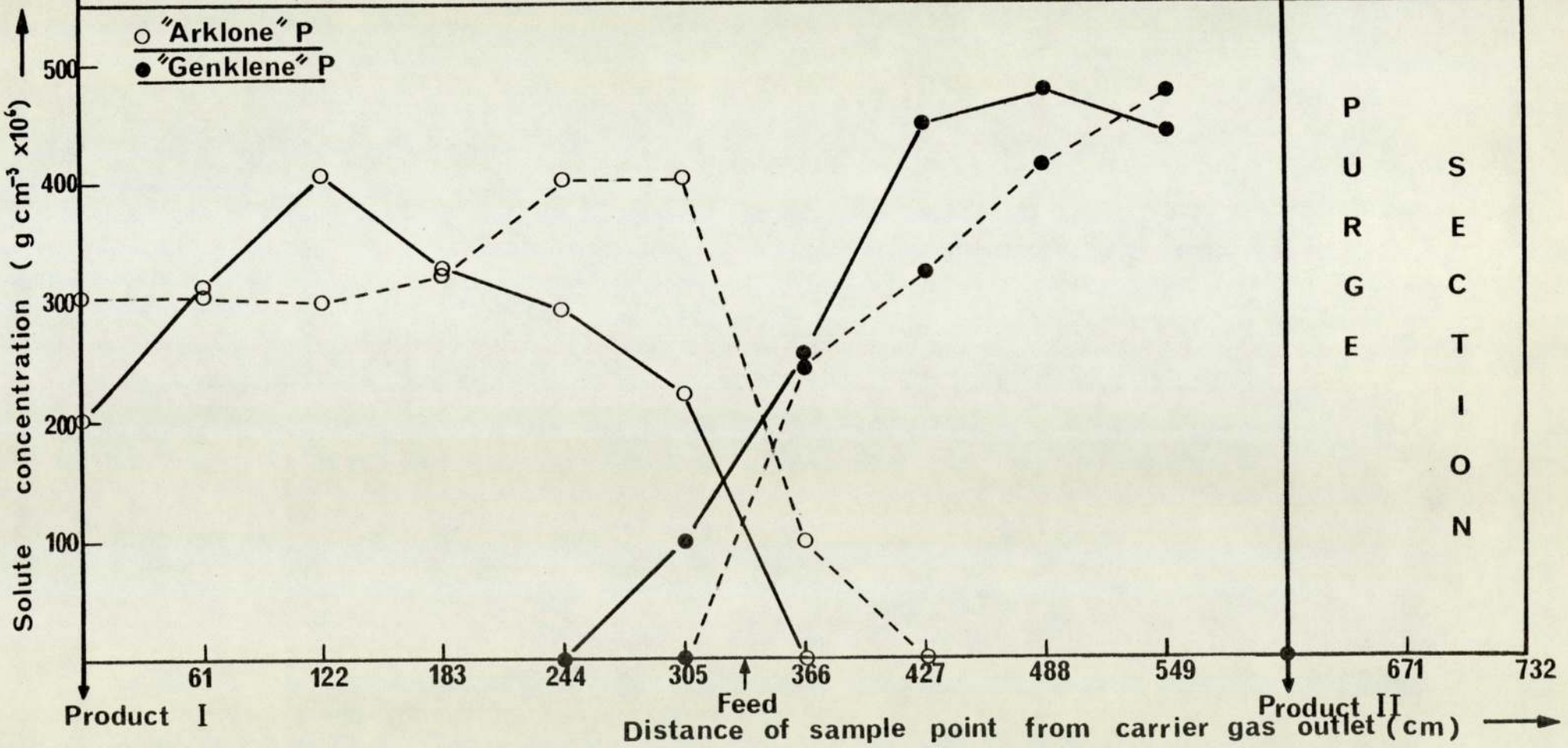


FIGURE 8.4.3 CONCENTRATION PROFILE FOR RUN 60 - 21 - 42 - 100
The samples were taken 70 sec after sequencing action ___ from column 10, on the 6th cycle
- - - from column 4, on the 11th cycle
○ "Arklone" P
● "Genklene" P
Solute concentration (g cm⁻³ x 10⁶)
400
300
200
100
PURGE SECTION
61
122
183
244
305
366
427
488
549
732
Product I
Feed
Product II
Distance of sample point from carrier gas outlet (cm)

FIGURE 8.4.4 CONCENTRATION PROFILE FOR RUN 60 - 21 - 43 - 130

The samples were taken, ——— from column 4, 120 sec after sequencing action on the 5th cycle
- - - - - from column 10, 80 sec after sequencing action on the 6th cycle



8.1.4 THE EFFECT OF "TEMPERATURE"* ON THE SEPARATION

8.1.4.1 RESULTS

Two further runs were performed, in which the operating temperature was increased from 55°C to 65°C, to show the effect of temperature on the performance of the SCCR-2 equipment for the "Genklene" P/"Arklone" P separation. These experimental runs were conducted at a constant feedrate of 21 cm^3h^{-1}, a $\frac{Gmc}{L'}$ ratio of 42, and a sequencing interval of 160 seconds.

Details of the above experimental runs are given in Table 8.3, Figures 8.5.1, 8.5.2 and Appendix A.3.1.

8.1.4.2 DISCUSSION

The above experimental study was restricted to only two runs, and this because of the necessity of operating the sequential unit above 50°C, which is the minimum recommended temperature of the F.F.A.P. liquid phase, and below 70°C in order to avoid partial vaporization of the "Arklone" P/"Genklene" P mixture in the feed distributor. The latter could alter the composition of the binary feed mixture which was introduced into the system, and was considered as an equivolume mixture.

Two experimental runs were performed at constant feedrate, $\frac{Gmc}{L'}$ ratio, and sequencing interval to show the effect of increasing the operating temperature from 55°C to 65°C.

As the operating temperature increased from 55°C to 65°C the partition coefficient values of solutes were reduced, and therefore the feed components increased their preference for the gas phase. However, these partition coefficient changes were small enough, within this limited range of temperatures, not to affect the column concentration

---

* NOTE: Only small range of temperature and two conditions considered.

profiles of "Arklone" P and "Genklene" P to any significant degree (see Figures 8.5.1, 8.5.2) except for the end columns near the "Arklone" P exit. Thus, the shape and degree of overlap of the two solute profiles remained almost the same in both experimental runs, while the product purities were retained the same.

Further tests were carried out in this section to observe the ability of the unit to reproduce concentration profiles; and again the reproducibility in terms of concentration levels and product purities was found to be quite satisfactory (See Figures 8.5.1, 8.5.2.).

TABLE 8.3 : The study of Temperature

SUMMARY OF OPERATING CONDITIONS

Run title	Temperature			Ambient conditions		Solute mixture feedrate	I_s	L'	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L'	Sa	Pin	Pout	J	Smc/L'
Θ-f-Gmc/L'-I_s	°C	°C	°C	°C	kNm^{-2}	$cm^3 h^{-1}$	s	$cm^3 s^{-1}$	$cm^3 s^{-1}$	kNm^{-2}	kNm^{-2}	—	—	$cm^3 s^{-1}$	kNm^{-2}	kNm^{-2}	—	—
55-21-42-160	55	57	75	19	102	21	160	0.071	5.0	198	181	0.95	42.3	173	184	163	0.94	1610
65-21-43-160	65	67	80	20	101	21	160	0.071	5.0	198	184	0.96	42.8	172	184	160	0.93	1641

SUMMARY OF RESULTS

Run title	K^∞		Separating section		Purge section	Total time of run	Total no. of cycles	Time to pseudo steady state	Concentration profile analysis				
	A.P	G.P	Gmin/L'	Gmax/L'	Smin/L'				Time to analysis	Table	Figure	Product Purities	
Θ-f-Gmc/L'-I_s						h		m	m			% A.P	% G.P
55-21-42-160	35	202	40.7	44.6	1517	5.9	11	64	128	A.3.1.8	8.5.1	>99.7	>99.9
65-21-43-160	28	151	41.4	44.6	1534	2.7	5	64	96	A.3.1.9	8.5.2	>99.7	>99.9

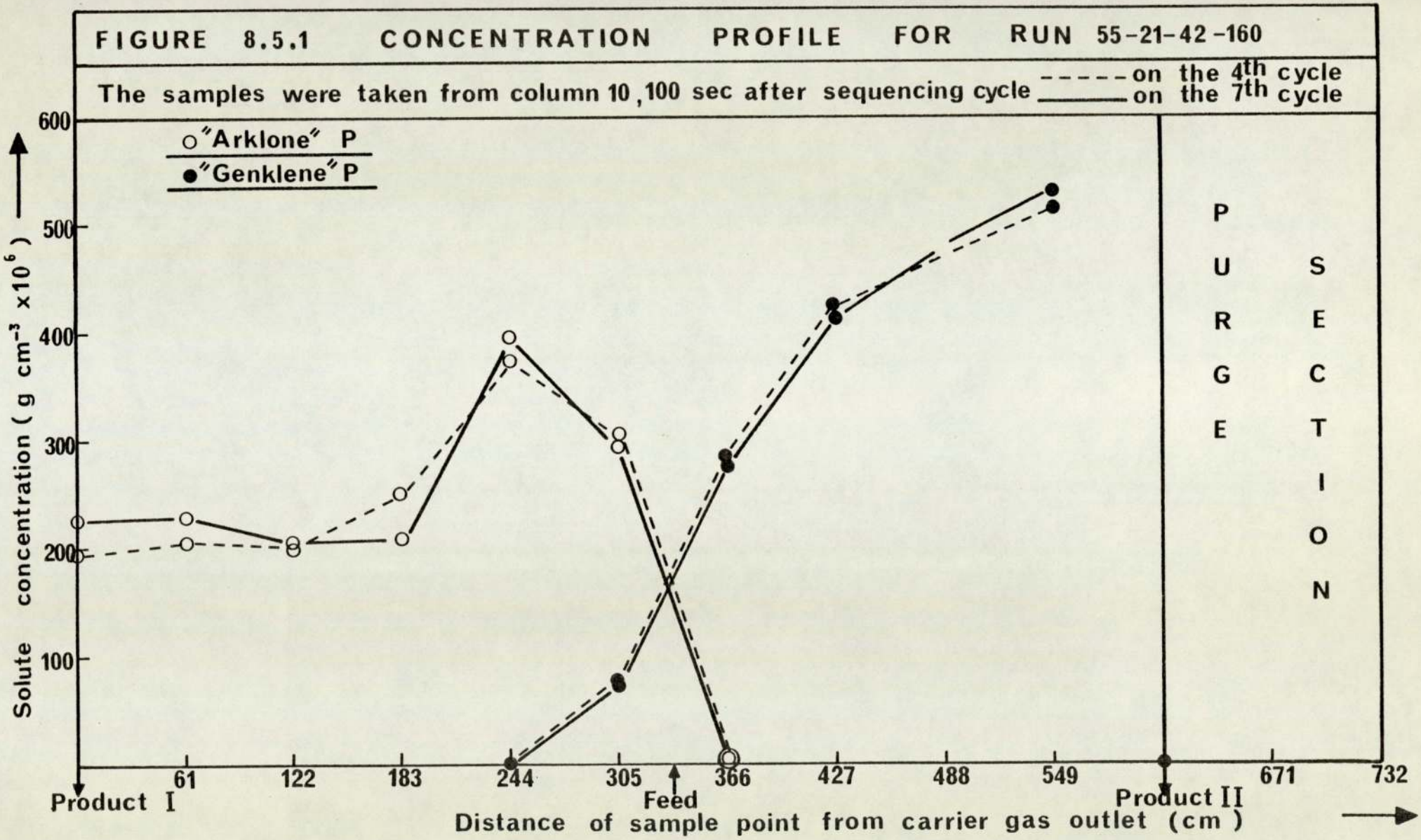
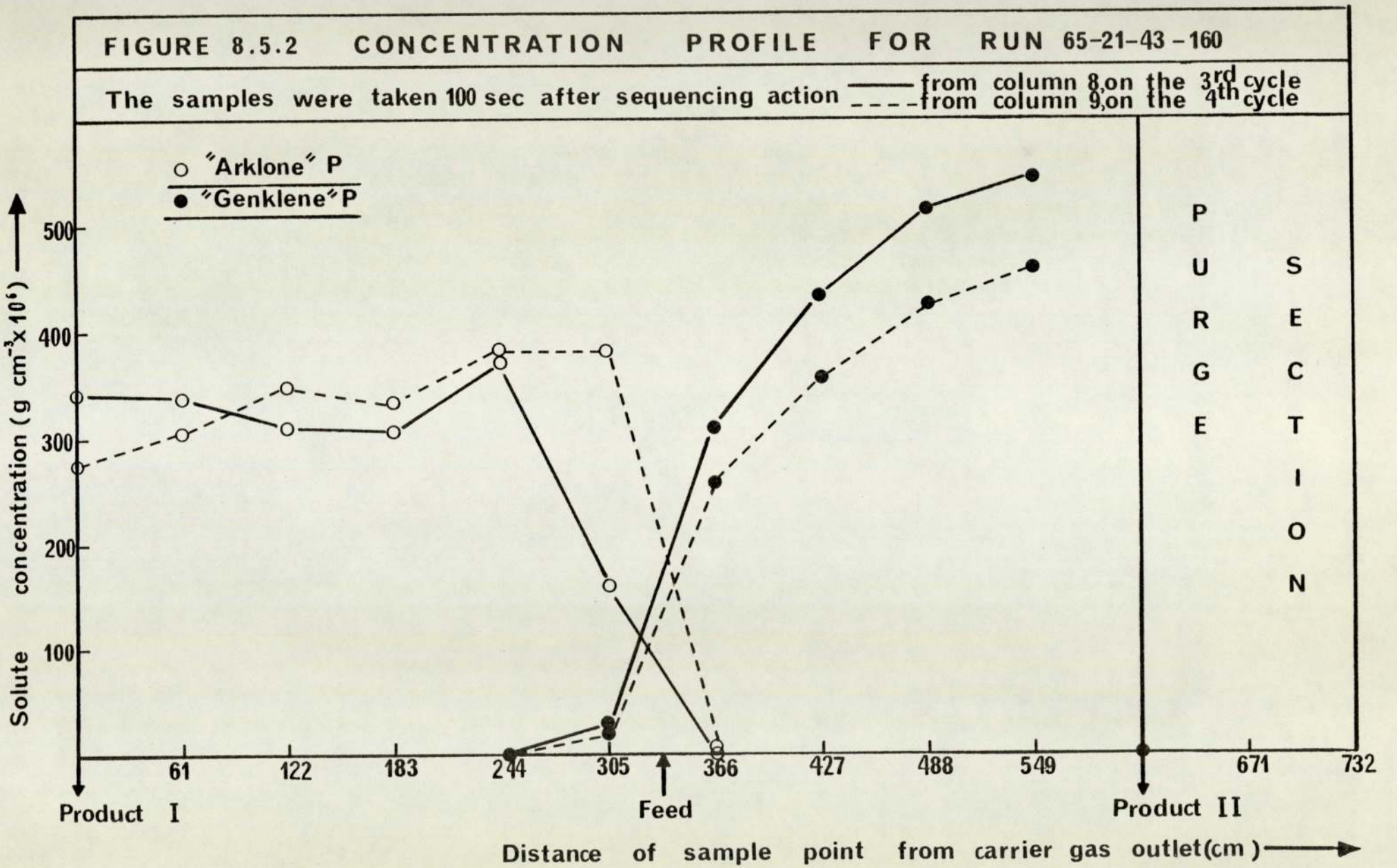


FIGURE 8.5.1 CONCENTRATION PROFILE FOR RUN 55-21-42-160
The samples were taken from column 10, 100 sec after sequencing cycle
----- on the 4th cycle
_____ on the 7th cycle
○ "Arklone" P
● "Genklene" P
Solute concentration (g cm⁻³ x10⁶)
600
500
400
300
200
100
PURGE SECTION
61
122
183
244
305
366
427
488
549
671
732
Product I
Feed
Product II
Distance of sample point from carrier gas outlet (cm)

FIGURE 8.5.2 CONCENTRATION PROFILE FOR RUN 65-21-43-160

The samples were taken 100 sec after sequencing action ——— from column 8, on the 3rd cycle
- - - - from column 9, on the 4th cycle



8.1.5 H.E.T.P. MEASUREMENTS OF THE SCCR-2 CHROMATOGRAPHIC COLUMNS

Before further separation studies were attempted, the efficiency of the sequential unit was estimated. For this reason the efficiency of the SCCR-2 chromatographic columns, measured in terms of H.E.T.P. values, was experimentally determined for the "Genklene" P solute.

8.1.5.1 INTRODUCTION AND EXPERIMENTAL PROCEDURE

Height equivalent to a theoretical plate (H.E.T.P.) as used in the chromatographic field is an empirical quantity relating the width of the eluted peak and column length. Despite the empirical nature of H.E.T.P. and the weakness of plate theory to relate some solute zone broadening mechanisms to it (partition phenomena, molecular diffusion and flow patterns through packed beds), H.E.T.P. has a considerable value for comparing the efficiency of chromatographic columns.

The H.E.T.P. values of two randomly chosen chromatographic columns of the SCCR-2 machine, were experimentally determined under various operating conditions such as gas flowrate and temperature. The purpose of this work was as follows.

(1) To compare the chromatographic efficiency (expressed as H.E.T.P.) of two individual columns of the SCCR-2 unit.

(2) To compare the average determined chromatographic efficiency of the SCCR-2 unit with those obtained by similar sequential units (SCCR-1, SCCR-3).

(3) To determine the effect of carrier gas flowrate and column temperature on the chromatographic efficiency of the SCCR-2 unit.

For this work, the Sternberg theory (178) was employed, which takes into consideration the contribution of factors such as "dead"

volume of column and detector response for the H.E.T.P. determination. According to this theory, H.E.T.P. is given by the following equation.

$$H = \frac{l.\,[(\sigma_t)^2_{r.o} - (\sigma_t)^2_{r.i}]}{[(t_{r.o.c.} + \bar{t}_{r.o}) - (t_{r.i.c.} + \bar{t}_{r.i})]^2} \qquad (8.1)$$

where l : column length

$(\sigma_t)^2$: time based 2nd moment or variance

$\bar{t}_{r.o}, \bar{t}_{r.i}$: peak mean or 1st moment in time units for the recorded outlet and injection profiles respectively

$t_{r.o.c.}, t_{r.i.c.}$: time from injection to commencement of recording the outlet and injection profiles respectively.

Also

$$\bar{t}_{r.o}, \bar{t}_{r.i} = \frac{S_1}{S} = \frac{\sum_{J=1}^{N'} [F(J).I.J]}{\sum_{J=1}^{N} F(J)}$$

$$(\sigma_t)^2 = \frac{S_2}{S} = \frac{\sum_{J=1}^{N'} [F(J).(I.J - \frac{S_1}{S})^2]}{\sum_{J=1}^{N} F(J)}$$

hence

I : time interval between data points (S)

$F(J)$: profile heights in order of recording (cm)

N' : number of profile height data points.

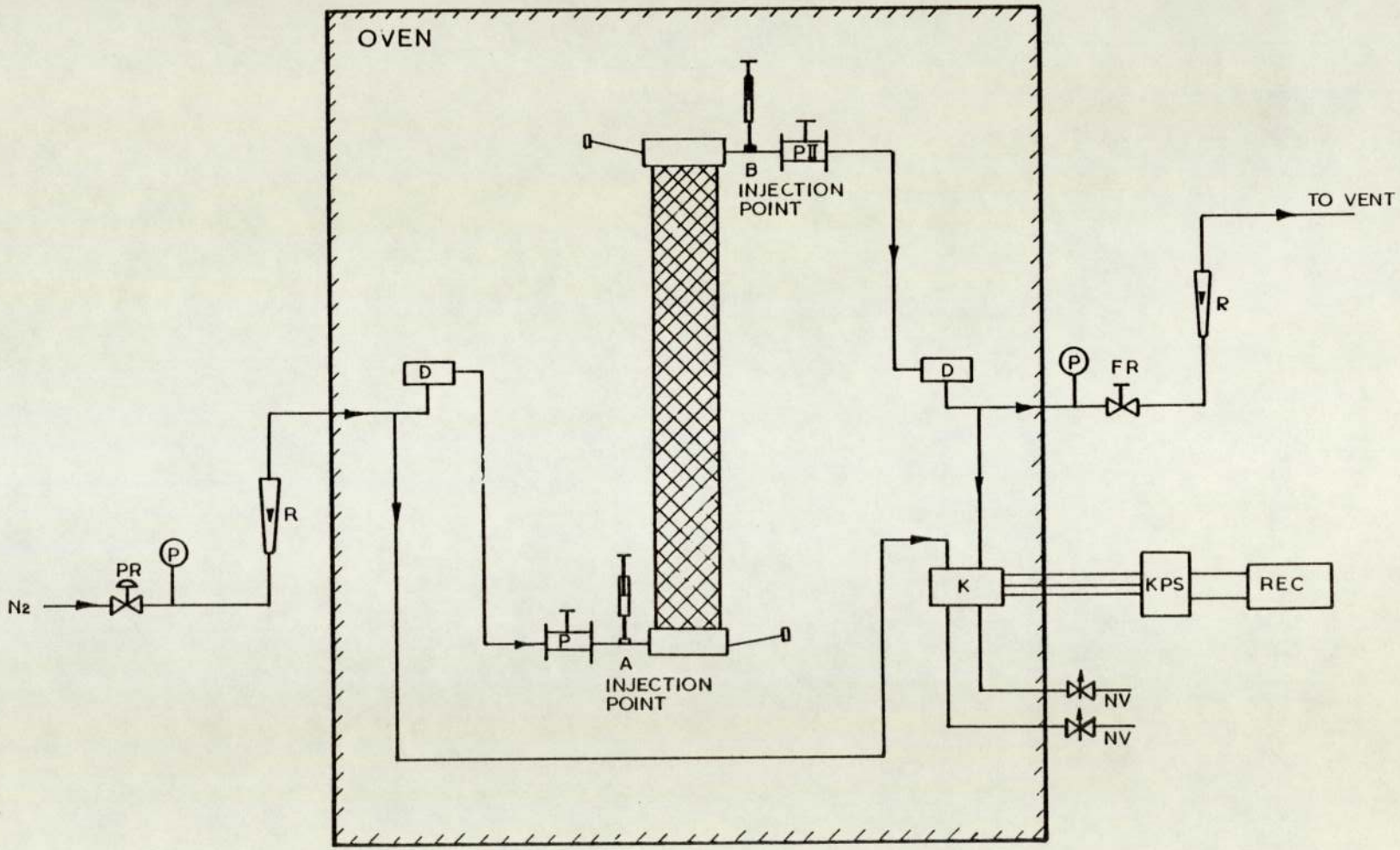
As shown in equation 8.1, the subtraction of the time-based variances or peak means calculated from the outlet and injection profiles cancels the contribution from the extra-column factors such

as the "dead" volume of the column inlet and outlet lines, detector response etc. Also, subtraction of the respective peak retention times gives the retention time solely attributable to the chromatographic column. Obviously, this implies that both the injection and outlet profiles are recorded under the same operating conditions (sample size, gas flowrate,temperature) with a common detection system.

For the H.E.T.P. measurements of the SCCR-2 columns, the arrangement illustrated in Fig. 8.6 was employed. Basically, one column was isolated from the sequential unit and a constant inlet gas pressure applied. The outlet volumetric flowrate was also held constant by a flow regulator, while the column temperature was adjusted by the oven's controller device. A 0.1 cm^3 sample of "Genklene" P was injected into the gas stream flowing into the column, at A (Fig 8.6). The solute profile obtained, which represents the outlet profile was monitored by the Katharometer in conjunction with the pen recorder. By injecting the same volume of "Genklene" P at position B, the injection profile was monitored by the Katharometer. The attenuation of the Katharometer bridge circuit meanwhile was adjusted so as to give a near full scale response for the emerging peaks on the recorder.

For each injection and outlet profiles the respective t r.i.c. and tr.o.c times were measured by an accurate stopwatch. In addition from each profile, the values of peak heights at equal time increments were read on the calibrated recorder chart. The time increment was chosen to give at least 30 values of peak height, which is the minimum for statistical significance. The data taken for a pair of injection and outlet profiles were then applied to equation 8.1 for the H.E.T.P. determination.

FIGURE 8·6 THE ARRANGEMENT OF SCCR-2 COLUMN FOR H.E.T.P. DETERMINATION



LEGEND			
	P = PRESSURE GAUGE	D = DISTRIBUTOR	K = KATHAROMETER
	R = ROTAMETER	P = PURGE DIAPHRAGM VALVE	KPS = KATHAROMETER POWER SUPPLY
	NV = NEEDLE VALVE	PII = PRODUCT II DIAPHRAGM VALVE	R = RECORDER

8.1.5.2 RESULTS AND DISCUSSION

H.E.T.P. determinations have been carried out with the equipment illustrated in Fig. 8.6, for the columns 8 and 12 of the sequential unit, using 0.1 cm^3 of "Genklene" P as the injected sample.

The reproducibility of the experimental technique was studied by repeating the injection and recording procedure for one column under the same operating conditions and reproducible H.E.T.P. values to within 5% were found.

A summary of the calculated H.E.T.P. values with the respective operating conditions employed for their determinations is shown in Table 8.4.

Comparing the chromatographic efficiencies (H.E.T.P.) of columns 8 and 12 under the same operating conditions (Table 8.4), it is suggested that a significant variation in H.E.T.P. values exists for the individual columns of the SCCR-2 unit. Similar findings were obtained by R. Deeble (20) and J. Ellison (61), using similar sequential units. However, this column to column variation in H.E.T.P. is less important to the successful operation of the SCCR-2 unit, since 10 columns are linked together and the variation in the total number of "plates", in the separating section at any time is considerably reduced. In addition, when the SCCR-2 unit is used at high solute concentrations, the H.E.T.P. values of individual columns would be expected to increase, and the column to column variation in H.E.T.P. to diminish. This effect has been recorded experimentally by R. Deeble (20).

The determined chromatographic H.E.T.P. values are relatively high but have the same order of magnitude to these obtained by similar sequential units (20,61). High H.E.T.P. values somehow represent a

TABLE 8.4 SUMMARY OF THE H.E.T.P. DETERMINATIONS FOR THE SCCR-2 UNIT

Assigned column number	Mean carrier gas velocity	Column Temperature	Injection profile			Outlet profile			Number of theoretical plates	H.E.T.P.
			$t_{r.i.c.}$	$\bar{t}_{r.i}$	$(\sigma_t)^2_{r.i}$	$t_{r.o.c.}$	$\bar{t}_{r.o}$	$(\sigma_t)^2_{r.o}$		
	$cm\ s^{-1}$	°C	s	s		s	s			cm
8	0.65	85	9	37.7	791.8	118	67.9	1508	27	2.25
8	1.39	85	9	37.1	912.5	100	59.8	1046	97	0.63
8	3.47	85	7	31.7	655.1	56	42.7	708.1	68	0.90
8	5.01	85	7	29.2	698.3	47	37.3	733.9	65	0.94
8	1.39	75	9	39.2	940.2	118	66.9	1174	80	0.76
8	1.39	60	9	40.3	967.9	138	72.4	1475	51	1.19
12	1.39	85	9	43.1	1811	151	114.6	1037	61	1.00
12	2.09	80	8	41.7	1365	120	101.7	959.9	73	0.83
12	2.82	75	9	37.1	1578	132	106.1	9529	61	1.0

limitation of the separating potential of the SCCR-2 unit with difficult separations. But it is expected by using finer packing particles and improved packing techniques a more efficient sequential system could be obtained.

Finally the variation of H.E.T.P. with carrier gas velocity and temperature for the column 8 of the sequential unit is illustrated in Fig. 8.7. This suggests the importance of identifying the operating conditions (solute, sample size, chromatographic column description, gas flowrate and temperature) for the H.E.T.P. determination and the expected wide range of H.E.T.P. values for the SCCR-2 unit, under the employed conditions for separation studies.

Consequently, the absolute H.E.T.P. values obtained, will not apply to each experimental run achieved with the SCCR-2 unit, unless similar operating conditions were used. For this to be achieved determination of H.E.T.P. values for each individual run would be required. In addition it should be emphasized that the above H.E.T.P. measurements were made in batch mode, while in practice the separation process which takes place in the sequential unit is semi-continuous. Therefore, the obtained H.E.T.P. data have only qualitative value in comparing the column to column variations in the sequential unit and also in comparing with the H.E.T.P. values obtained by other workers on similar sequential units.

FIGURE 8.7a The effect of carrier gas velocity on the chromatographic efficiency of SCCR-2 columns

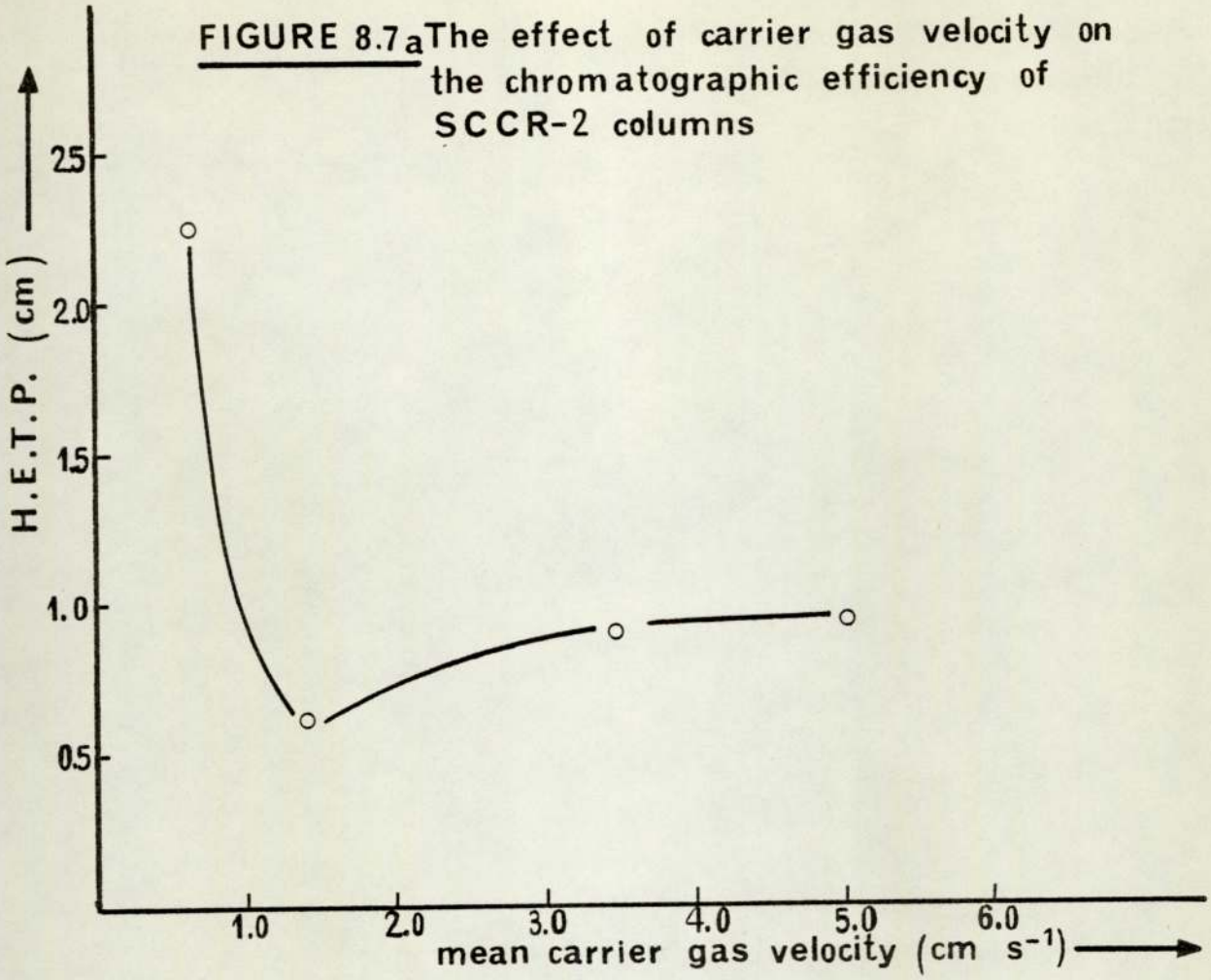
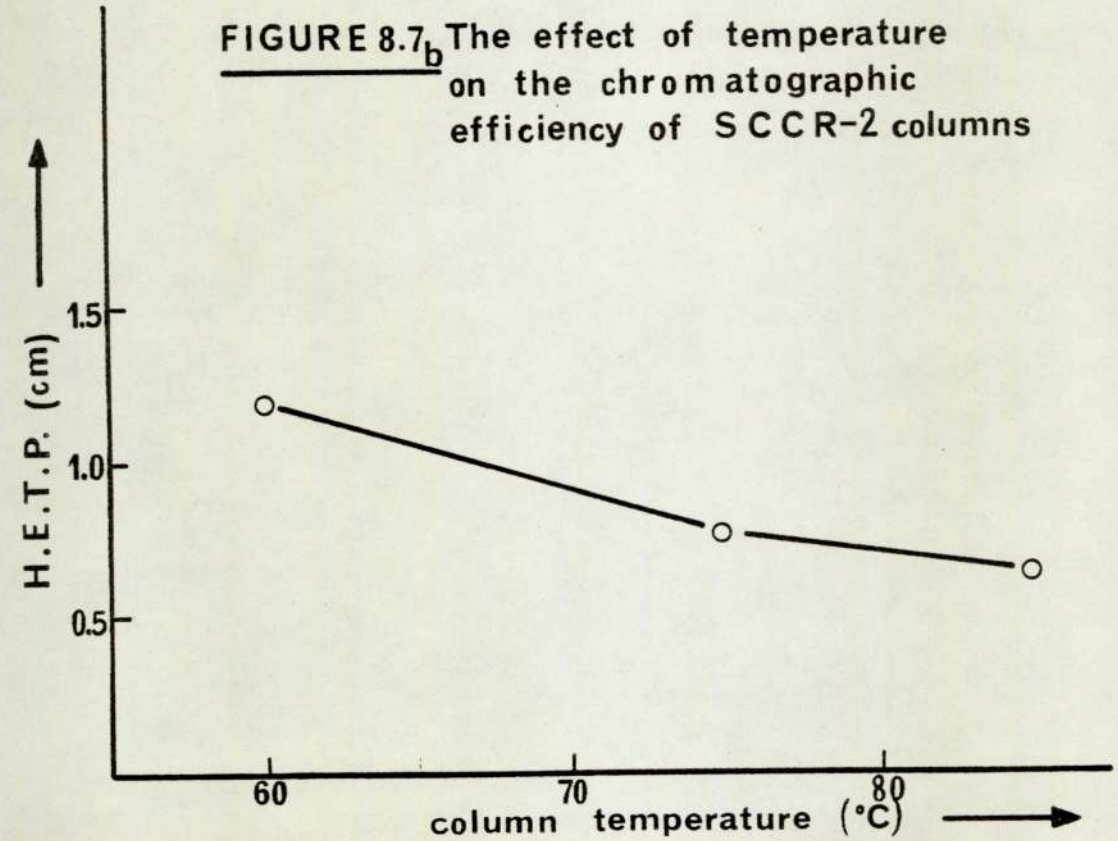


FIGURE 8.7b The effect of temperature on the chromatographic efficiency of SCCR-2 columns



8.2 THE SEPARATION OF METHYL CHLOROACETATE/ETHYL LACTATE

The separation of more difficult systems such as a 50/50 V/V mixture of methyl chloroacetate/ethyl lactate has been studied on the SCCR-2 equipment. The factors governing the choice of chemical systems for separation study have been outlined in Section 6, along with the properties of the selected chemicals.

The partition coefficient values at infinite dilution for methyl chloroacetate and ethyl lactate, which were experimentally determined in Section 4.1, give a separation factor of 1.5 at 120°C. This indicates a relatively difficult separation in comparison with that of "Arklone" P/"Genklene" P, previously studied.

In the present study 17 experimental runs were performed to show the effect of four significant operating variables such as feedrate, temperature, sequencing rate and apparent gas to liquid rate ratio, on the performance of the sequential unit. The range of throughputs covered was 21-80 cm^3h^{-1} and the operating temperatures were within the range of 105-130°C. The main records of performance of the sequential unit on these separation studies were again the column to column concentration profile analysis and the separating product purities.

The presentation of the experimental results followed the same format as the "Arklone" P/"Genklene" P separation studies.

8.2.1 THE STUDY OF $\frac{"Gmc"}{L^1}$

8.2.1.1 RESULTS AND DISCUSSSION

Two sets of experimental runs were performed to show the effect of increasing the $\frac{Gmc}{L^1}$ ratio by increasing the carrier gas flowrate, while holding constant the sequencing rate.

The first set, includes the experimental runs 105-21-378-300, 105-21-413-300 and 105-21-444-300, which were conducted at 105°C, a sequencing rate of 300 s and at a constant solute feedrate of 21 cm^3s^{-1}. Details of these experimental runs are presented in Table 8.5, Figures 8.8.1-8.8.3 and Appendix A.3.2.

Increasing the $\frac{Gmc}{L'}$ ratio from 378 to 444 by proportionately increasing the carrier gas flowrate, Ga, from 21.3 to 25.0 cm^3s^{-1}, permitted observation of the concentration profiles from one extreme, loss of purity of product II, to the other, product I impure (see Table 8.5 and Figures 8.8.1-8.8.3).

For run 105-21-378-300, the values of $\frac{Gmc}{L'}$ and $\frac{G_{min}}{L'}$ being quite close to the partition coefficient, K^{∞}, of methyl chloroacetate, resulted in severe loss of product II purity, the methyl chloroacetate profile covering the entire length of the separating section.

Increasing the value of $\frac{Gmc}{L'}$ leads to the two components exhibiting a greater preference to move in the direction of the flowing carrier gas stream towards the product I exit port. This resulted in a general reduction in the concentration level of methyl chloroacetate, while that for ethyl lactate increased. Consequently, as run 105-21-413-300 demonstrates the expected increase in product II occurs without any loss of product I purity.

Further increase of $\frac{Gmc}{L'}$ ratio, however results in some loss of product I purity. Thus, at a $\frac{Gmc}{L'}$ ratio of 444 (run 105-21-444-300) the ethyl lactate had developed a long leading edge which contaminated the methyl chloroacetate exiting as product I. In this case the $\frac{Gmc}{L'}$ and $\frac{G_{max}}{L'}$ values were too close to the partition coefficient value, K^{∞}, of ethyl lactate so that the inequality defining the upper limit for successful separation was unfulfilled (see equations 7.7-7.8).

The reproducibility of concentration profile analysis has been again demonstrated, for the methyl chloroacetate/ethyl lactate system, by comparing solute concentration profiles obtained at different sequencing cycles from varying sample points. As is shown for the runs 105-21-378-300 and 105-21-444-300, the reproducibility of separation in terms of concentration levels and product purities was satisfactorily retained during an experimental run.

For the second series of runs (see Table 8.6) similar findings were obtained, which re-emphasises the importance of $\frac{Gmc}{L'}$ to the successful separation of the methyl chloroacetate/ethyl lactate system. The purpose of these further experimental studies was to provide a better insight into the operating limits of the $\frac{Gmc}{L'}$ ratio for a successful separation, and to experimentally determine the "optimum" $\frac{Gmc}{L'}$ ratio for which high purities for both product streams are obtained.

The operating conditions for this second series of runs were different to those of the previous set of experimental runs. Thus, the effect of increasing the $\frac{Gmc}{L'}$ ratio is now studied at constant temperature of 110°C, a sequencing rate of 200 s, and at an approximately constant feedrate of 40 cm^3h^{-1}.

Details of the experimental runs 110-38-273-200, 110-40-313-200, 110-40-351-200, 110-37-365-200 and 110-40-425-200, which provide the second series of runs, are presented in Table 8.6, Figures 8.8.4-8.8.8 and Appendix A.3.2.

The shape of the solute concentration profiles, given in Figures 8.8.4-8.8.8, were as expected similar to those experi enced in the previous set of runs, having the same effects on the $\frac{Gmc}{L'}$ ratio variations.

At the "optimum" experimentally determined $\frac{Gmc}{L'}$ ratio (365) for which the best experienced separation is effected (run 110-37-365-200),

the solute concentration profiles had sharp leading and trailing edges, while the degree of overlap of the two solute profiles was within four column-lengths around the feed point. Similar findings were recorded for run 105-21-413-300, which was considered as the most successful in the first series of runs; only the solute concentration levels changed due to the lower feed throughputs employed for the latter run.

For both series of runs the $\frac{Gmc}{L'}$ ratio for which the most successful separation is effected was found to be quite close to the K^{∞} of ethyl lactate, being approximately equal to $0.92 \times K^{\infty}$. This could be justified if all terms, such as that one accounting for the sequential nature of operation or for the finite concentration effects, were included in the inequality defining the separating limits of the sequential unit (see equation 7.7).

Inspection of all results obtained in this study shows the sensitivity of methyl chloroacetate/ethyl lactate separation to changes in $\frac{Gmc}{L'}$, particularly when these changes occur in a range quite close to the "optimum" $\frac{Gmc}{L'}$ value for successful separation. Thus, for run 110-37-365-200 decreasing the $\frac{Gmc}{L'}$ value by only 14 i.e. run 110-40-351-200, the separation is significantly affected. This suggests the importance of experimentally determining the $\frac{Gmc}{L'}$ values for which the separation of methyl chloroacetate/ethyl lactate is effected. These $\frac{Gmc}{L'}$ values compared to the "Arklone" P/"Genklene" P system lie within a much closer range.

TABLE 8.5 THE STUDY OF G_{mc}/L'

SUMMARY OF OPERATING CONDITIONS

Run title	Temperature			Ambient conditions		Solute mixture feedrate	l_s	L'	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L'	Sa	Pin	Pout	J	Smc/L'
Θ-f-Gmc/L'-l_s	°C	°C	°C	°C	kNm^{-2}	$cm^3\,h^{-1}$	s	$cm^3\,s^{-1}$	$cm^3\,s^{-1}$	kNm^{-2}	kNm^{-2}	—	—	$cm^3\,s^{-1}$	kNm^{-2}	kNm^{-2}	—	—
105-21-378-300	105	108	135	26	100	21	300	0.041	21.3	198	146	0.84	378	232	184	136	0.84	4418
105-21-413-300	105	108	135	25	102	21	300	0.041	23.0	205	144	0.82	413	248	198	143	0.83	4597
105-21-444-300	105	108	135	28	102	21	300	0.041	25.0	205	146	0.83	444	245	191	139	0.84	4625

SUMMARY OF RESULTS

Run title	K^∞		Separating section		Purge section	Total time of run	Total no. of cycles	Time to pseudo steady state	Concentration profile analysis				
	M.C	E.L	Gmin/L'	Gmax/L'	Smin/L'				Time to analysis	Table	Figure	Product Purities	
Θ-f-Gmc/L'-l_s						h		h	h			% M.C	% E.L
105-21-379-300	302	457	332	450	3887	5:00	5	2.00	3.00	A.3.2.1	8.8.1	> 99.8	>99.2
105-21-413-300	302	457	354	504	3952	3.00	3	2.00	2.00	A.3.2.2	8.8.2	> 99.8	>99.5
105-21-444-300	302	457	381	535	4007	5.00	5	2.00	3.00	A.3.2.3	8.8.3	> 99.3	>99.7

FIGURE 8.8.1 CONCENTRATION PROFILE FOR RUN 105-21-379-300

The samples were taken 150 sec after sequencing action —— from column 8, on the 4th cycle ---- from column 10, on the 5th cycle

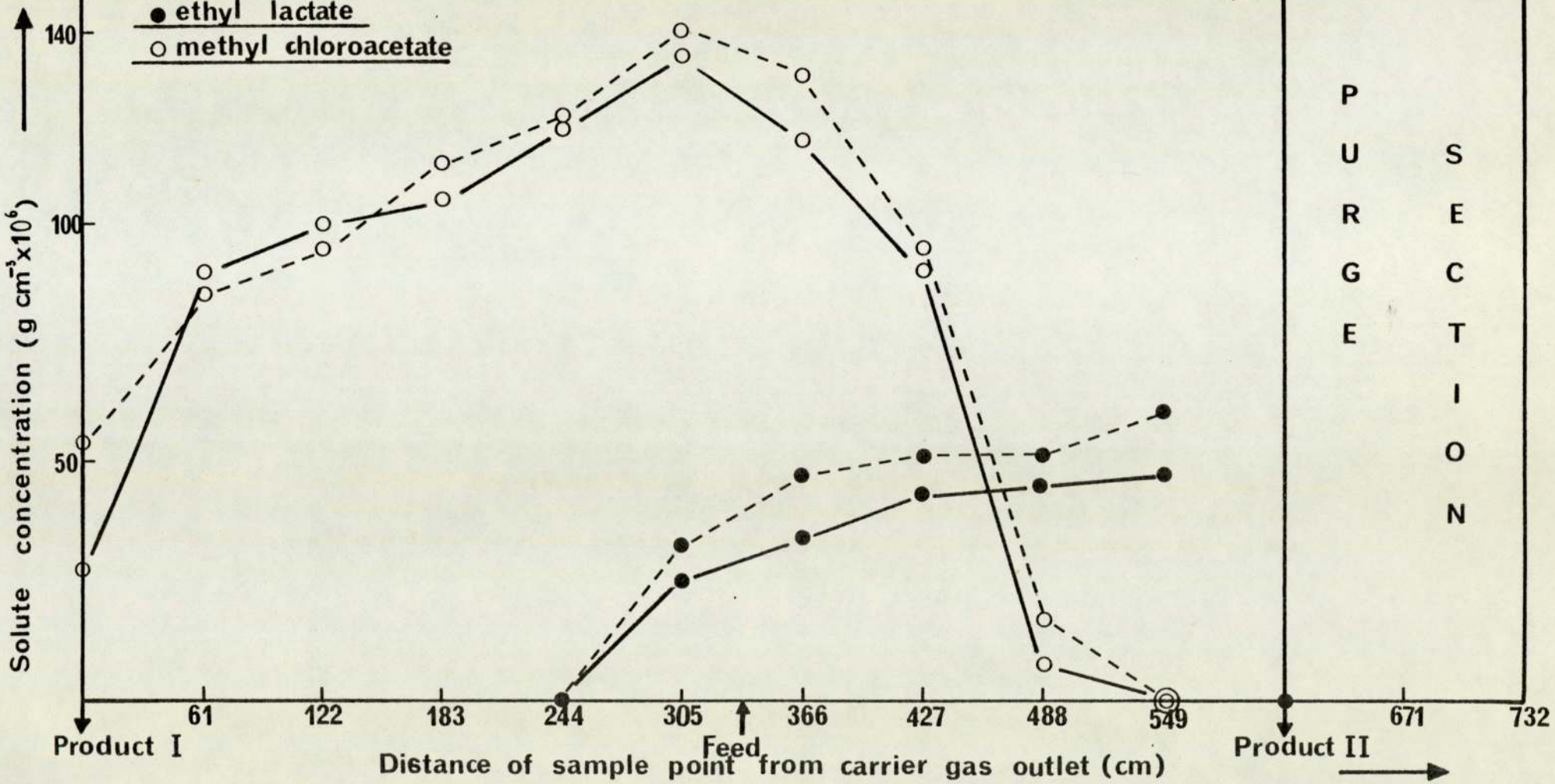


FIGURE 8.8.2 CONCENTRATION PROFILE FOR RUN 105 - 21 - 413 - 300

The samples were taken from column 8, 200 sec after sequencing action, on the 3rd cycle

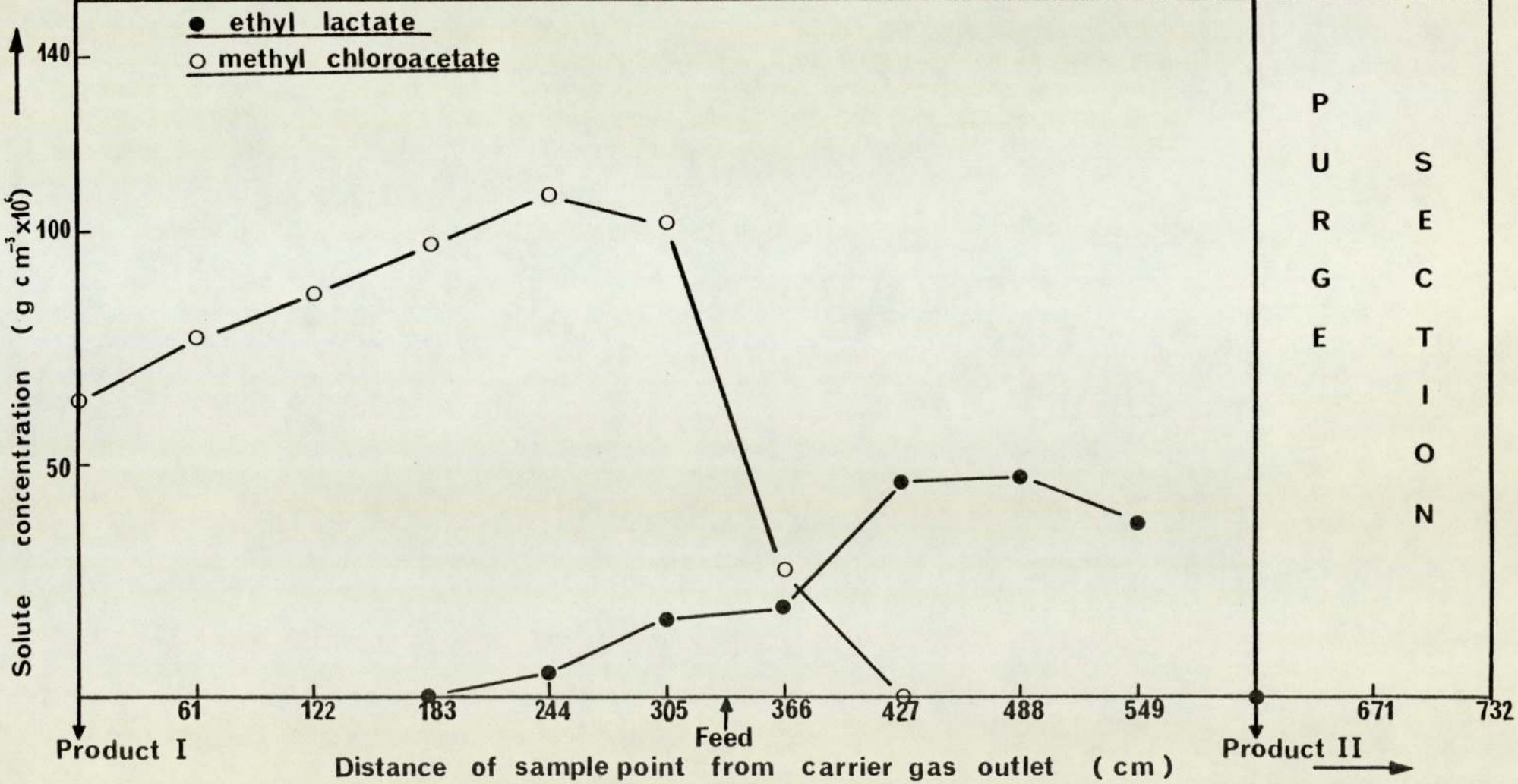


FIGURE 8.8.3 CONCENTRATION PROFILE FOR RUN 105-21-444-300

The samples were taken 150 sec after sequencing action ——— from column 8, on the 4th cycle
– – – – from column 10, on the 5th cycle

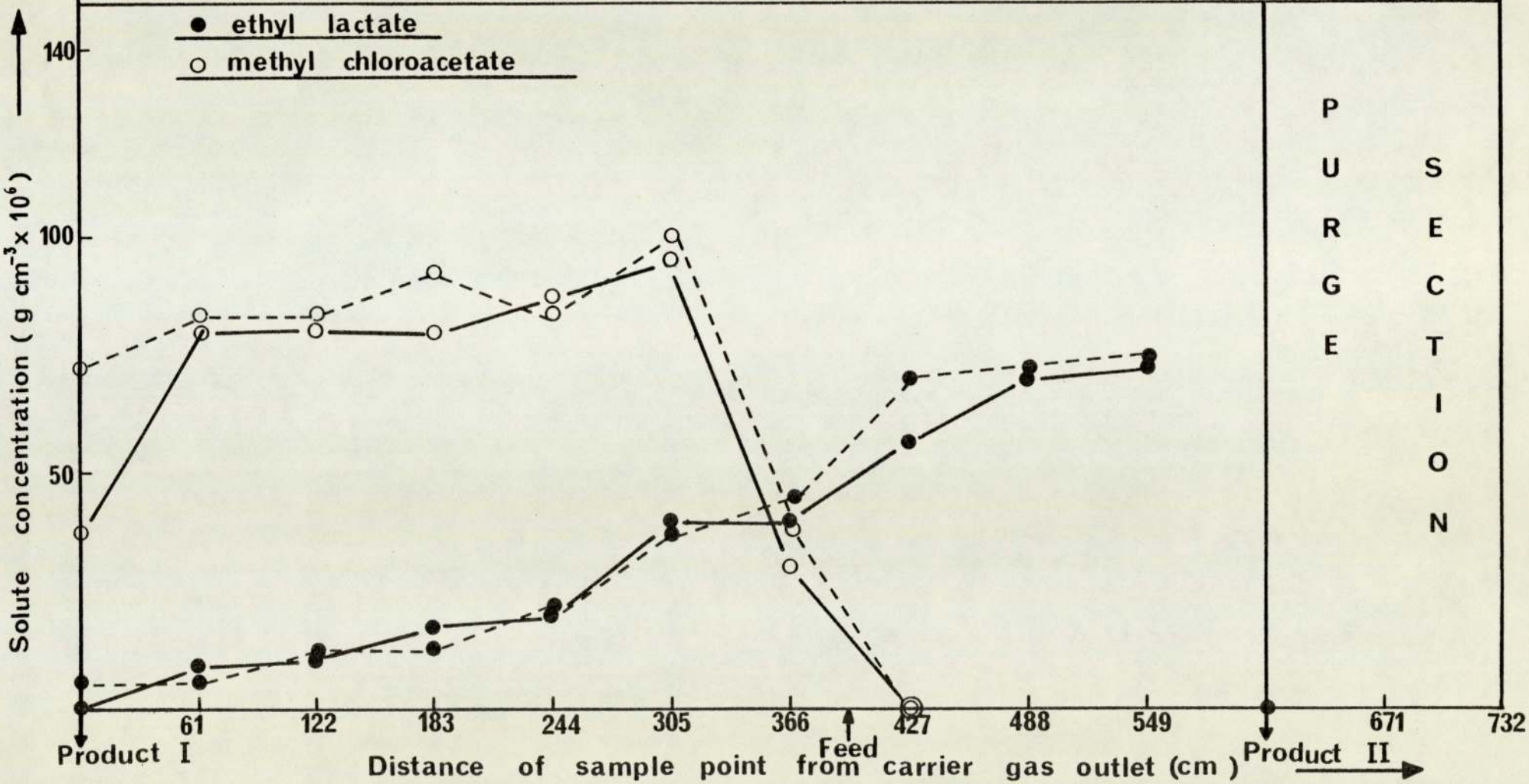


TABLE 8.6 : THE STUDY OF G_{mc}/L'
SUMMARY OF OPERATING CONDITIONS

Run title	Temperature			Ambient conditions		Solute mixture feedrate	I_s	L'	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L'	Sa	Pin	Pout	J	Smc/L'
Θ-f-Gmc/L'-I_s	°C	°C	°C	°C	kNm^{-2}	$cm^3 h^{-1}$	s	$cm^3 s^{-1}$	$cm^3 s^{-1}$	kNm^{-2}	kNm^{-2}	—	—	$cm^3 s^{-1}$	kNm^{-2}	kNm^{-2}	—	—
110-38-273-200	110	113	120	29	100	38	200	0.062	23.0	198	143	0.83	273	197	184	143	0.87	2451
110-40-313-200	110	112	120	28	100	40	200	0.062	26.3	205	136	0.79	313	195	184	150	0.90	2401
110-40-351-200	110	112	120	30	102	40	200	0.062	30.0	212	137	0.77	351	183	184	150	0.90	2283
110-37-365-200	110	112	120	30	101	37	200	0.062	35.0	239	150	0.76	365	183	184	151	0.90	2246
110-40-425-200	110	112	120	29	100	40	200	0.062	43.3	260	148	0.71	425	170	184	156	0.92	2050

SUMMARY OF RESULTS

Run title	K^∞		Separating section		Purge section	Total time of run	Total no. of cycles	Time to pseudo steady state	Concentration profile analysis				
	M.C	E.L	Gmin/L'	Gmax/L'	Smin/L'				Time to analysis	Table	Figure	Product Purities	
Θ-f-Gmc/L'-I_s						h		h	h			% M.C	% E.L
110-38-273-200	257	389	238	329	2190	2.67	4	1.33	2.00	A.3.2.4	8.8.4	>99.9	-
110-40-313-200	257	389	263	397	2175	4.67	7	1.33	4.00	A.3.2.5	8.8.5	>99.9	-
110-40-351-200	257	389	294	455	2068	3.33	5	1.33	2.67	A.3.2.6	8.8.6	>99.9	>99.6
110-37-365-200	257	389	301	480	2048	3.33	5	1.33	2.67	A.3.2.7	8.8.7	>99.9	>99.8
110-40-425-200	257	389	341	598	1890	4.00	6	1.33	3.33	A.3.2.8	8.8.8	>99.9	>99.8

FIGURE 8.8.4 CONCENTRATION PROFILE FOR RUN 110 - 38 - 273 - 200

The samples were taken from column 10, 150 sec after sequencing action, on the 4th cycle

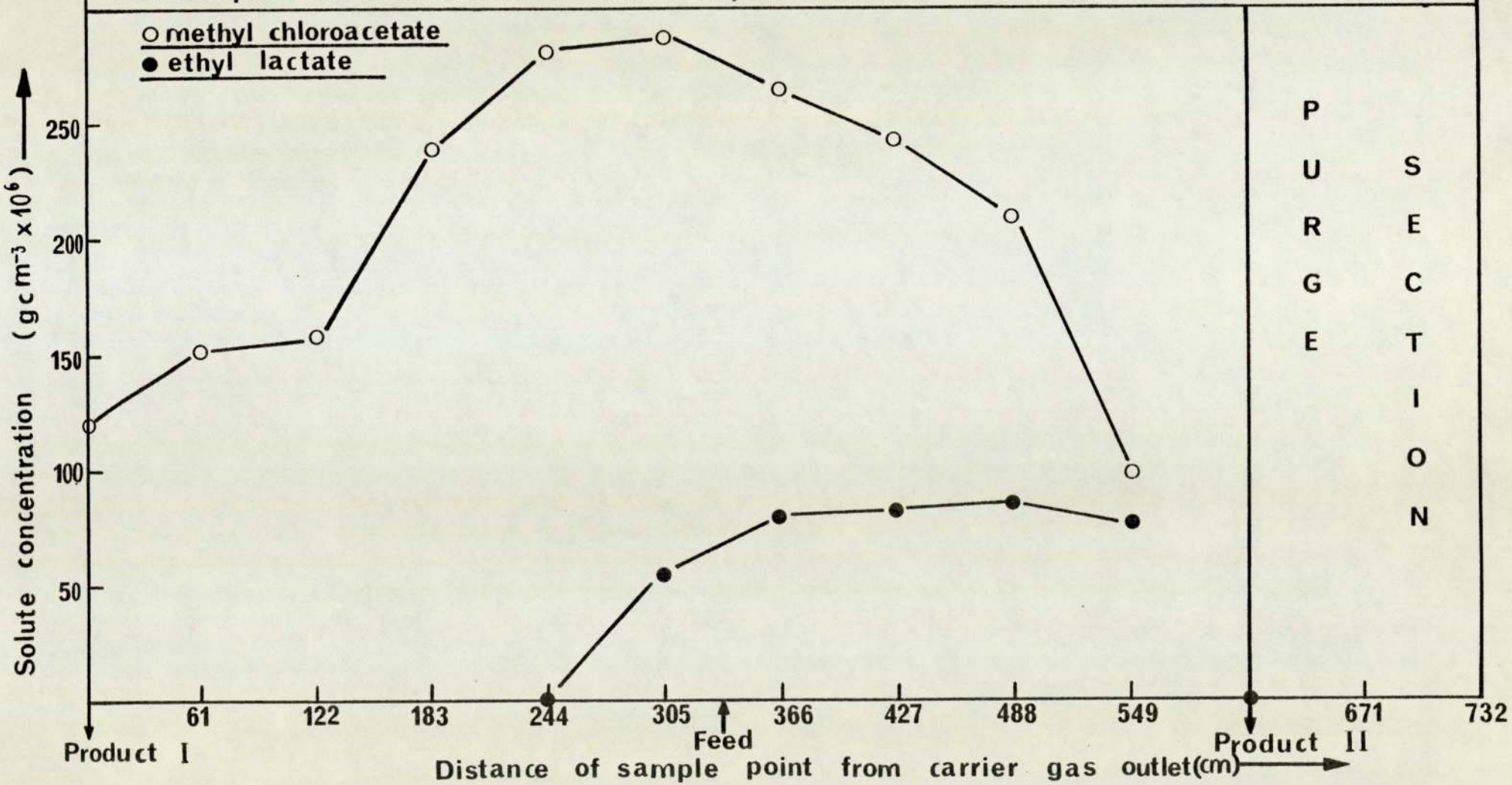


FIGURE 8.8.5 CONCENTRATION PROFILE FOR RUN 110-40-313-200

The samples were taken from column 10,150 sec after sequencing action, on the 7th cycle

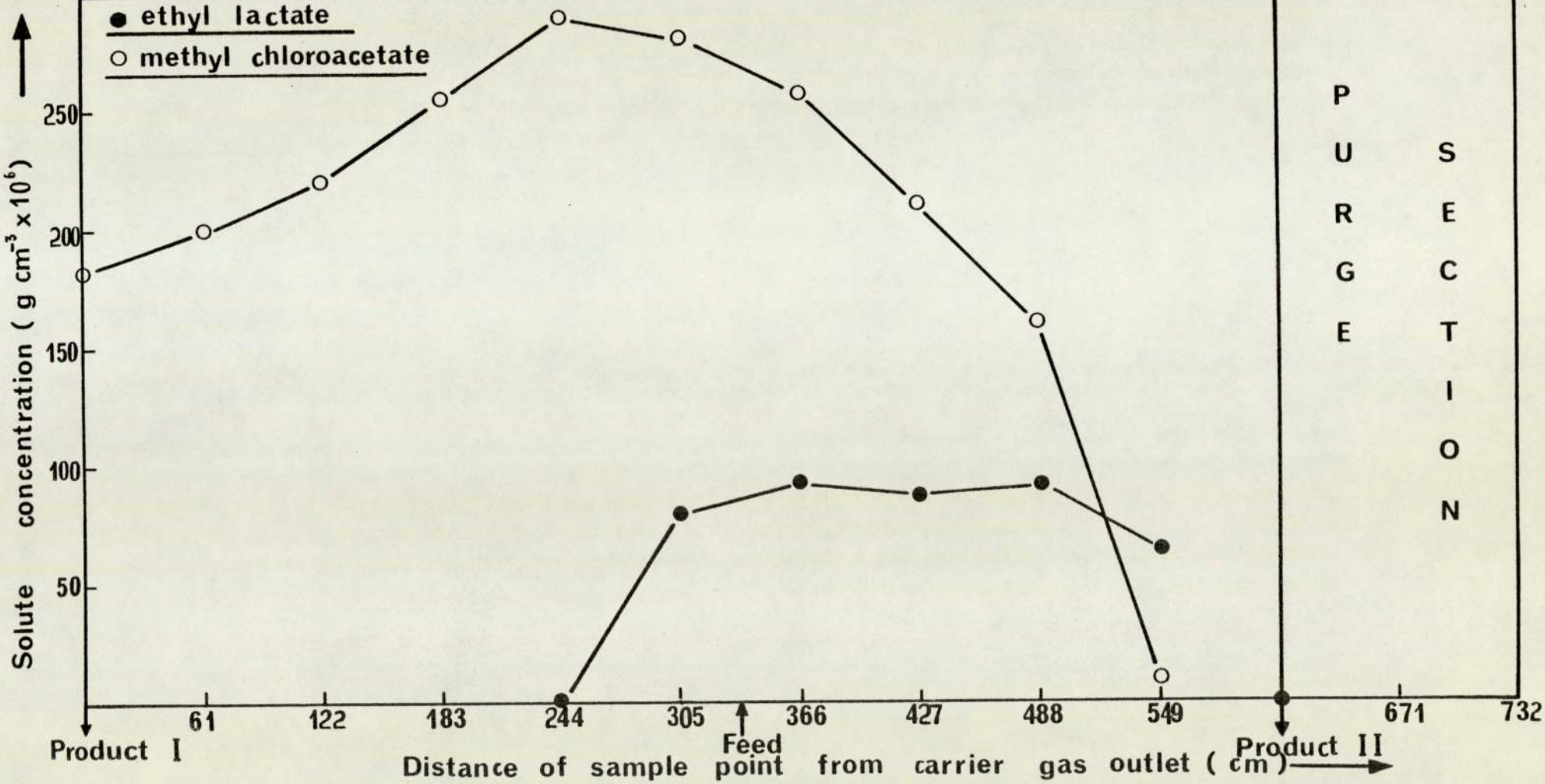


FIGURE 8.8.6 CONCENTRATION PROFILE FOR RUN 110-40-351-200

The samples were taken from column 10, 150 sec after sequencing action, on the 5th cyde

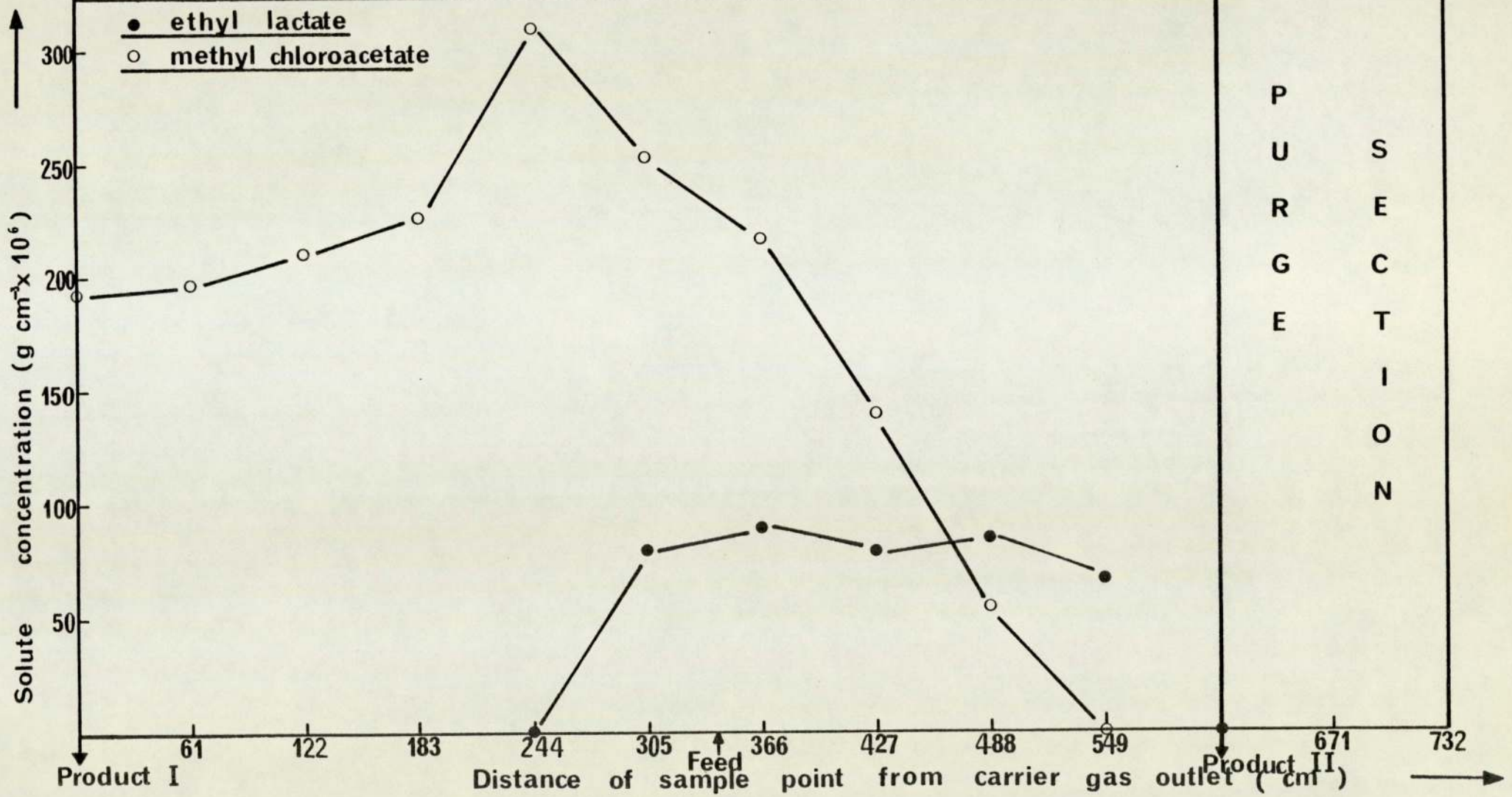


FIGURE 8.8.7 CONCENTRATION PROFILE FOR RUN 110-37-365-200

The samples were taken from column 10, 150 sec after sequencing action, on the 5th cycle

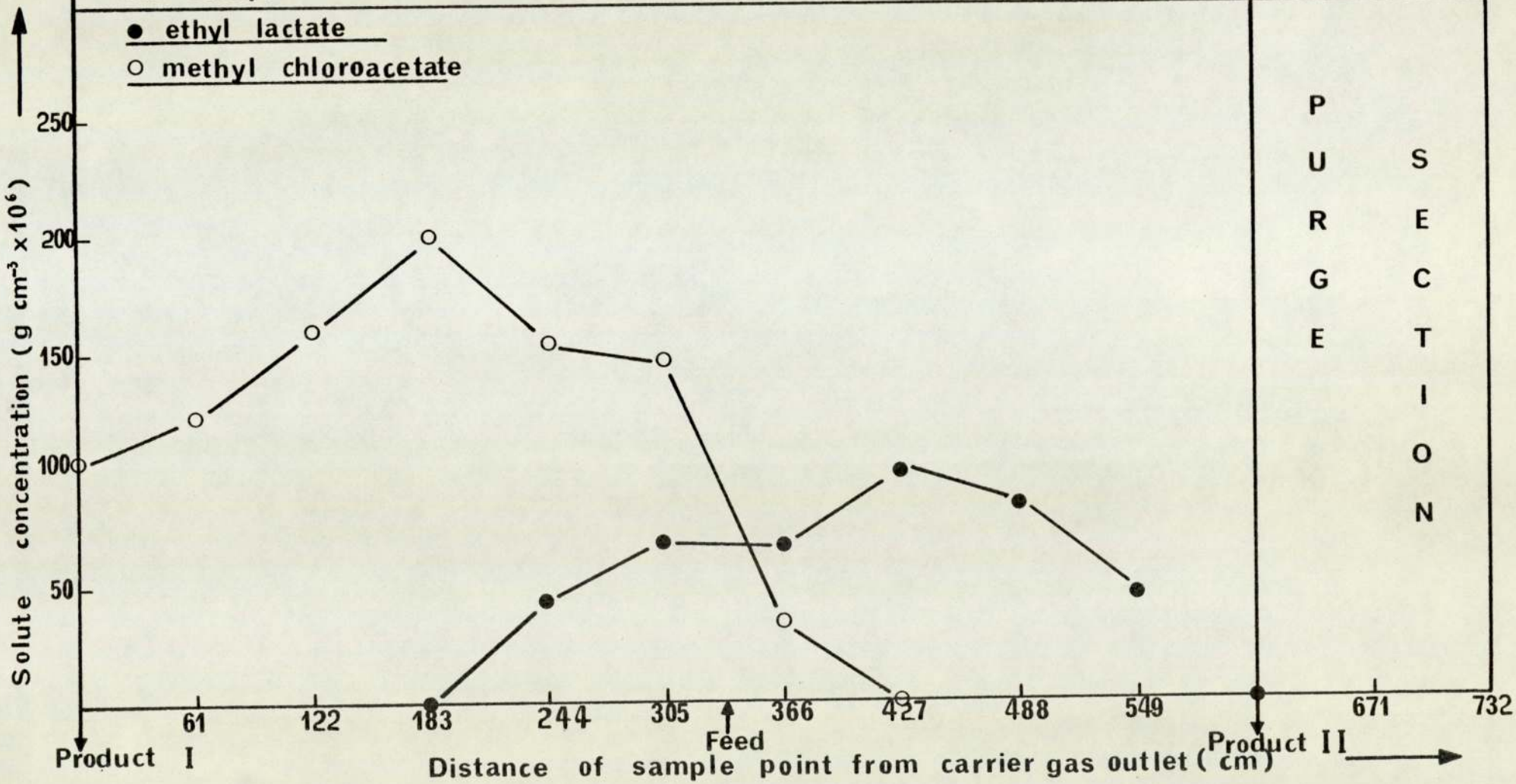
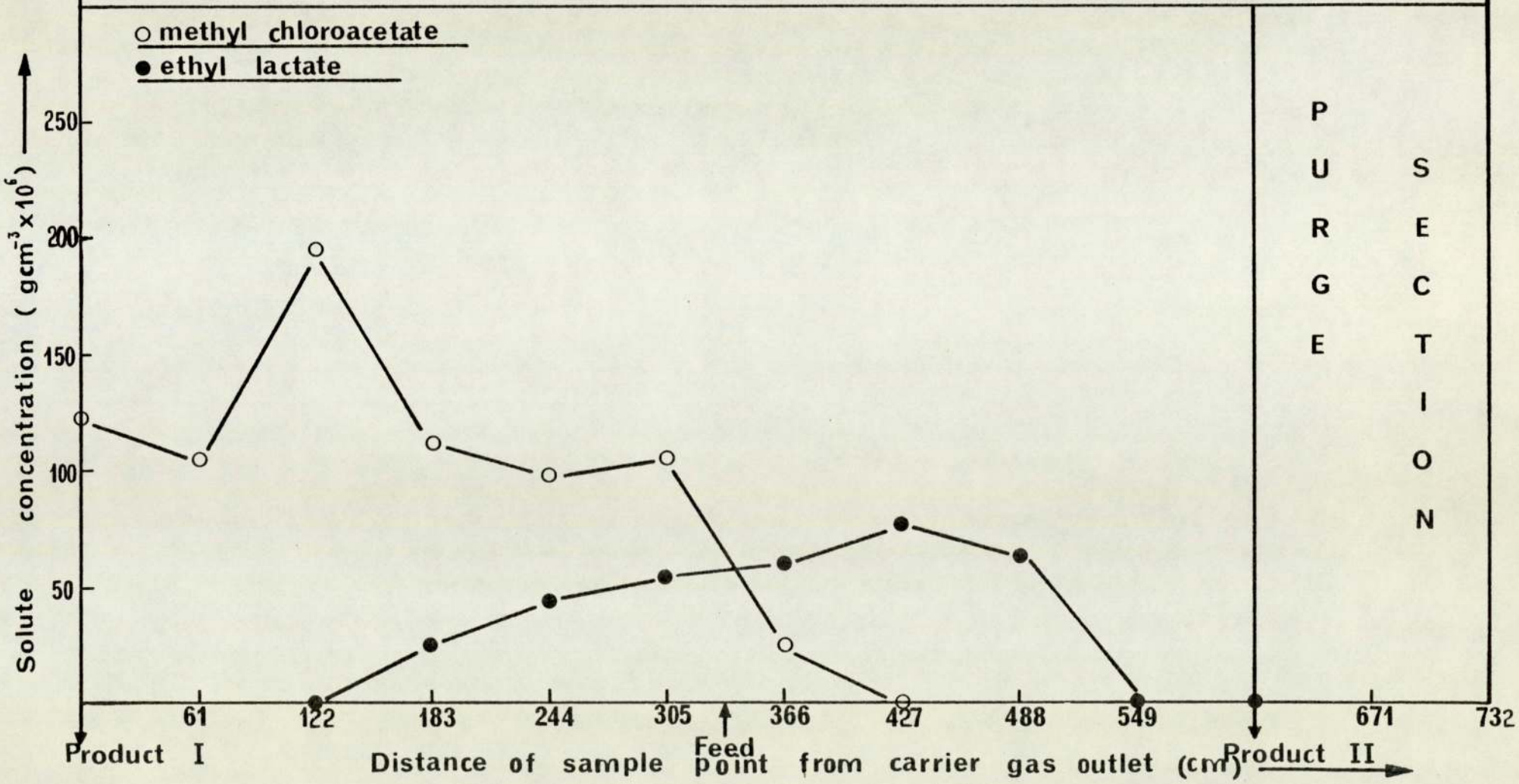


FIGURE 8.8.8 CONCENTRATION PROFILE FOR RUN 110-40-425-200

The samples were taken from column 10, 150 sec after sequencing action, on the 6th cycle



8.2.2 THE STUDY OF "SEQUENCING RATE"

8.2.2.1 RESULTS AND DISCUSSION

The experimental runs 110-37-365-200, 110-36-366-250, 110-41-367-300 and 110-40-375-350 performed in this study, show the effect of increasing the sequencing rate while maintaining the value of $\frac{Gmc}{L^{\dagger}}$ approximately constant by proportionately reducing the carrier gas flowrate.

The $\frac{Gmc}{L^{\dagger}}$ ratio throughout these experimental runs was held constant within 370 ± 5, while the solute feedrate was maintained within 38 ± 2 cm^3h^{-1}, and the operating temperature approximately constant at 110°C.

Further details of the above experimental runs are given in Table 8.7, Figures 8.9.1-8.9.4 and Appendix A.3.2.

As is shown in Table 8.7 and Figures 8.9.1-8.9.4, on increasing the sequencing interval from 200 s to 350 s, with a corresponding reduction in the carrier gas flowrate, Ga, from 35 to 20 cm^3s^{-1}, the performance of the sequential unit has not been noticably affected. Only some increase in the concentration level of ethyl lactate and decrease for that of methyl chloroacetate was recorded as the sequencing interval was increased.

Apart from that the performance of the sequential unit has shown very little sensitivity to the sequential rate variations. Thus, the shape of the concentration profiles has remained the same throughout these experimental runs, with sharp leading and trailing edges, while the degree of overlap of the two solute profiles was retained within four to five column-lengths around the feed point. Also the product purities were retained at about the same levels throughout these runs.

Increasing the sequencing time interval reduces the required carrier gas flowrate and hence the pressure drop across the separating section, which results in a significant reduction in the variation of $\frac{G}{L'}$ values between the carrier gas inlet and outlet (see Table 8.7); and this is beneficial to the successful separation. However, for very long sequencing time intervals the accompanied high solute concentrations, as a result of the corresponding reduction in the carrier gas flowrate, are expected to severely affect the performance of the sequential unit, particularly when high feed throughputs are used. Thus, a compromise between those two effects seems to dictate the choice of a sequencing time interval, Is, for a particular separation problem. Other factors, which also should be considered in choosing Is values, are the maximum/minimum pressures and flowrates permitted by the controlling and measuring devices of the SCCR-2 equipment.

Despite the above limitations the sequential rates, for which the separation of methyl chloroacetate/ethyl lactate is effected, were found to cover a wide range of values.

TABLE 8.7 : THE STUDY OF I_s

SUMMARY OF OPERATING CONDITIONS

Run title	Temperature			Ambient conditions		Solute mixture feedrate	I_s	L′	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L′	Sa	Pin	Pout	J	Smc/L′
Θ-f-Gmc/L′-I_s	°C	°C	°C	°C	kNm^{-2}	cm^3 h^{-1}	s	cm^{3}s^{-1}	cm^{3}s^{-1}	kNm^{-2}	kNm^{-2}	—	—	cm^{3}s^{-1}	kNm^{-2}	kNm^{-2}	—	—
110-37-365-200	110	112	120	30	101	37	200	0.062	35.0	239	150	0.76	365	183	184	151	0.90	2246
110-36-366-250	110	112	120	28	101	36	250	0.050	28.3	232	157	0.79	366	165	184	151	0.90	2527
110-41-367-300	110	112	120	28	101	41	300	0.041	23.3	232	163	0.82	367	165	184	151	0.90	3082
110-40-375-350	110	112	120	26	102	40	350	0.035	20.0	232	163	0.82	375	162	184	155	0.91	3550

SUMMARY OF RESULTS

Run title	K^∞		Separating section		Purge section	Total time of run	Total no. of cycles	Time to pseudo steady state	Concentration profile analysis				
	M.C	E.L	Gmin/L′	Gmax/L′	Smin/L′				Time to analysis	Table	Figure	Product Purities	
Θ-f-Gmc/L′-I_s						h		h	h			% M.C	% E.L
110-37-365-200	257	389	301	480	2048	3.33	5	1.33	2.67	A.3.2.7	8.9.1	>99.9	>99.8
110-36-366-250	257	389	313	463	2305	3.33	4	1.67	2.50	A.3.2.9	8.9.2	>99.9	>99.8
110-41-367-300	257	389	315	448	2810	4.00	4	2.00	3.00	A.3.2.10	8.9.3	>99.9	>99.8
110-40-375-350	257	389	322	458	3286	5.83	5	2.33	4.67	A.3.2.11	8.9.4	>99.9	>99.9

FIGURE 8.9.1 CONCENTRATION PROFILE FOR RUN 110-37-365-200

The samples were taken from column 10,150 sec after sequencing action, on the 5th cycle

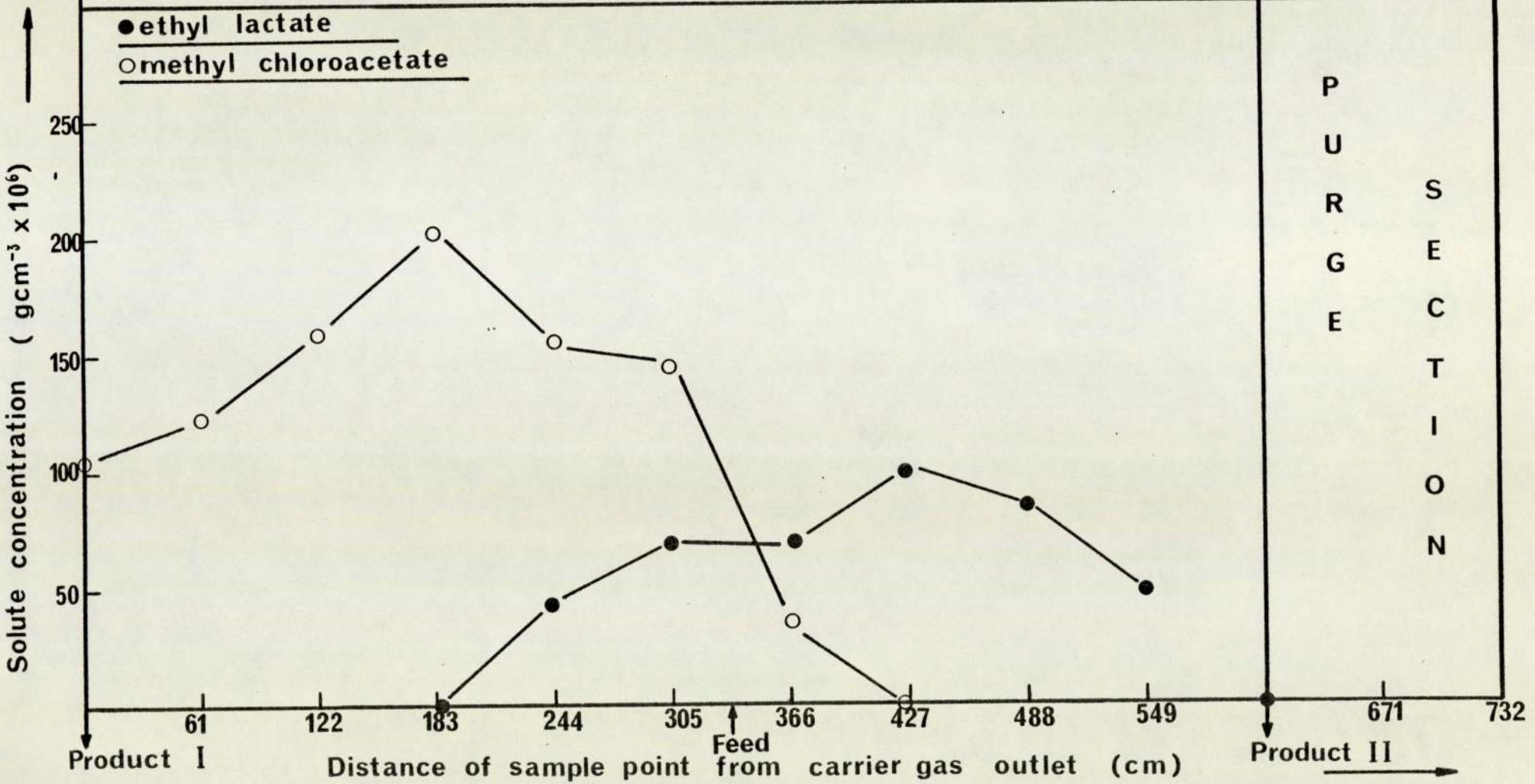


FIGURE 8.9.2 CONCENTRATION PROFILE FOR RUN 110-36-366-250

The samples were taken from column 10, 150 sec after sequencing action, on the 4th cycle

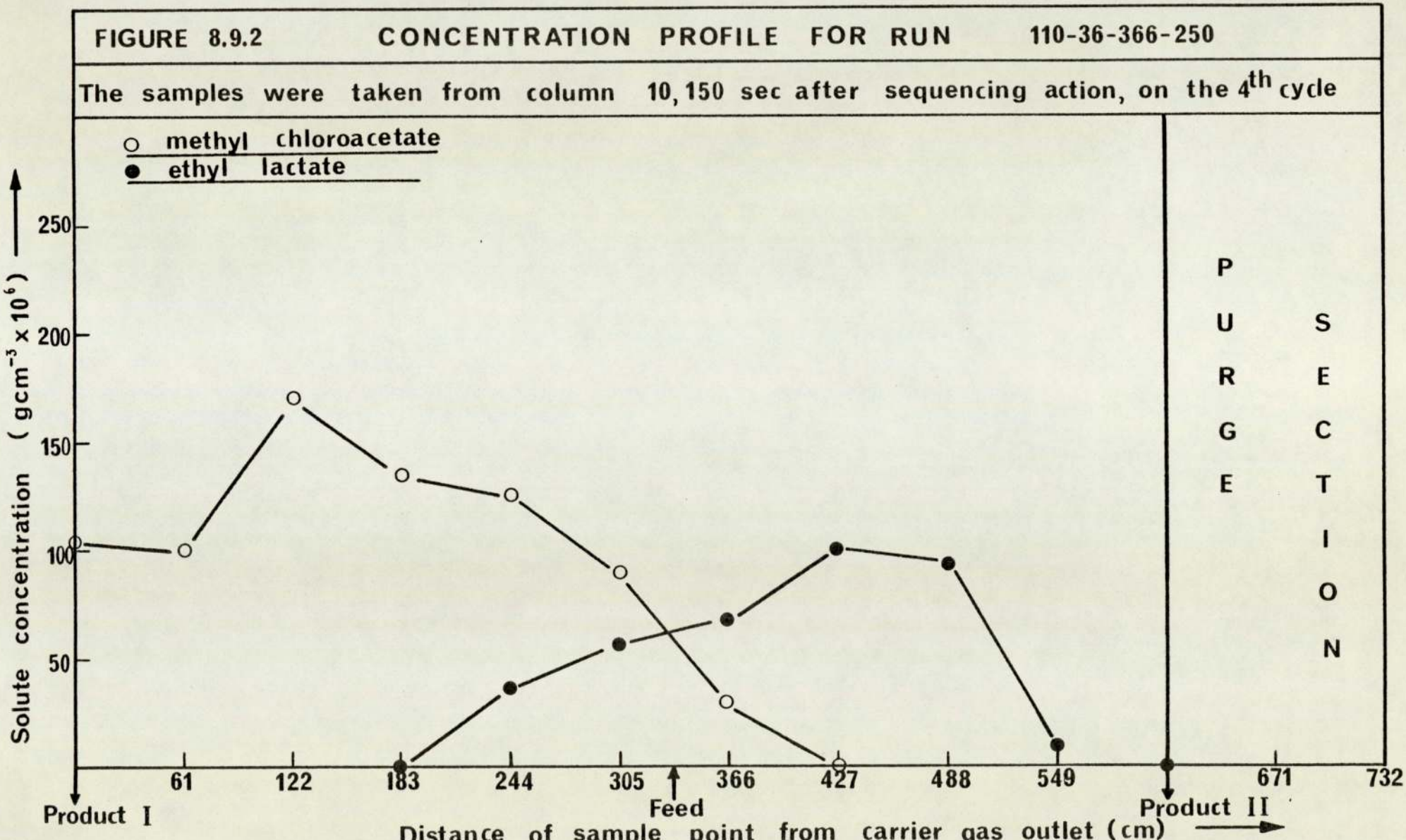


FIGURE 8.9.3 CONCENTRATION PROFILE FOR RUN 110-41-367-300

The samples were taken from column 10, 200 sec after sequencing action, on the 4th cycle

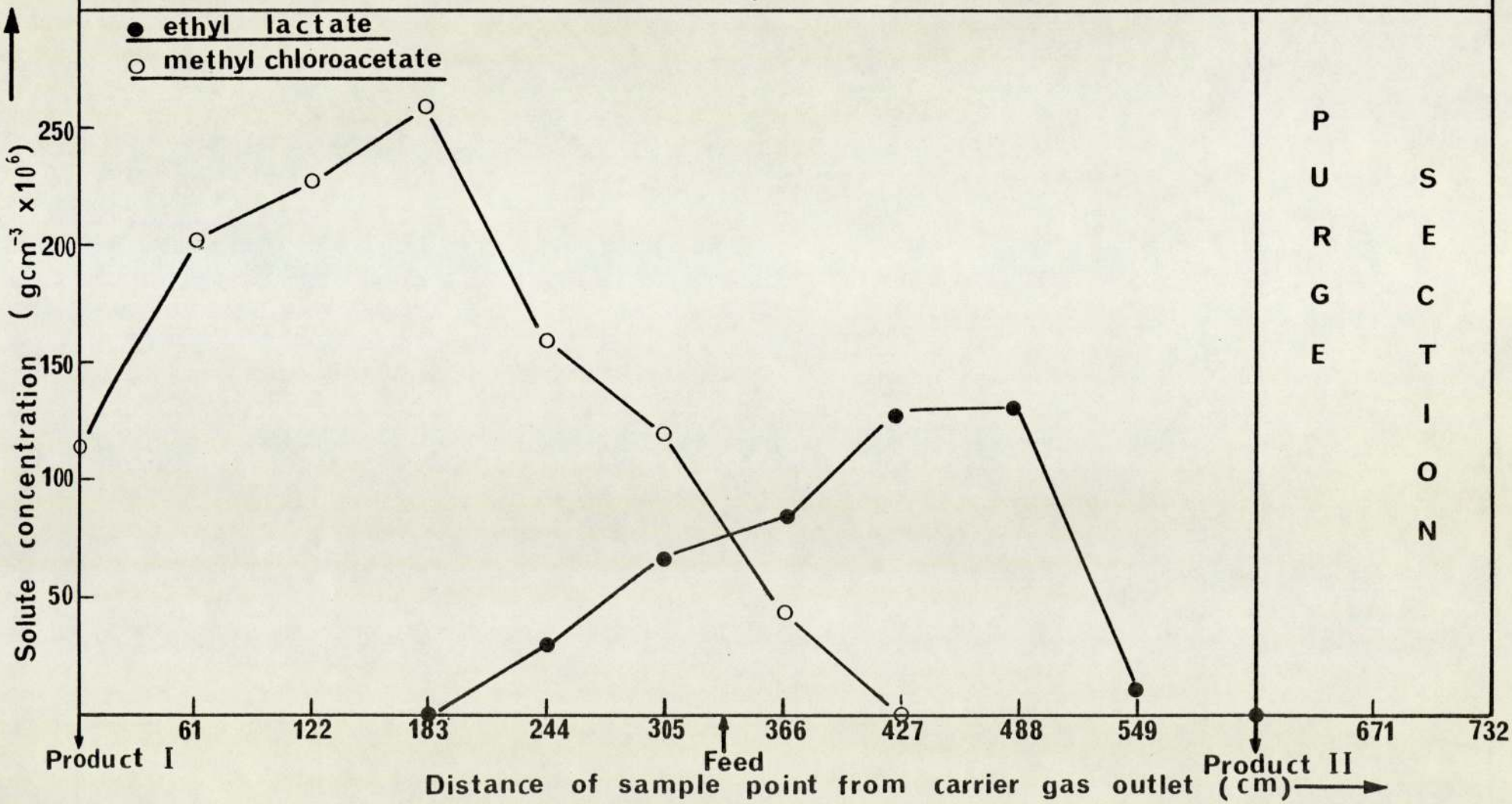
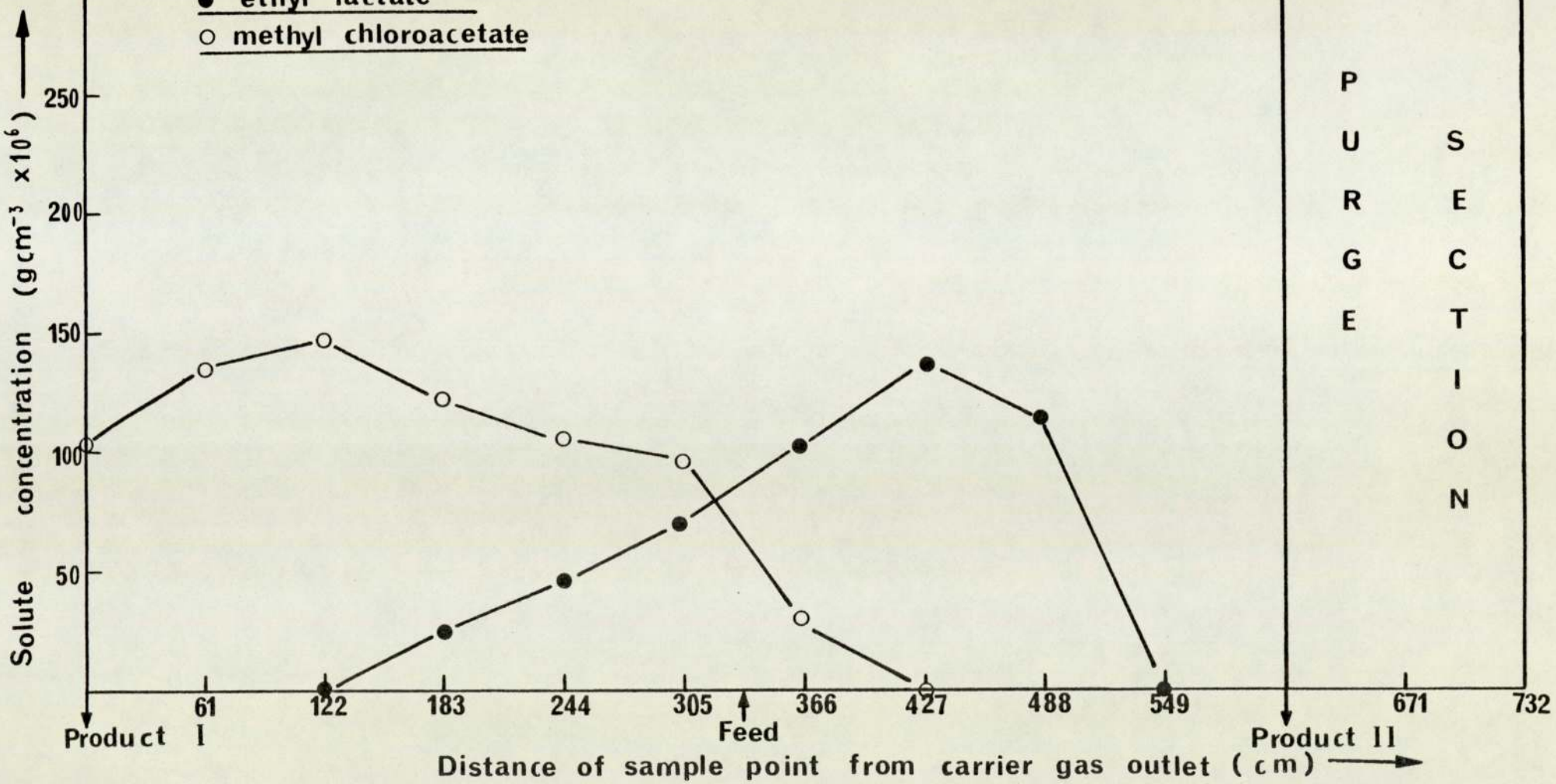


FIGURE 8.9.4 CONCENTRATION PROFILE FOR RUN 110-40-375-350

The samples were taken from column 10,200 sec after sequencing action, on the 5th cycle



8.2.3 THE STUDY OF "FEEDRATE"

8.2.3.1 RESULTS AND DISCUSSION

Details of the experimental runs 110-37-365-200, 110-60-374-200 and 110-80-427-200, which record the effect of feed throughput on the performance of the sequential unit, are presented in Table 8.8, Figures 8.10.1-8.10.3 and Appendix A.3.2. These runs were carried out at a solute feedrate of 37, 60 and 80 cm^3h^{-1} respectively, with all the other operating conditions, except $\frac{Gmc}{L'}$, approximately constant.

On increasing the feedrate from 37 to 60 cm^3h^{-1} a tendency for both methyl chloroacetate and ethyl lactate solutes to extend towards the purge section was observed (see Figures 8.10.1, 8.10.2). However, in both runs $\frac{Gmc}{L'}$ was maintained within 370 ± 5, a range lying between the limits for successful separation, which were defined by the respective partition coefficients of methyl chloroacetate and ethyl lactate at infinite dilution (see Section 7.1).

The results obtained from the above runs show that the defining separating limits of the sequential unit, based on the assumption of dilute operating conditions, are unjustified as the feed throughput is increased (see Equations 7.7, 7.8). This is due to the concentration dependence of partition coefficient, K, which in the case of the methyl chloroacetate/ ethyl lactate system, is indicated by the results of experimental runs as an anti-Langmuir type of adsorption isotherm; K increases with increasing concentration.

Further increase in feedrate would lead to some loss of product II purity, as the methyl chloroacetate profile would be extended over the whole of the separating section contaminating the ethyl lactate exiting as product II. To avoid this, the $\frac{Gmc}{L'}$ ratio was increased from 374 to 427, by increasing the carrier gas flowrate, Ga, from 35.3 to 41.7 cm^3s^{-1},

when feed throughputs of 80 cm^3h^{-1} were applied for the separation, i.e. run 110-80-427-200. Under these conditions, the product purities were retained at high levels, although the shape of column concentration profile shown in Fig. 8.10.3, suggeststhat a further increase in the $\frac{Gmc}{L'}$ value would be beneficial for the separation.

No attempts have been made to find the maximum feed throughput for a successful separation in order to avoid stripping the liquid phase from the packing. However, studying the results of the experimental runs, presented in Figures 8.10.1-8.10.4, it is observed that at a feedrate of 37 cm^3h^{-1} the separation was largely achieved within a distance of four column-lengths, while at 80 cm^3h^{-1} the degree of overlap of the two solute profiles is only increased to five column-lengths. These observations favour the possibility of the SCCR-2 unit for higher throughput capabilities with this sytem.

It should be noted that for each separation problem studied on the sequential unit, a maximum solute concentration limit in the gas phase is expected, for which the separation is successfully achieved; and this is likely to be lower than the saturation level for the gas phase.

TABLE 8.8 : THE STUDY OF FEEDRATE

SUMMARY OF OPERATING CONDITIONS

Run title	Temperature			Ambient conditions		Solute mixture feedrate	l_s	L′	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L′	Sa	Pin	Pout	J	Smc/L′
Θ-f-Gmc/L′-l_s	°C	°C	°C	°C	kNm^{-2}	$cm^3\,h^{-1}$	s	$cm^3\,s^{-1}$	$cm^3\,s^{-1}$	kNm^{-2}	kNm^{-2}	—	—	$cm^3\,s^{-1}$	kNm^{-2}	kNm^{-2}	—	—
110-37-365-200	110	112	120	30	101	37	200	0.062	35.0	239	150	0.76	365	183	184	151	0.90	2246
110-60-374-200	110	112	120	25	101	60	200	0.062	35.3	239	148	0.75	374	183	184	150	0.90	2299
110-80-427-200	110	112	120	25	101	80	200	0.062	41.7	253	143	0.70	427	183	184	150	0.90	2299

SUMMARY OF RESULTS

Run title	K^∞		Separating section		Purge section	Total time of run	Total no. of cycles	Time to pseudo steady state	Concentration profile analysis				
	M.C	E.L	Gmin/L′	Gmax/L′	Smin/L′				Time to analysis	Table	Figure	Product Purities	
Θ-f-Gmc/L′-l_s						h		h	h			% M.C	% E.L
110-37-365-200	257	389	301	480	2048	3.33	5	1.33	2.67	A.3.2.7	8.10.1	>99.9	>99.8
110-60-374-200	257	389	309	499	2082	2.67	4	1.33	2.00	A.3.2.12	8.10.2	>99.9	>99.9
110-80-427-200	257	389	345	610	2082	2.67	4	1.33	2.00	A.3.2.13	8.10.3	>99.9	>99.8

FIGURE 8.10.1 CONCENTRATION PROFILE FOR RUN 110-37-365-200

The samples were taken from column 10, 150 sec after sequencing action, on the 5th cycle

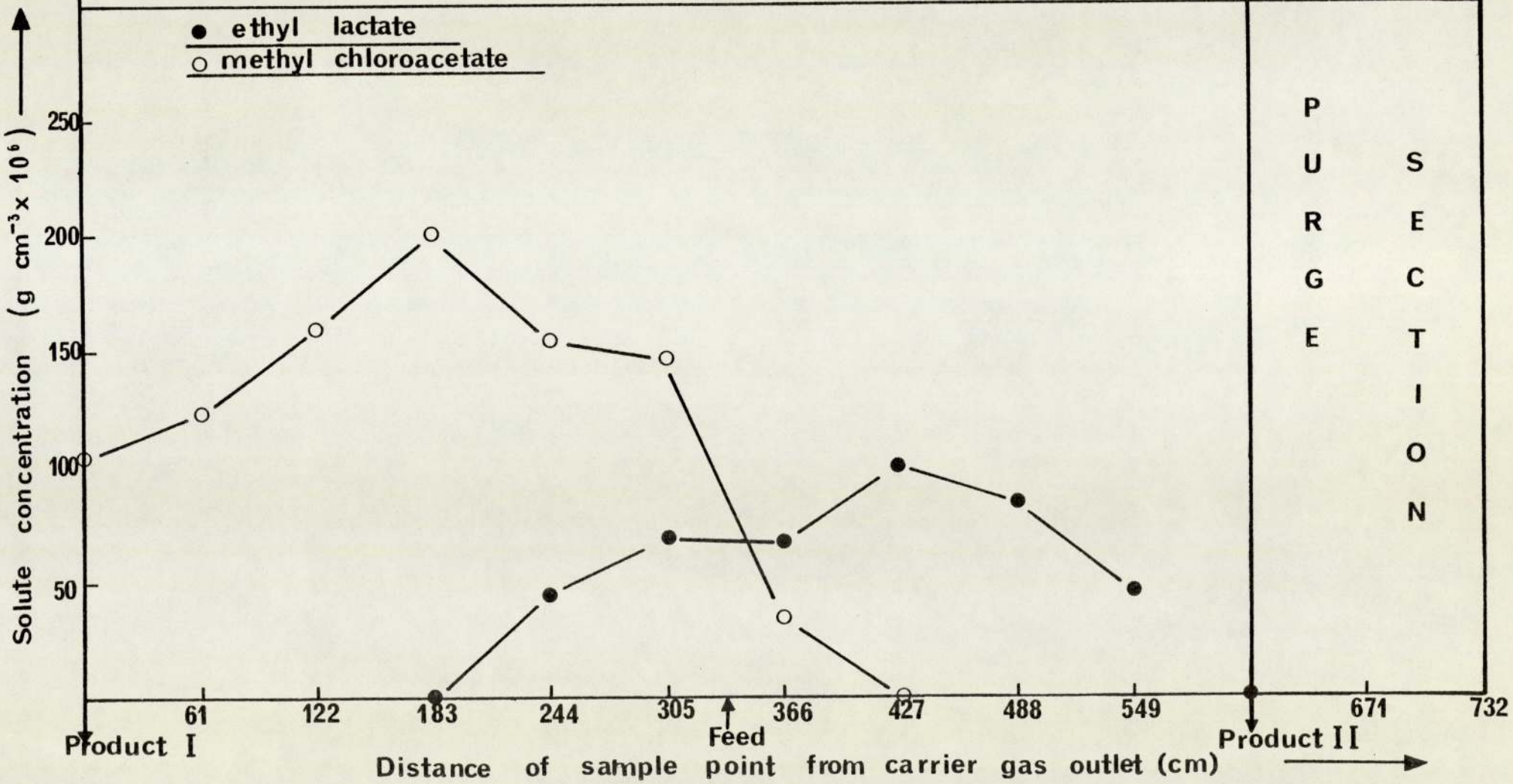


FIGURE 8.10.2 CONCENTRATION PROFILE FOR RUN 110-60-374-200

The samples were taken from column 10, 150 sec after sequencing action, on the 4th cycle

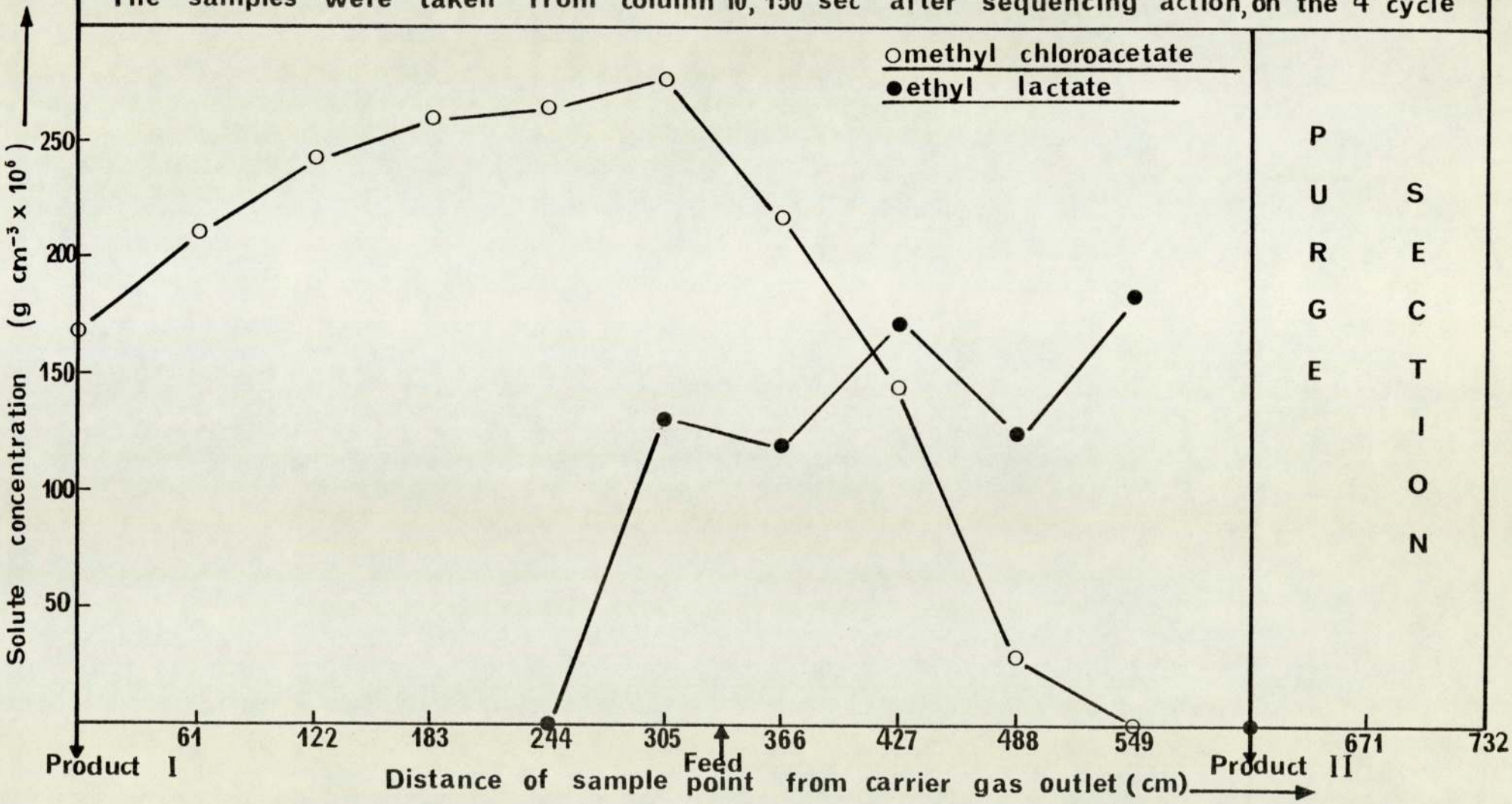
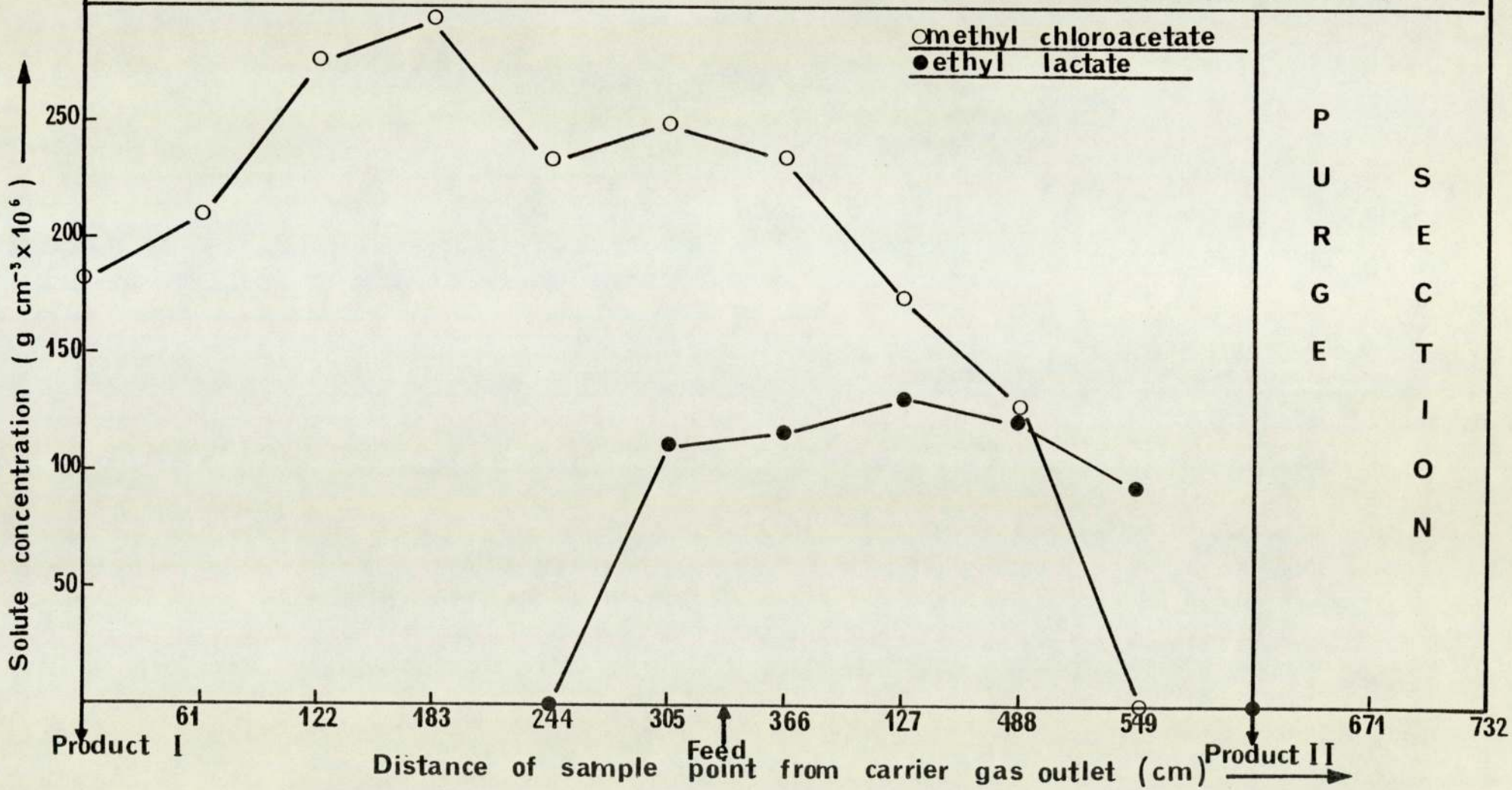


FIGURE 8.10.3 CONCENTRATION PROFILE FOR RUN 110-80-427-200

The samples were taken from column 10, 150 sec after sequencing action, on the 4th cycle



8.2.4 THE STUDY OF "TEMPERATURE"

8.2.4.1 RESULTS AND DISCUSSION

Five experimental runs were performed in which the operating temperature varied between 110 and 130°C to show the effect of temperature on the successful separation of the methyl chloroacetate/ethyl lactate system. Table 8.9 summarizes the operating conditions employed and the results obtained for each experimental run, while Figures 8.11.1-8.11.5 illustrate the column concentration profiles for the respective runs. Further details of the runs are given in Appendix A.3.2.

The results of the experimental runs 110-40-351-200 and 120-40-346-200 show the effect of increasing the operating temperature from 110 to 120°C, while holding all the other operating conditions approximately constant. Increasing the temperature from 110 to 120°C, the associated significant reduction in the partition coefficient values, K^{∞}, is obviously responsible for the observed tendency of the solute profiles to stretch towards the product I off-take, contaminating the methyl chloroacetate (see Figures 8.11.1 and 8.11.2). In order for the separation to be successfully achieved at 120°C, the $\frac{Gmc}{L^{T}}$ ratio should be changed so as to justify the new operating conditions for separation, set by the reduced partition coefficient values (see Equation 7.8). The run 120-38-241-200 is an example of such a separation.

The pair of runs 120-38-241-200 and 110-38-248-200 demonstrate again the sensitivity of the system to changes in temperature and the importance of selecting the $\frac{Gmc}{L^{T}}$ ratio within the operating limits for successful separation, defined by the K^{∞} values of solutes at the respective temperature.

For the experimental run 130-40-182-150, conducted at 130°C, high product purities were recorded but the degree of overlap between

the two solute profiles was extended to seven column-lengths instead of about four column lengths (see Fig.8.11.5). Also the methyl chloroacetate profile was not extending as gently as usually towards the product I exit. This could be caused because of the high solute concentrations experienced in the gas phase, as the K^{∞} values decreased with increasing temperature.

No further increase in the operating temperature was attempted in order to avoid partial vaporization of the methyl chloroacetate/ ethyl lactate mixture in the feed distributor. The presence of gas phase in the feed distributor would result in non-uniform feeding around the 12-columns which is undesirable for successful separation.

Decreasing the temperature below 110°C would not be beneficial for the separation as the K^{∞} values are increased and higher $\frac{Gmc}{L'}$ values required for the operation. This would increase the pressure drop across the separating section and hence increase the variation in the point values of the gas to apparent liquid rate ratio.

TABLE 8.9 : THE STUDY OF TEMPERATURE
SUMMARY OF OPERATING CONDITIONS

Run title	Temperature			Ambient conditions		Solute mixture feedrate	l_s	L´	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L´	Sa	Pin	Pout	J	Smc/L´
Θ-f-Gmc/L´-l_s	°C	°C	°C	°C	kNm^{-2}	$cm^3\,h^{-1}$	s	cm^3s^{-1}	cm^3s^{-1}	kNm^{-2}	kNm^{-2}	—	—	cm^3s^{-1}	kNm^{-2}	kNm^{-2}	—	—
110-40-351-200	110	112	120	30	102	40	200	0.062	30.0	212	137	0.77	351	183	184	150	0.90	2283
120-40-346-200	120	122	125	30	100	40	200	0.062	29.2	212	136	0.77	346	182	184	150	0.90	2284
120-38-241-200	120	122	125	29	100	38	200	0.062	19.8	198	143	0.83	241	180	184	147	0.88	2261
110-38-248-200	110	112	120	27	101	38	200	0.062	20.8	198	150	0.86	248	197	184	143	0.87	2492
130-40-182-150	130	132	135	27	102	40	150	0.083	20.0	212	145	0.80	182	163	198	160	0.89	1497

SUMMARY OF RESULTS

Run title	K^∞		Separating section		Purge section	Total time of run	Total no. of cycles	Time to pseudo steady state	Concentration profile analysis				
	M.C	E.L	Gmin/L´	Gmax/L´	Smin/L´				Time to analysis	Table	Figure	Product Purities	
Θ-f-Gmc/L´-l_s						h		h	h			% M.C	% E.L
110-40-351-200	257	389	294	455	2068	3.33	5	1.33	2.67	A.3.2.6	8.11.1	>99.9	>99.6
120-40-346-200	184	275	288	449	2069	4.67	7	1.33	4.00	A.3.2.14	8.11.2	-	>99.8
120-38-241-200	184	275	210	291	2053	2.67	4	1.33	2.00	A.3.2.15	8.11.3	>99.9	>99.8
110-38-248-200	257	389	218	288	2226	3.33	5	1.33	2.67	A.3.2.16	8.11.4	>99.9	-
130-40-182-150	138	202	156	228	1359	2.00	4	1.00	1.50	A.3.2.17	8.11.5	>99.9	>99.7

FIGURE 8.11.1 CONCENTRATION PROFILE FOR RUN 110-40-351-200

The samples were taken from column 10, 150 sec after sequencing action, on the 5th cycle

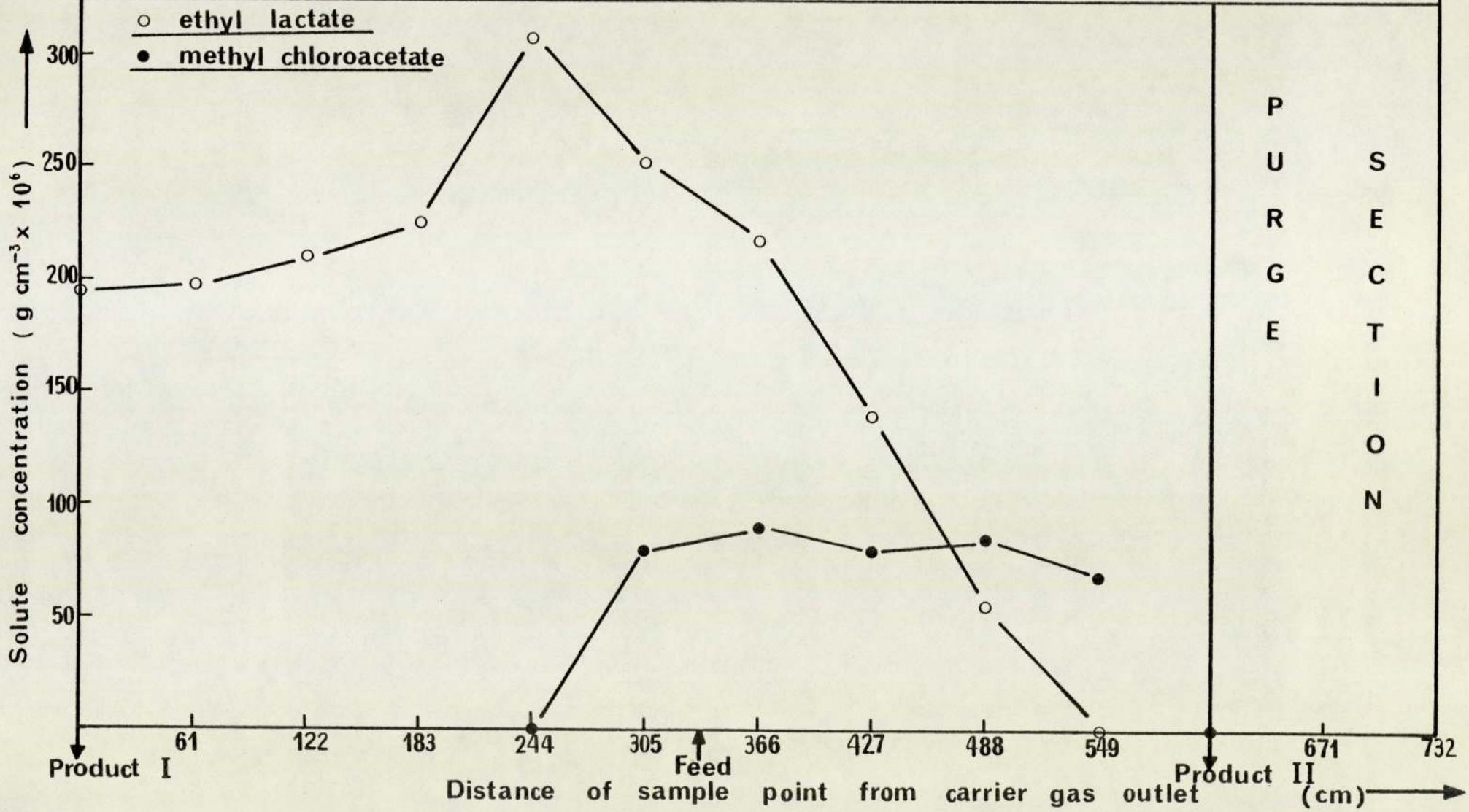


FIGURE 8.11.2 CONCENTRATION PROFILE FOR RUN 120-40-346-200

The samples were taken from column 10, 150 sec after sequencing action, on the 7th cycle

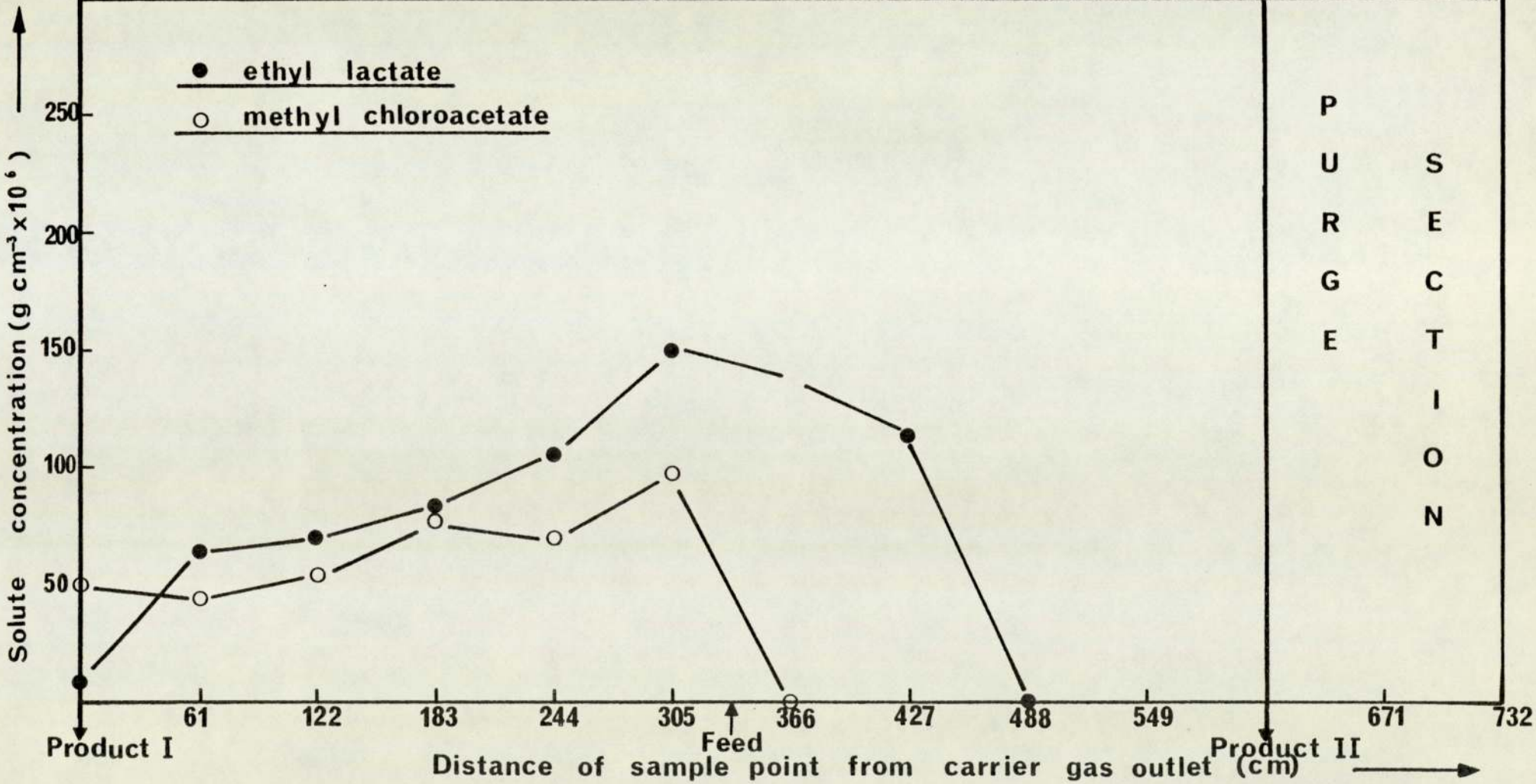


FIGURE 8.11.3 CONCENTRATION PROFILE FOR RUN 120-38-241-200

The samples were taken from column 10, 150 sec after sequencing action, on the 4th cycle

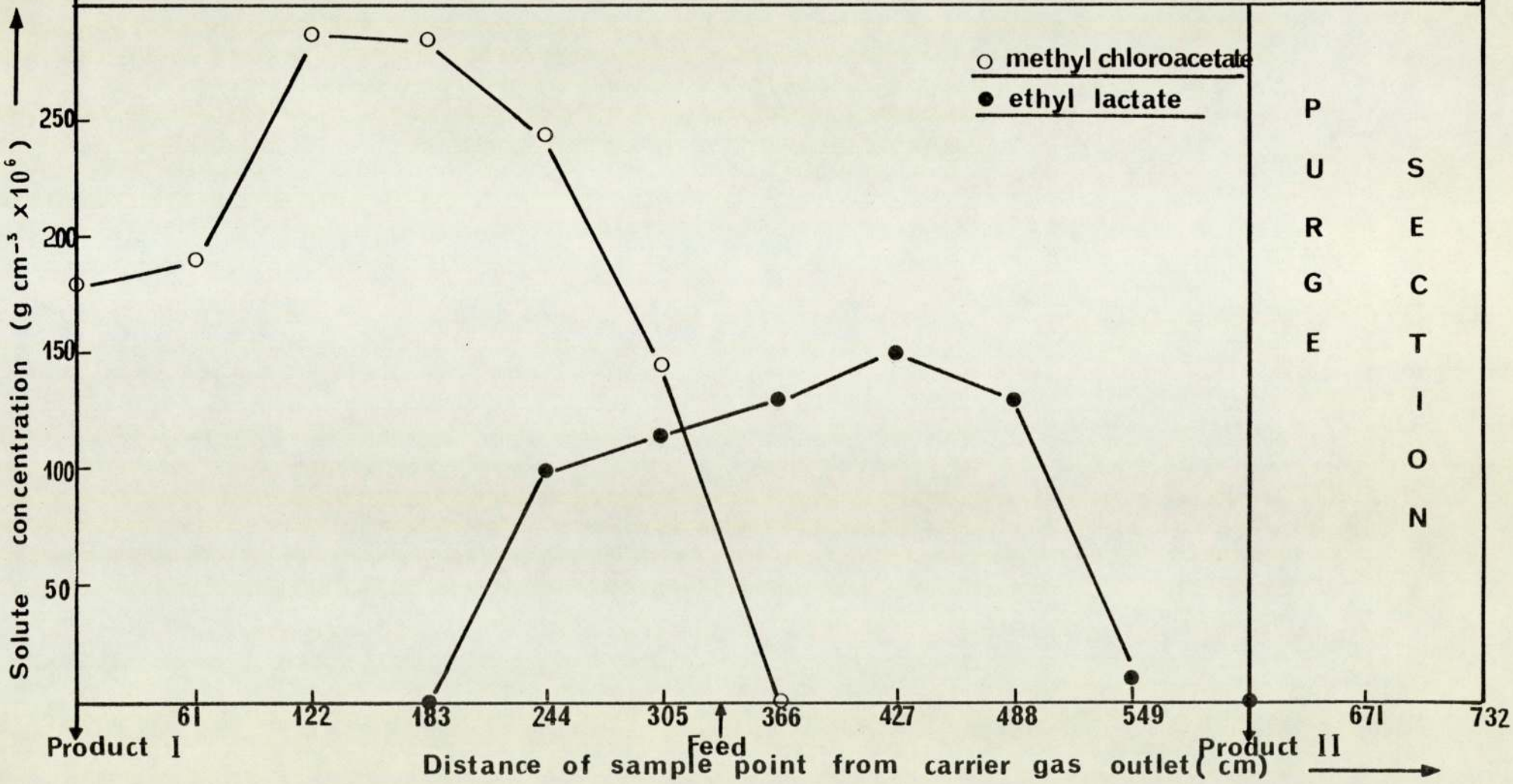


FIGURE 8.11.4 CONCENTRATION PROFILE FOR RUN 110-38-248-200

The samples were taken from column 10, 150 sec after sequencing action, on the 5th cycle

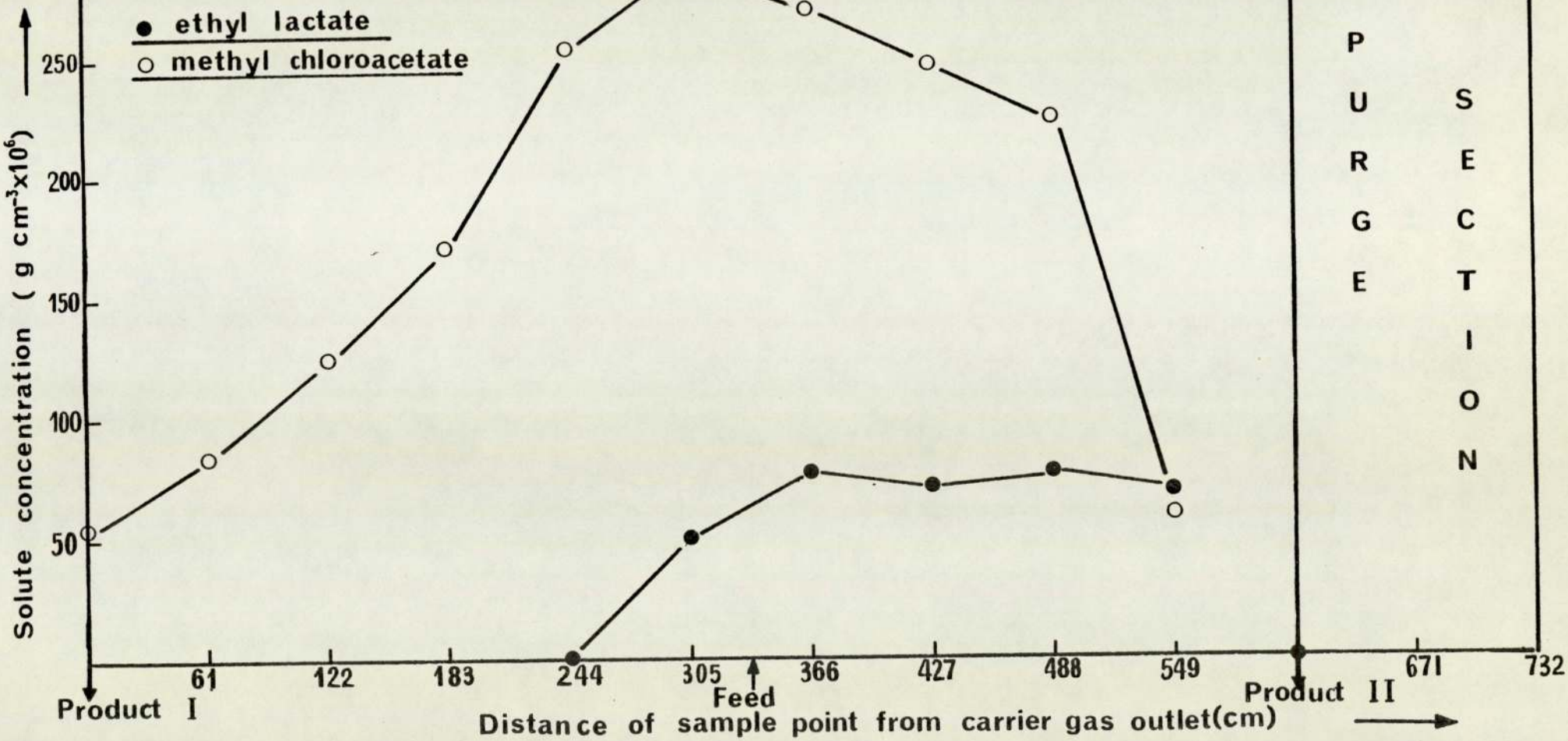
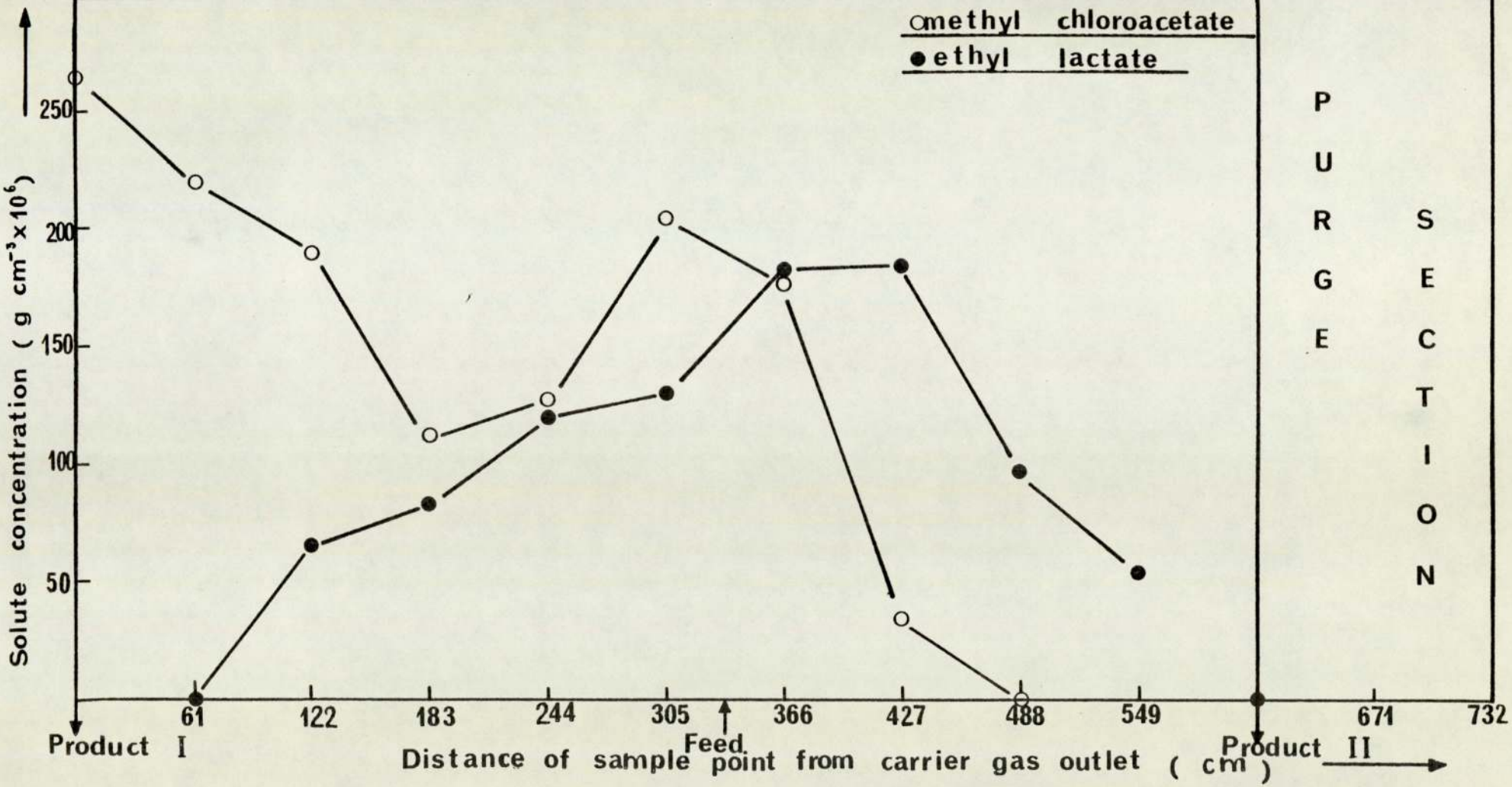


FIGURE 8.11.5 CONCENTRATION PROFILE FOR RUN 130-40- 182-150

The samples were taken from column 10, 100sec after sequencing action, on the 4th cycle



8.3 THE SEPARATION OF ETHYL CHLOROACETATE/ETHYL LACTATE

The separating capabilities of the SCCR-2 unit have been further examined by using a system of higher separation difficulty, such as ethyl chloroacetate/ethyl lactate.

The partition coefficient values of ethyl chloroacetate and ethyl lactate at infinite dilution, experimentally determined as is shown in Section 4.1, indicate separation factors within the range 1.26-1.17 for the system in the respective temperature range of 108-135°C. These low separation factor values indicate a very difficult separation for this equipment, particularly if the drawbacks of the sequential unit are to be considered such as the temperature fluctuations experienced during operation (± 2°C) and the $\frac{G}{L}$, variations across the separating section.

The relevant physical properties of the above chemicals are summarised in Table 6.1.

The studies with the system ethyl chloroacetate/ethyl lactate were not as extensive as those of "Arklone" P/"Genklene" P and methyl chloroacetate/ethyl lactate systems. Also the column to column concentration profiles were not obtained, because difficulties were encountered in analysing the gas samples taken through the sampling valve. In particular, the adsorption of solutes in the inlet/outlet lines of the sampling valves caused some tailing in the elution peaks which owing to the low separation factor system resulted in some degree of overlapping between the elution peaks, making the quantitative analysis inaccurate.

Thus, the only record of performance of the sequential unit on these experimental studies was the products' purities, which could

be determined at the end of each experimental run by analysing liquid samples taken from the condensing traps.

8.3.1 RESULTS

Details of four experimental runs are presented in Table 8.10 in which the operating temperature varied between 108 and 125°C, and the $\frac{Gmc}{L'}$ ratio was proportionately reduced from 414 to 201 according to the requirements for successful separation.

A trial and error procedure followed to determine the range of $\frac{Gmc}{L'}$ over which a measure of separation could be achieved. This was found, as with the previously studied methyl chloroacetate/ethyl lactate system, to be quite close to the upper theoretical limit for successful separation, defined by the partition coefficient of ethyl lactate at infinite dilution, at the respective temperature (see Equation 7.8).

The above findings could be justified if the finite solute concentration effects upon the partition coefficients were included in the inequality defining the limits for successful separation (see Section 7.1). The results however are consistent with the anti-Langmuir type of absorption isotherms; i.e. the partition coefficients of solutes increase with increasing concentration.

All experimental runs were performed at a constant solute feedrate of 33 cm^3h^{-1}. It was decided to keep feedrates at relatively low levels in order to avoid to some extent the effect of solute concentration on the performance of the sequential unit, which in the case of low separation factor systems is expected to be very important.

TABLE 8.10 : SYSTEM ETHYL CHLOROACETATE/ETHYL LACTATE
SUMMARY OF OPERATING CONDITIONS

Run title	Temperature			Ambient conditions		Solute mixture feedrate	l_s	L'	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L'	Sa	Pin	Pout	J	Smc/L'
Θ-f-Gmc/L'-l_s	°C	°C	°C	°C	kNm^{-2}	$cm^3\ h^{-1}$	s	cm^3s^{-1}	cm^3s^{-1}	kNm^{-2}	kNm^{-2}	—	—	cm^3s^{-1}	kNm^{-2}	kNm^{-2}	—	—
108-33-414-300	108	110	111	27	100	33.3	300	0.041	25.4	226	150	0.79	414	160	184	159	0.93	2898
118-33-292-240	118	120	121	27	101	33.5	240	0.051	22.2	229	163	0.83	292	172	184	156	0.92	2618
125-33-201-240	125	127	128	27	102	33.3	240	0.051	15.0	226	168	0.85	201	167	184	151	0.90	2641
125-33-243-240	125	127	128	28	102	33.5	240	0.051	18.3	226	165	0.83	243	165	184	153	0.91	2595

SUMMARY OF RESULTS

Run title	K^∞		Separating section		Purge section	Total time of run	Total no. of cycles	Time to pseudo steady state	Product purities	
	E.C	E.L	Gmin/L'	Gmax/L'	Smin/L'				%E.C	% E.L
Θ-f-Gmc/L'-l_s						h		h		
108-33-414-300	324	407	348	524	2693	3.50	4	2.50	74.8	80.7
118-33-292-240	228	276	250	351	2412	4.00	5	2.00	91.6	76.0
125-33-201-240	185	223	176	237	2408	4.80	6	2.00	95.0	65.2
125-33-243-240	185	223	214	293	2348	4.00	5	2.00	85.8	70.4

8.3.2 DISCUSSION

The results presented in Table 8.10 demonstrate the limited capability of the SCCR-2 unit in dealing with systems having very low separation factors. The product purities indicat e that the equipment has inadequate separating length for close separation factor systems.

In particular for the ethyl chloroacetate/ethyl lactate system, the purity of one product could be improved at the expense of the other product purity. This indicates the difficulty of the separation which requires equipment operation at conditions very close to the limits of its separating power.

The operating conditions employed on these experimental runs may be far from being the optimum, and in any further investigations the concentration profile analysis for the runs would be required for determining the optimum values. The use of capillary analytical columns or improved means of heating the inlet/outlet lines of the sampling valve could overcome the problems encountered in determining the column concentration profiles for this sytem.

Particularly a study into the optimum operating temperature is essential. Increasing the temperature reduces the partition coefficient of solutes and therefore lower $\frac{Gmc}{L'}$ values would be required for the separation. The advantage is that the pressure drop across the separating section can be reduced and hence the variation in the point values of $\frac{G}{L'}$, between the carrier gas inlet and outlet, which is very restrictive to the successful separation. This however must be balanced against the reduction in the value of separation factor with increasing temperature.

Apart from optimising the operating conditions several changes can be suggested to improve the separating capabilities of the sequential units when processing chemical systems with a low separation factor.

A larger sized solid suppprt would reduce the pressure drop, for a given flowrate, across the separating section and hence reduce the variation in the point values of the gas to apparent liquid rate ratio. The associated increase in H.E.T.P. with increased particle size could be counteracted by employing an improved packing technique. Also selecting another liquid phase to give comparatively lower values for the respective partition coefficients would be advantageous for the same reasons.

The significant effect of temperature on the gas chromatographic process was well demonstrated in previous experimental studies. A better temperature control for the unit, at present giving rise to temperature fluctuations of about ± 2°C, would be essential for improving its separating capabilities.

An improvement in the performance of the sequential unit would be gained by introducing the solute feed in the vapour phase. The latter has been experimentally demonstrated by Bell (21), using a low separation factor system on the SCCR-1 unit.

8.4 PRELIMINARY SEPARATION STUDIES OF OTHER CHEMICAL SYSTEMS

8.4.1 THE SEPARATION OF ACETIC-PROPIONIC ACIDS

The separation of the equivolume mixture of acetic-propionic acids has been preliminarily studied on the sequential unit. The relevant physical properties of the acids are given in Table 6.1, while their experimentally determined partition coefficient data at infinite dilution are presented in Table 4.1.

The partition coefficients, K^{∞}, of acetic and propionic acids at 108°C are 706 and 1102 respectively, giving a separation factor of 1.56. This separation factor is of the same order of magnitude as that of the methyl chloroacetate/ethyl lactate system for which a number of successful separations were demonstrated in Section 8.2.

Preliminary studies however have shown that separations of the acetic-propionic acids were not as successful as those carried with the methyl chloroacetate/ethyl lactate mixture. Typical purities of about 95% for product I (acetic acid) and 85% for product II (propionic acid) were achieved, when operating the unit at 110°C with feed throughputs of approximately 25 cm^3h^{-1}. The loss of separation with this mixture is mainly due to the large partition coefficient values of the solutes which are typical of the free fatty acids (see Section 4.1). The disadvantage in dealing with high K^{∞} values, is that high $\frac{Gmc}{L'}$ values are required for the separation and the associated pressure drop increase across the separating section results in high $\frac{G}{L'}$ variations.

Reducing the K^{∞} values of acetic and propionic acids by simply increasing the operating temperature does not facilitate the separation, as the present design of feed distributor requires equipment operation below the boiling point of solutes so that vaporization of the feed mixture in the distributor is avoided. Presence of gas phase in the

feed distributor would result in non-uniform feeding around the 12-columns which is undesirable for successful separation.

Several other problems associated with the G.L.C. separation of free fatty acids have been reported in the literature for analytical-scale chromatographs, such as the molecular association of acids in the stationary phase or their adsorption in the column. These are comprehensively reviewed in Section 2.5.1.2.

To conclude, converting the fatty acids into their esters eliminate most of the above mentioned problems and better separations would be expected on the sequential unit, as happens on analytical-scale chromatographs (see Sections 2.5.1, 4.1).

8.4.2 THE RECOVERY OF γ-LINOLENIC ACID FROM "FUNGAL OIL"

The recovery of γ-linolenic acid from "fungal oil" is a problem with high industrial interest to pharmaceutical companies.

Recent research by Bio-Oils Research Ltd. has shown the remarkable ability of γ-linolenic acid to reduce blood clotting, even at very low doses. This effect is believed to derive from the fact that γ-linolenic acid may redirect natural biosynthetic pathways in the body. Specifically, γ-linolenic acid is normally metabolised by a series of steps to form either a prostaglandin or arachidonic acid. In a healthy man these two products are in balance but a patient prone to heart attacks tends to produce excessive amounts of arachidonic acid. γ-Linolenic acid has been found able to redirect these natural biological processes, allowing the body to increase the production of prostaglandin, which in turn prevents blood clotting.

The "fungal oil", an oil derived from the seeds of the wild flower, "Evening Primrose", has been found by the Bio-Oils Research Ltd. to be a good source of the γ-linolenic acid. In particular the

hydrolysed and methylated "fungal oil" provides a multicomponent fatty acid esters mixture, approximately 20% "rich" in γ-linolenic acid methyl ester.

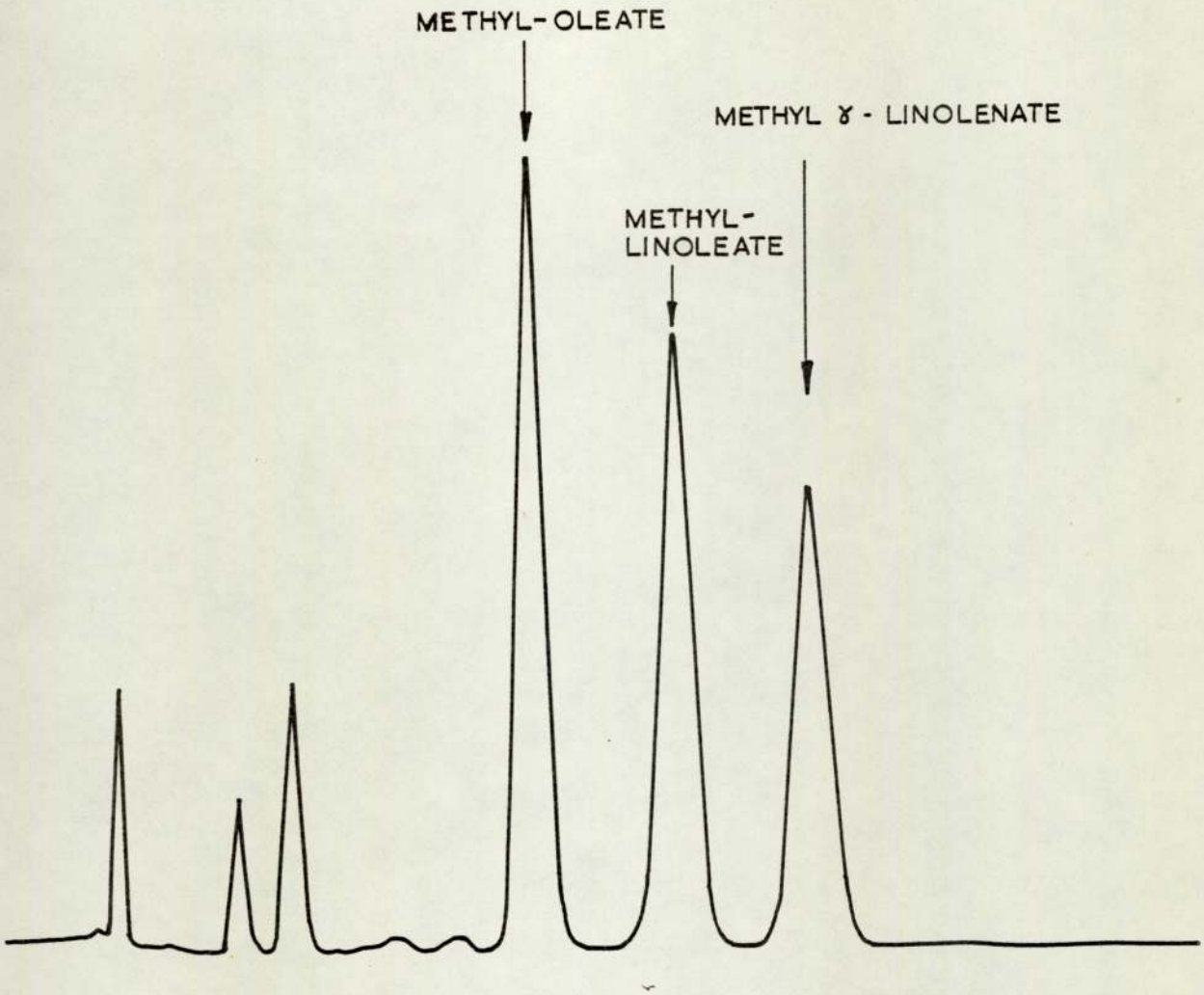
However, as the major components of the mixture are methyl oleate and methyl linoleate, which have very close boiling points to the methyl γ-linolenate, the recovery of γ-linolenic acid from "fungal oil" by the common separation methods i.e. distillation has been found to be impossible. The investigations of Bio-Oils Research Ltd. have indicated crystalization and chromatography as the leading possibilities for the above purification problem.

In the present work the recovery of γ-linolenic acid from "fungal oil" was studied on the SCCR-2 equipment.

From the G.L.C. analysis of hydrolysed and methylated "fungal" oil, shown in Fig. 8.12, it is indicated that the heaviest component in the mixture (the most soluble in the liquid phase) is the methyl γ-linolenate, while the nearest lighter component to it is methyl linoleate. Consequently, as the SCCR-2 equipment is capable of producing only two products for a single pass operation, the "cut" position for the above purification problem should be between the methyl γ-linolenate and methyl linoleate components. The partition coefficient values, K^{∞}, of methyl linoleate and methyl γ-linolenate, experimentally determined at infinite concentration conditions on F.F.A.P. phase, are 1478 and 1813 respectively at 197°C (see Table 4.2).

Initial experimental studies on the sequential unit have shown that the recovery of γ-linolenic acid is impossible with the equipment presently available. The reason for that is the excessively high K^{∞} values of the above mentioned solutes on F.F.A.P. phase and their relatively low separation factor. Solutes with such high K^{∞} values, required excessively high carrier gas flowrates in order for the

FIG 8.12 G.L.C. ANALYSIS OF HYDROLYSED - METHYLATED "FUNGAL OIL"



inequality defining the conditions for successful fractionation to be justified (see Equation 7.8). This resulted in unusually high pressure drops across the separation section, leading to extremely high $\frac{G}{L'}$ variations for which the condition $K_I < \frac{G_{min}}{L'} < \frac{G_{max}}{L'} < K_{II}$ required for the fractionation was not fulfilled (see Section 7.1).

In addition, when operating the sequential unit at about 200°C which is far below the boiling point of the fatty acid ester solutes, it is expected that most of the feed mixture will remain as liquid during the whole of the chromagraphic process.

Obviously some of the above problems can be eliminated by operating the sequential unit at higher temperatures; reduced K^{∞} values would be obtained and the vaporization of the feed mixture would be easier. Unfortunately the construction of the SCCR-2 unit dictated operation below 210°C, while the degree of unsaturation of the long chain-length fatty solutes involved in this purification problem required operation below 200°C in order for polymerization, cyclization or stereomutation of the double bonds to be avoided. In fact indications are of the thermal instability of fatty solutes at operating conditions of around 200°C.

To overcome these drawbacks certain modifications had to be made on the sequential unit.

Firstly the initial packing had to be replaced by a more suitable one. The selection of a new solvent phase was made from consideration of the partition coefficient values of methyl γ-linolenate and methyl linoleate on three recommended phases (see Table 4.2). OV-275 (a cyanosilicone) was finally chosen because it gave comparatively low values for the respective partition coefficients and has high thermal stability. The chromatographic packing material which was used for

repacking the SCCR-2 columns consisted of 15% by weight of OV-275 on 353-251 μm Chromosorb P, while the employed packing procedure was similar to the one previously used for the F.F.A.P. packing, described in Section 5.2.3.2. The exact weights of new packing material used for each SCCR-2 column, are given in Table 5.3.

Secondly the design of the feed introduction system was modified so that the presence of liquid feed onto the chromatographic columns was eliminated during the separation process. Thus, it was decided to introduce the "fungal oil" feed in the vapour phase. This was essentially achieved by passing a flow regulated nitrogen stream through two feed tanks in series, located inside the SCCR-2 oven. Each feed tank was made from a stainless-steel tube of 2.5 cm in I.D. and 30.5 cm in length, which was half-filled with the "fungal oil" mixture. From the feed tanks the nitrogen stream, carrying solute vapours enters the feed distributor and then enters the chromatographic columns through the energized feed diaphragm valves.

It should be noted that the composition of solutes in the nitrogen stream was considered the same as in the original feed mixture. This assumption arises from the fact that vapour pressures of the components of the "fungal oil" mixture are approximately the same (see Table 6.1).

The major operating restriction involved for the latter feed system is that the nitrogen gas flow through the liquid feed must be relatively low compared to the main carrier gas flow so that the preset flow conditions through the chromatographic columns remain unaffected. It was experimentally found that the nitrogen-feed vapour flowrate should be lower than one tenth of the mean carrier gas flowrate for this not to happen. Consequently, the feed throughputs which could be introduced into the system were at very low levels, i.e. 1 $cm^3 h^{-1}$ for the hydrolysed-

methylated "fungal oil". The operated feed throughput for each experimental run could be determined from the measured volume of solute mixture in the feed tanks prior and after the run and the recorded total time of operation.

The preliminary experimental studies performed with the "fungal oil" mixture after the above modifications are presented in Table 8.11.

The results obtained, demonstrate the rather unsatisfactory performance of the sequential unit in dealing with low separation factor systems such as the separation of γ-linolenic acid from "fungal oil", which has a separation factor of 1.23 at 183°C. This is mainly due to the $\frac{G}{L}$, variations across the separation section and the temperature fluctuations caused by the presently available temperature control system of the unit. However, the lighter components of the "fungal oil" mixture were satisfactorily removed from the product II, which now contained up to 49.4% of methyl γ-linolenate compared to the 20% initially present in the feed mixture.

Further investigations should be directed towards optimising the operating conditions so that a product II, "richer" in methyl γ-linolenate, may be achieved. Also recycling procedures for the product II should be considered in order to improve its concentration levels in methyl γ-linolenate.

Several design changes were suggested in Section 8.3.2. for improving the separating capabilities of the sequential unit which may in due course be proved very useful for the above purification problem.

At the time of writing M. Howari, a member of the Separation-Purification Research Group in the Chemical Engineering Department of University of Aston, has been engaged on further experimental studies

on the SCCR-2 unit. These include a more comprehensive study for the recovery of γ-linolenic acid from "fungal oil".

TABLE 8.11 : SYSTEM "FUNGAL OIL"

SUMMARY OF OPERATING CONDITIONS

Run title	Temperature			Ambient conditions		Solute mixture feedrate	l_s	L′	Separating section					Purge section				
	Operation	Carrier inlet	Purge inlet	Θa	Pa				Ga	Pin	Pout	J	Gmc/L′	Sa	Pin	Pout	J	Smc/L′
Θ-f-Gmc/L′-l_s	°C	°C	°C	°C	kNm^{-2}	$cm^3\ h^{-1}$	s	cm^3s^{-1}	cm^3s^{-1}	kNm^{-2}	kNm^{-2}	—	—	cm^3s^{-1}	kNm^{-2}	kNm^{-2}	—	—
183-1-391-300	183	185	185	28	101	1.2	300	0.051	33.7	322	186	0.72	391	171	246	193	0.88	2339
183-1-450-300	183	185	185	29	101	1.1	300	0.051	37.5	322	157	0.63	450	174	236	181	0.86	2472
181-1-427-300	181	183	188	27	101	1.1	300	0.051	30.8	281	134	0.62	427	181	218	155	0.82	2869

SUMMARY OF RESULTS

Run title	K~		Separating section		Purge section	Total time of run	Total no. of cycles	Time of pseudo steady state	% Methyl γ-linolenate in product II
	M.L	M.γ.L	Gmin/L′	Gmax/L′	Smin/L′				
Θ-f-Gmc/L′-l_s						h		h	
183-1-391-300	295	363	314	543	2085	6.00	6	2.50	38.6
183-1-450-300	295	363	348	714	2204	5.00	5	2.50	49.4
181-1-427-300	320	398	328	689	2488	6.00	6	2.50	46.6

8.5 CONCLUDING DISCUSSION OF THE SEPARATION STUDIES

The results presented in this Chapter demonstrate the performance of the SCCR-2 unit for the separation of various systems over a wide range of temperatures.

For relatively easy systems such as that of "Arklone" P/ "Genklene" P, which has a separation factor of 5.8 at 60°C and requires equipment operation at around 60°C, quite successful separations were achieved under various operating conditions (temperature, carrier gas flowrate, sequencing rate). This was to be expected because of the wide range of conditions for which the Equations 7.7, 7.8, which define the limits for successful separation, are justified for the "Arklone" P/ "Genklene" P system.

For the more difficult separation of the methyl chloroacetate/ ethyl lactate system, which has a separation factor of 1.5 at 120°C and requires operation at temperatures in the range of 110-130°C, an optimisation of the operating conditions (particularly for the $\frac{Gmc}{L'}$ ratio) was found to be necessary in order to obtain high product purities. This again is consistent with the limits defined from Equations 7.7, 7.8 for successful separation which in the case of the methyl chloroacetate/ ethyl lactate system are in a close range.

The separating capabilities of the SCCR-2 unit have been further studied using the lower separation factor systems ethyl chloroacetate/ ethyl lactate and "fungal oil" which have separation factors of around 1.2 at temperatures of 125 and 180°C respectively, and require that the unit be operated at temperatures of up to 200°C. However, unsatisfactory results were obtained for both ethyl chloroacetate/ethyl lactate and "fungal oil" fractionations, although the optimisation of operating conditions is still required.

Five factors have been considered as restricting the separating capabilities of the SCCR-2 unit, namely:

1. the changes in the partition coefficient values of solutes with finite concentrations (absorption isotherm effect).
2. the $\frac{G}{L}$, variations across the separation section due to the pressure drop across the columns
3. the finite column length of the separation section and therefore the finite number of theoretical plates
4. the semi-continuous nature of operation
5. the temperature fluctuations during operation caused either by the inaccurate temperature control system or the enthalpic overloading effects.

In practice factor (2) appeared to be the most significant, and it was found advantageous to deal with systems having low partition coefficient solutes as lower pressure drops across the columns are involved and the $\frac{G}{L}$, variations reduced. Also the temperature fluctuations within the packed bed (± 2°C) during operation caused mainly by the oven's temperature control system should be considered quite restirctive because of the high temperature dependence of the partition coefficients.

Operating the sequential unit at temperatures close to the boiling points of solutes was found to be beneficial for the separation, as lower partition coefficient values, K, were involved (K decreases with increasing temperature) and the feed mixture was easily vaporized into the columns. However, for the "fungal oil" mixture operation at such temperatures was not possible because of the high thermal instability of the mixture and the operating limitations of the SCCR-2 equipment.

Finally several design changes are suggested in Section 8.3.2 to improve the separating capabilities of the SCCR-2 unit.

CHAPTER 9

Theoretical Treatment of the Sequential Counter-Current Chromatographic Process

9.1 FACTORS RESTRICTING THE PERFORMANCE OF OPERATION

As is shown in Section 7.1 the conditions for the separation of a binary feed mixture on an ideal counter-current chromatographic unit with a separate purging section, are as follows:

$$K_I < \frac{G}{L} < K_{II}$$

$$\frac{S}{L} > K_{II} \qquad (9.1)$$

where, G : mobile phase flow in the separating section

L : stationary phase flow

S : mobile phase flow in the purge section

K_I : partition coefficient of component I. Hence component I is the component of feed mixture with the least affinity for the stationary phase.

K_{II}: partition coefficient of component II. Hence component II is the component of feed mixture with the most affinity for the stationary phase.

However, when applying this idealised model to the practical case of the SCCR-2 equipment, several factors can impose restrictions upon the above equations namely,

(1) chromatographic zone broadening

(2) finite column length

(3) the sequential nature of operation

(4) finite solute concentration effects

(5) mobile phase pressure gradient.

9.1.1 CHROMATOGRAPHIC ZONE BROADENING

The chromatographic solute zone broadening theories have been reviewed in Sections 2.1.1 and 2.1.2. Zone dispersion has the effect of causing a component with a partition value of K_I to elute from a chromatographic column over a range of K values, from $K_I-\delta_I$ to $K_I+\delta_I$, where $2\delta_I$ is the total baseline peak width in K units. Consequently, the G/L ratio must be maintained within narrower limits to ensure a successful separation, as is shown in the following inequality.

$$K_I + \delta_I < \frac{G}{L} < K_{II} - \delta_{II} \tag{9.2}$$

Similarly, the gas flowrate in the purge section must be increased so that,

$$\frac{S}{L} > K_{II} + \delta_{II} \tag{9.3}$$

9.1.2 FINITE COLUMN LENGTH

It has been previously indicated (see Section 2.3.2.1) that the required column length or number of theoretical plates for a successful separation increases with the difficulty of separation. The closer together the values of K_I and K_{II} become, the more that the G/L ratio approaches the limits for successful separation and the tendency of the feed solutes to move in opposing directions is reduced. Thus, a longer column length is required to achieve the same degree of separation as the K_{II}/K_I ratio approaches unity. Consequently, for a finite column length the range of G/L values for a successful separation is further reduced, as follows

$$K_I + \delta_I + \delta'_I < \frac{G}{L} < K_{II} - \delta_{II} - \delta'_{II} \tag{9.4}$$

Hence δ'_I and δ'_{II} may be regarded as functions of the number of theoretical plates for the system, as well as the criteria for a "successful" separation.

9.1.3 THE SEQUENTIAL NATURE OF OPERATION

The counter-current movement of the stationary phase relative to the mobile phase in the sequential unit does not occur in a continuous manner but as a step movement of one column length of packing every sequencing interval. Within a sequencing interval, the unit is operating as a co-current system till the next sequencing action of the valves, when the whole of the material in a column is transported in the direction of packing movement in a discontinuous manner. This has the effect of further reducing the selectable range for the G/L ratio.

$$K_I + \delta_I + \delta'_I + S_I < \frac{G}{L} < K_{II} - \delta_{II} - \delta'_{II} - S_{II} \qquad (9.5)$$

where, L' = the apparent volumetric liquid phase flowrate

$$= \frac{\text{total volume of liquid phase in columns}}{\text{cycle time}}$$

and S_I, S_{II} = factors to allow for the reduction in the limits of G/L' attributable to the sequencing action, which are functions of the number of columns in the unit and the sequencing time interval.

9.1.4 MOBILE PHASE PRESSURE GRADIENT

In chromatographic columns the small particle size packing materials usually employed present a considerable flow resistance. The consequent pressure drop associated with the flow of gas across

the column results in a continual change in the volumetric gas flowrate. Thus, at the column inlet the carrier gas flowrate, G, has a minimum value, while as the pressure falls G increases to a maximum value at the outlet.

The effect of this pressure drop on the performance of the sequential unit is better understood by considering the two ends of the separating section, the carrier gas inlet and product I outlet. In the region close to the carrier gas inlet the flowrate is relatively lower and therefore the rate of migration of both solute molecules in the direction of gas flow is reduced. Consequently the solute molecules (component I) which should be travelling preferentially with the carrier gas could eventually be retarded enough so as to cause contamination of Product II (component II).

Approaching the other end of the separating section (product I outlet) the opposite effect could occur so that the migration rate of component II molecules being relatively high could produce a long leading edge contaminating the product I (component I).

A further restriction should therefore be imposed on the limits of G/L' to ensure a successful separation.

$$K_I + \delta_I + \delta'_I + S_I < \frac{G_{min}}{L'} < \frac{G_{max}}{L'} < K_{II} - \delta_{II} - \delta'_{II} - S_{II} \qquad (9.6)$$

where G_{min} = inlet gas phase volumetric flowrate in the separating section of the sequential unit

G_{max} = outlet gas phase volumetric flowrate in the separating section of the sequential unit.

9.1.5 FINITE SOLUTE CONCENTRATION EFFECTS

It has been previously shown (see Section 2.3.1.1) that at finite concentrations the partition coefficient values of solutes are affected by three major effects: the absorption isotherm, the sorption effect and enthalpic overloading effect.

The majority of systems in G.L.C. exhibit a non-linear absorption isotherm. Consequently the partition coefficient, K, changes with solute concentration. With increasing concentration K decreases for a Langmuir isotherm while for an anti-Langmuir isotherm K increases.

The sorption effects always lead to migration rates for the solute molecules which are higher than the specified solely by the ratio of the liquid and gas phase solute concentrations, $K = \frac{q}{c}$. This is due to the additional presence of vapor of the solute in the carrier gas stream which results in higher mobile phase flowrates.

At finite solute concentrations the heats of absorption and desorption of the solute become significant and generate temperature fluctuations in chromatographic columns (enthalpic overloading effect). In practice any temperature variations accompanying the solute band will be counteracted by heat conduction through the column packing and column wall. However an axial and radial temperature will still exist because of the low thermal conductivity of packing materials. Axial and radial temperature gradients will have the following effects on a separation.

(1) The leading edge of the solute band will be at a relatively high temperature giving an increased solute migration rate, whilst the trailing edge of the solute band will be retarded due to a lower temperature being experienced.

(2) Radial temperature gradients will lead to non-uniform cross-column solute migration rates.

The above discussed finite concentration effects on the partition coefficient may be expressed by the following equation.

$$K = K^{\infty} + \Delta K \tag{9.7}$$

where, K^{∞} = the partition coefficient at infinite dilution

ΔK = the positive or negative deviation of partition coefficient at finite concentration, K, from the K^{∞} value.

Therefore, a further restriction should be imposed on the limits of G/L' so as to ensure the successful separation of components I and II on the sequential unit.

$$K_I^{\infty} + \Delta K_I + \delta_I + \delta_I' + S_I < \frac{G_{min}}{L'} < \frac{G_{max}}{L'} < K_{II}^{\infty} + \Delta K_{II} - \delta_{II} - \delta_{II}' - S_{II} \tag{9.8}$$

Similarly for the purge section the final relation is,

$$\frac{S_{min}}{L'} > K_{II}^{\infty} + \Delta K_{II} + \delta_{II} + \delta_{II}' + S_{II} \tag{9.9}$$

9.1.6 DISCUSSION

Equation 9.8 represents the limits for complete separation of components I and II. However, the use of this equation requires detailed knowledge of the parameters involved which in turn necessitate an extensive experimental and theoretical study.

To evaluate individually the effect of the parameters on the performance of the sequential unit based purely upon experimental data would be extremely difficult, if not impossible. This is due to the complex interaction between the parameters of Equation 9.8. For example, the effect of a finite column length is related to column characteristics, sequencing rate and pressure drop. Also, the finite solute concentration effects are related to zone broadening.

A theoretical model is required to enable a study of the individual factors to be made. The operating data of the SCCR-2 unit (see Section 8) could provide the basic information required to prove the validity of this model.

Since the numerical values of the parameters of Equation 9.8 were not obtained in this work, the limits of the SCCR-2 unit for successful separation were approximated by the respective partition coefficients of solutes at infinite dilution (see Equation 7.8). Equation 7.8 was used as a practical guide to the selection of operating conditions for the separation of a binary feed mixture with the SCCR-2 unit. Experimental studies however have indicated that the effect of pressure drop across the column as well as the effect of finite solute concentrations sometimes cause the approximate equation 7.8 not to hold true (see Section 8).

9.2 MATHEMATICAL MODELLING OF THE COUNTER-CURRENT CHROMATOGRAPHIC PROCESS

9.2.1 INTRODUCTION

Theoretical models of mass transfer processes are usually based on either the "transfer unit" or "equilibrium stage" concepts. Both concepts have been used by Barker and co-workers for the theoretical

analysis of the various counter-current chromatographic units proposed by them.

Barker and Lloyd (16,179) approach to the theoretical treatment of the counter-current chromatographic process is based on the transfer unit concept of Chilton and Colburn (196), in which the H.T.U. (height of a transfer unit) is used to express the efficiency of chromatographic columns. They derived the following equationsfor a G.L.C. system.

$$(N_{OG})_R = \frac{1}{G/(KL-L)} \ln \left[\frac{E_I/KL - c_a\,(G/KL-1)}{E_I/KL - c_b\,(G/KL-1)}\right] \qquad (9.10)$$

$$(N_{OG})_S = \frac{1}{(1-G/KL)} \ln \left[\frac{E_{II}/KL - c_a\,(1-G/KL)}{E_{II}/KL - c_b\,(1-G/KL)}\right]$$

where,

$(N_{OG})_R, (N_{OG})_S$ = number of overall gas phase transfer units in the "rectifying" and "stripping" sections respectively

E_I, E_{II} = mass flowrate of solute leaving the column in the product I and product II streams respectively

c_a, c_b = gas phase solute concentrations at points a and b in the column

G = gas volumetric flowrate

L = liquid volumetric flowrate.

This method has been applied by Barker and Lloyd (7,16,179) to a moving-bed G.L.C. system for which a first order relationship was found between the logarithm of H_{OG} and the liquid phase flowrate,

with H_{OG} values of the order of 10 cm for the chemical systems and conditions studied.

Sunal (47) developed a computer model for the counter-current chromatographic process, using the H.T.U. concept and based on the "two film theory" of mass transfer. Comparing his computer calculations with the experimental results of Huntington (180) for a moving-bed G.L.C. system he concluded that the effect of axial mixing on separation efficiency was negligible.

Barker and Al-Madfai (13,14) based on the random walk model derived the following equation to express the solute zone broadening in terms of H (height equivalent to a theoretical plate) for a counter-current G.L.C. system.

$$H = d_p + \frac{2 D_m}{u} + \frac{2 r_1 r_2}{u r_2 - u_L r_1} \left(\frac{u + u_L}{r_1 + r_2}\right)^2 \qquad (9.11)$$

whhre,

r_1 = rate of transfer of molecules from gas to liquid

r_2 = rate of transfer of molecules from liquid to gas

u_L = liquid phase velocity.

For a co-current operated chromatographic column a similar expression (see Equation 9.12) is valid, only that the last equation does not include contribution to solute zone broadening caused by movement of the liquid phase.

$$H = d_p + \frac{2 D_m}{u} + \frac{2 r_1 u}{(r_1 + r_2)^2} \qquad (9.12)$$

Further, Al-Madfai (13) gives an expression to relate the number of theoretical plates required to separate a binary mixture using a co-current G.L.C. column, N, to the required number, N_{cc}, for a counter-current chromatographic column.

$$\frac{N_{cc}}{N} = 3\,(\alpha-1) \qquad (9.13)$$

hence,

N_{cc} = number of counter-current theoretical plates

N = number of co-current theoretical plates

α = separation factor, $\frac{K_{II}}{K_I}$

From the above equation it is indicated that for systems having a separation factor below 1.33, less theoretical plates would be required for a counter-current column than for a co-currently operated column, which suggests that the counter-current operation may be particularly viable for difficult separations. Rony (181-183) also derived a relationship between N and N_{cc}, which is as follows.

$$\frac{N_{cc}}{N} = \frac{(1 + K_I)^2}{\sqrt{2\pi}\,(u_{m.t}/\sigma)} \qquad (9.14)$$

where,

K_I = the partition coefficient for component I

u_m = the molar velocity of the mobile phase

t = time

σ = peak standard deviation (units of length).

Quoting the work of Fitch et al. (103), Barker and Huntington (10,16,180) treated the counter-current moving-bed process in a manner similar to the theoretical treatment of stagewise liquid-liquid extraction given by Alders (184) to obtain the following relationship between the difficulty of separation, the number of theoretical plates and the products purities.

$$\log \frac{\psi_{max}}{\psi_{min}} = \log a + \frac{2}{N_{cc}} \left[\log\left(1 - \frac{E_I^I}{f_I}\right) + \log \frac{E_{II}^I}{f_{II}}\right] \qquad (9.15)$$

where,

ψ_{max}, ψ_{min} = the maximum and minimum allowable values of u/u_L to produce products of the required purity

E_I^I, E_{II}^I = the mass production rate of components I and II at the top of the column

f_I, f_{II} = the mass feedrate of component I and II to the column

α = the separation factor

N_{cc} = the number of counter-current theoretical plates.

One major disadvantage of Equations 9.14 and 9.15 is the inherent assumption of a constant partition coefficient, which is not usually obtained in practice. Tiley (185) overcame this drawback by developing a computer program to perform stage-to-stage calculations for a vertical moving-bed column which allows the introduction of a non-linear absorption isotherm. Tiley (185) studying the effect of stage number, flow conditions and temperature on the column concentration profiles concluded that,

(1) there is a limiting feed throughput for a given solvent rate, product purity and number of stages which is dependent on the phase equilibrium characteristics

(2) the optimum operating temperature is just below the mean boiling points of the feed mixture.

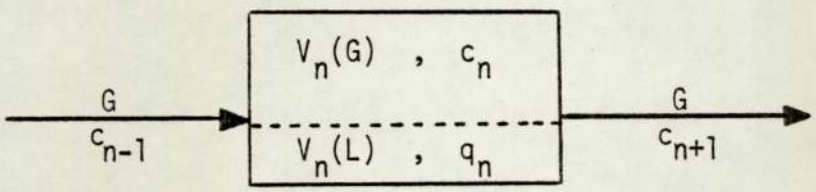
All the theoretical treatments of the counter-current chromatographic process discussed here are based on a true steady-state operation which is only achieved in the moving-packing systems (see Section 2.4.2.2).

The latter schemes of counter-current chromatographs developed by Barker such as the moving-column or sequential units (see Section 2.4.2.2) operate in a manner similar to "frontal elution chromatography", as the stationary phase, maintained in a fixed position within a series of packed columns, is exposed to the solute carrying gas stream in finite volumes. The overall behaviour of these chromatographs is then described by imposing a switching mechanism on the basic process that simulates the relative movements of the gas and stationary phases. Thus, time must be introduced as an additional variable for the theoretical analysis of this chromatographic process. Sunal (47) has developed a computer program based on plate-to-plate calculations to simulate the operation of a compact circular counter-current chromatograph (see Section 2.4.2.2). This approach was also used by Deeble (20) for the simulation of the SCCR-1 unit, while Bell (21) has modified this computer model by introducing other factors, i.e. temperature profiles to improve the accuracy of simulation. Based on the same model Ellison (61) developed a program to simulate gel-permeation chromatographic separations on a 5.2 cm diameter sequential unit. The above computer simulations of the sequential counter-current gas-liquid chromatographic process are reviewed in the following Section.

9.2.2 COMPUTER MODELS FOR THE SIMULATION OF THE SEQUENTIAL COUNTER-CURRENT OPERATION

The computer models for the simulation of the sequential counter-current chromatographic process mentioned in the previous section are all based on a plate model developed by Sunal (47). According to this model, the chromatographic column is considered to consist of a series of idealized mixing stages or theoretical plates. A mass balance over the n^{th} plate and for the time increment $t \rightarrow t+\Delta t$ led Sunal to the following equation (see Fig. 9.1).

FIGURE 9.1 : MASS BALANCE OVER PLATE "n"



$$G.c_{n-1} = G.c_n + V_n(G).\frac{d\,c_n}{dt} + V_n(L).\frac{d\,q_n}{dt} \qquad (9.16)$$

where, G = volumetric gas flowrate

c_n, q_n = solute concentration in gas and liquid phase in plate n over a small time increment $t \rightarrow t+\Delta t$

$V_{n(G)}, V_{n(L)}$ = the volumes of gas and liquid phase occupying the n^{th} plate.

Noting that the partition coefficient is defined as $K_n = \frac{q_n}{c_n}$, a rearrangement of equation 9.16 gives

$$G.c_{n-1} = G.c_n + V_n.\frac{d\,c_n}{dt} \qquad (9.17)$$

where, $V_n = V_{n(G)} + K_n.V_{n(L)}$ the "effective plate volume".

If the time increment, Δt, over which the above equation is integrated, is sufficiently small so that c_{n-1} may be considered constant, integration of equation 9.16 yields:

$$c_n = c_{n-1}(1 - e^{-\frac{G.\Delta t}{V_n}}) + c_n(0)\, e^{-\frac{G.\Delta t}{V_n}} \qquad (9.18)$$

In the above equation c_n is the gas phase concentration in plate n at the end of the time increment, Δt, while the first term on the right hand side is the contribution to it from the inlet concentration (this may be the output from the previous plate and/or an external feed) and the second term is the contribution of the concentration which was present in the plate at the beginning of the time increment.

Commencing from time zero, a plate to plate calculation for a single solute over a small time increment can be performed by substituting successive values of c_{n-1} into Equation 9.18, with $c_n(0)$ being zero for the first time increment. The resultant concentration profile is then updated by repeating the entire calculation for successive time increments. Meanwhile, the sequencing action occurring in the SCCR equipments may be imposed onto the plate-to-plate calculations by stepping the concentration profile backwards, by one column, at the end of a sequencing interval.

The inclusion of a second solute on the computer model is achieved by duplicating the calculation at each plate with different variable names for the respective solute concentrations ($c_{n(I)}$, $c_{n(II)}$) and partition coefficients (K_I, K_{II}). Thus, the assumption being made

is that the solute concentration profiles are independent. For simplicity it was also assumed that the solute feed was introduced as vapour onto a single plate in the centre of the feed column. For the plate which was receiving the solute feed the term, c_f, was included in Equation 9.18 to give the total input gas phase concentration to that plate.

The above model proposed initially by Sunal (47) and further developed by Deeble (20) and Bell (21) for the simulation of the SCCR-1 unit, although very simple, is very flexible. Thus, it can easily be made to incorporate non-linear absorption isotherms, sorption effects, column pressure gradients and temperature profiles (20,21). Despite the number of simplifying assumptions being made by Deeble (20) and Bell (21), the major drawback of the model is the enormous amount of computer time required. These assumptions however represent an idealised picture of the actual process taking place within the sequential and some of them must be removed in order to improve the accuracy of simulation. Thus, a balance between the accuracy of simulation and the corresponding increase in computation time must be made.

9.2.3 DISCUSSION

A simple chromatographic plate model has been developed by Sunal, Deeble and Bell (20,21,47) to simulate the performance of the sequential counter-current operation. Although the model has been found by Deeble (20) and Bell (21) to reproduce the experimental concentration profiles of the first sequential unit (SCCR-1) with reasonable accuracy, several suggestions for improving the accuracy of simulation were made by them. However, the extremely long computation time required for a simulated run represent a limitation on the practical value of this model.

The development of a reliable computer model to simulate accurately the sequential counter-current process would be very useful for further studies on the SCCR-2 equipment. Information that could be extracted from such a model are:

(1) the determination of optimum operating conditions

(2) investigations for the operation of the SCCR-2 equipment above 446 kN m^{-2} and 200°C, which is impossible to be experimentally studied because of the limitations of the sequential unit

(3) determination of minimum number of theoretical plates required for a given separation

(4) to investigate in isolation, the individual factors affecting the performance of the sequential unit, defined by Equation 9.8.

Due to time limitations it has not been possible to undertake any computer simulations studies, but my successor Mr. Howari (186) is engaged in a study of the computer simulation of the SCCR-2 unit using some of the data reported in this thesis and using the model developed by Bell (21).

CHAPTER 10

Conclusions and Recommendations for Future Work

The sequential counter-current mode of continuous chromatography has been successfully applied to G.L.C. separations at temperatures up to 200°C.

Economic considerations dictated the design of the SCCR-2 equipment developed for this study which consisted of 12 columns, each 61 cm long and 2.54 cm in diameter. Column dimensions, however, can be increased without further complexity for higher throughputs, while an increase in the separating capabilities of the unit can be achieved by simply increasing the number of columns.

Vapour-liquid equilibrium determinations with an analytical-scale chromatograph indicated a number of chemical systems suitable for separation studies on the SCCR-2 unit. The selected chemicals provided a combination of mixtures of different separation difficulty and volatility. Hence, a systematic study of the SCCR-2 unit performance at various temperatures (55-200°C) and with different separation difficulty (SF = 1.1-5.8) could be achieved.

The factors affecting the performance of the sequential unit have been identified (solute concentration effects, pressure gradient across the columns, sequential nature of operation etc.) but their quantitative determination is still required. A modified version of the computer program suggested by previous workers (20,21) in the field of sequential chromatography could be used to achieve this. In practice, as the difficulty of separation increased, the factors restricting the performance of the sequential unit were more pronounced and this led to a loss of product purity.

Consequently, for the relatively easy separation of "Arklone" P/ "Genklene" P, which has a separation factor of 5.8 at 60°C on F.F.A.P.

liquid phase, product purities in excess of 99.8% were obtained at feedrates of 21 $cm^3 s^{-1}$ under various operating conditions. The performance of the SCCR-2 unit for this feed mixture has shown very little sensitivity to column conditions within the defined theoretical limits for successful separation (see Equation 9.1).

For the more difficult system of methyl chloroacetate/ethyl lactate, which has a separation factor of 1.5 at 120°C on F.F.A.P. phase, the effects of pressure drop and finite solute concentration were the most pronounced. However, an optimisation of the operating conditions has led to 99.8% pure products at feedrates up to 80 $cm^3 h^{-1}$ and operating temperatures within the range of 110-130°C.

Preliminary studies with the lower separation factor systems ethyl chloroacetate/ethyl lactate and "fungal oil" at temperatures up to 200°C, indicated that the sequential unit had inadequate column length for close separation factor mixtures i.e. separation factors lower than 1.2.

Apart from increasing the number of columns, several suggestions can be given for improving the separating capabilities of the SCCR-2 unit.

1. The use of an improved packing technique to increase the chromatographic column efficiency e.g. Reese and Grushka method (5).
2. The use of larger size solid support to minimize the pressure drop effects which were found to severely affect the performance of the sequential equipment.
3. The cross-column variation in volumetric gas flowrate could be reduced by operating the unit at high pressures which would also increase the solute capacity of the gas phase.

4. Improving the temperature control system of the sequential unit, at present giving rise to temperature fluctuations within the packed bed of about ± 2°C, would also be beneficial for the equipment because as was shown the gas chromatographic process is very sensitive to temperature variations.

5. Introducing the feed mixture in the vapour phase would withdraw the present limitation which requires that the unit operate at temperatures below the boiling point of feed solutes in order to effect uniform feeding around the 12-columns. Also the heat of vaporisation, which at high feedrates is expected to cause significant temperature variations in the system, would be avoided.

The development of a reliable computer model to simulate the performance of the SCCR-2 unit is also recommended as facilitating:

a. the determination of optimum operating conditions for a given separation

b. quantitative investigations of the individual effect of key parameters on the overall performance of the SCCR-2 unit

c. investigation of the performance of the unit at conditions not experimentally possible, i.e. operation at temperatures above 200°C

d. indication of other means of improving the throughput capacity and selectivity power of the sequential unit.

Although the mixtures used in this study (with the exception of "fungal oil") can be separated relatively cheaply in larger quantities by other methods, it is thought that the application of the SCCR-2 unit will lie in the separation of thermally unstable and close boiling point chemical mixtures when high purity products are required. Such separations are encountered in most chemical industries but in particular in the pharmaceutical, perfume and food industries, where separations of essential oils and fatty acids are important.

To summarize, the recommended future work on the SCCR-2 equipment should be concentrated on studies aimed at increasing its separating power. This is because most of the industrially important problems deal with mixtures having low separation factors on the liquid phases presently available e.g. the separation of oleic/linoleic/ linolenic acids. Meanwhile, the scale-up of this equipment has been already investigated in columns up to 2.54 cm in diameter and successful separations at feedrates up to 1500 cm^3h^{-1} have been achieved (21) at ambient temperature.

NOMENCLATURE

A	term accounting for eddy diffusion in chromatographic theoretical plate height equation
Ai, A', A*	constants in empirical equations for the determination of vapour pressure data
B	term accounting for longitudinal diffusion in chromatographic theoretical plate height equation
B_{ii}	second virial coefficient of component i
B_{ij}	cross second virial coefficient of components i and j
B_o^*, B_1^*	reduced second virial coefficient functions
B_i, B', B*	constants in empirical equations for the determination of vapour pressure data
C_i	constant in the Antoine equation
C_m	term accounting for mobile phase resistance to mass transfer in chromatographic theoretical plate height equation
C_s	term accounting for stationary phase resistance to mass transfer in chromatographic theoretical plate height equation
c	concentration of solute in the gas phase
D_s	stationary phase molecular diffusivity
d	thickness of stationary phase liquid film
d_c	column diameter
d_p	mean particle diameter
E_I, E_{II}	mass flowrate of product leaving in the product I and Product II streams respectively
E_I^I, E_{II}^{II}	mass production rate of components I and II as product I
F	mobile phase flowrate at ambient conditions
F°	mobile phase flowrate at the column outlet pressure
F'_m	fractional volume of mobile phase in chromatographic column
F'_s	fractional volume of stationary phase in chromatographic column
f	solute mixture feedrate

f_I, f_{II}	feedrate of component I and II to the column
G	gas phase volumetric flowrate in the main separating section of the sequential unit
G_a	gas phase volumetric flowrate measured at ambient conditions
G_{mc}	gas phase volumetric flowrate measured at mean column pressure
G_{min}	gas phase volumetric flowrate at the column inlet
G_{max}	gas phase volumetric flowrate at the column outlet
H	height equivalent to a chromatographic theoretical plate, H.E.T.P.
$\bar{h}^E$	excess partial molar enthalpy of mixing
I_s	the length of a sequencing interval
J_n^m	correction factor for gas phase compressibility
K	partition coefficient
K^∞	partition coefficient at infinite dilution
ΔK	change in the value of the partition coefficient from the value at infinite dilution with increasing solute concentration
k	capacity ratio, $K.F'_s/F'_m$
k_f	solute exchange rate between mobile and stationary phases
L	liquid phase volumetric flowrate
L'	apparent liquid phase volumetric flowrate in the sequential unit
L_M	distance migrated by the centre of a component zone
l	column length
l'	root mean square step length in random walk model
M	molecular weight
M_L	molecular weight of liquid phase
N	number of co-current chromatographic theoretical plates within a column

N_{cc}	number of counter-current theoretical plates within a column
$(N_{OG})_R$	number of overall gas phase transfer units in the rectifying section of a column
$(N_{OG})_S$	number of overall gas phase transfer units in the stripping section of a column
n	constant in the O'Connell-Prausnitz equation
n'	number of steps in random walk model
n_L	number of moles of liquid phase in the column
P	pressure
P_a	ambient pressure
P_c	critical pressure
P_i	column inlet pressure
P_o	column outlet pressure
P_R	reduced pressure
P_{co}	outlet pressure in the separation section of the sequential unit
P_{so}	outlet pressure in the purge section of the sequential unit
P°	vapour pressure
$\bar{P}$	mean column pressure
ΔP	atomic and structural contribution to P_c
R	relative solute band migration rate
R_g	gas constant
r_1	rate of transfer of molecules from gas to liquid phase in random walk model of continuous counter-current G.L.C.
r_2	rate of transfer of molecules from liquid to gas phase in random walk model of continuous counter-current G.L.C.
S	volumetric gas flowrate in the purge section of the sequential unit
S_a	volumetric purge gas flowrate measured at ambient conditions

S_{mc}	volumetric gas flowrate measured at mean purge column pressure
SF	separation factor, K_{II}/K_I
s	correction to the operating G/L' limits for a successful separation on the sequential unit attributable to the sequencing action
$\bar{s}^E$	excess partial molar entropy of mixing
T	temperature (absolute)
T_a	ambient temperature (absolute)
T_b	boiling point temperature (absolute)
T_c	critical temperature (absolute)
T_R	reduced temperature, T/T_c
T_{co}	column temperature (absolute)
T_{mc}	mean column temperature in the separation section of the sequential unit (absolute)
T_{ms}	mean column temperature in the purge section of the sequential unit (absolute)
t	time
t_R	elution or retention time
t'_R	adjusted retention time, $t_R - t_m$
t_m	elution or retention time for an unabsorbed component
t_w	width of an eluted peak (time units)
$t_{r.i.c}, t_{r.o.c}$	time from injection to the commencement of the recording of the inlet and outlet profiles
$\bar{t}_{r.i}$, $\bar{t}_{r.o}$	peak mean or first moment in time units for the recorded inlet and outlet profiles
u	average interstitial mobile phase velocity
u_L	stationary phase velocity in continuous counter-current chromatography
u_m	molar velocity of the gas phase
V°	molar volume of pure component
$\bar{V}$	partial molar volume

$\bar{V}^{\infty}$	partial molar volume at infinite dilution
V_c	critical volume
V_m	volume of mobile phase in column
V_N	net retention volume, $V_R - V_m$
V_N^o	corrected net retention volume, $J_3^2 . V_N$
$V_n(G)$, $V_n(L)$	gas phase volume and liquid phase volume in plate n
V_R	retention or elution volume
ΔV	atomic and structural contribution to V_c
W	accentric factor
W_H	accentric factor of a polar molecule's homomorph
W_L	weight of liquid phase in a column
y	mole fraction of solute in the gas phase
y_o	mole fraction of solute in the gas phase at the column outlet

Greek

α	separation factor, K_{II}/K_I
γ	activity coefficient
γ^{∞}	activity coefficient at infinite dilution
γ'	labyrinth factor
δ, δ'	factors to correct theoretical operating (G/L) limits of the sequential unit
θ	temperature in °C
θ_a	ambient temperature in °C
λ	eddy diffusion factor
μ	dipole moment
μ_R	reduced dipole moment
ρ	density

ρ_L	density of liquid phase
σ	standard deviation
σ^2	variance
$(\sigma_t)^2_{r.i}$	time based variance of the eluted peak recorded at the column inlet
$(\sigma_t)^2_{r.o}$	time based variance of the eluted peak recorded at the column outlet
ψ	operating mobile phase/stationary phase velocity ratio in moving-bed chromatography

Abbreviations

A.P.	"Arklone" P
B.S.P	British Standard Pipe Fitting
Component I	the least soluble component in the feed mixture which exits from the sequential unit with the carrier gas
Component II	the most soluble component in the feed mixture which exits from the purge section of the sequential unit
E.C	ethyl chloroacetate
E.L	ethyl lactate
F.F.A.P.	free fatty acid phase
F.I.D.	flame ionization detector
G.L.C.	Gas-liquid Chromatography
G.P	"Genklene" P
G.P.C.	Gel-Permeation Chromatography
L.L.C.	Liquid-Liquid Chromatography
M.C	methyl chloroacetate
M.γ-L	methyl γ-linolenate
SCCR	Sequential Continuous Chromatographic Refiner
S.T.P.	shake, turn, pressurise method of packing columns

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APPENDIX 1

Calibration Charts

FIGURE A.I.I ROTAMETER CALIBRATION

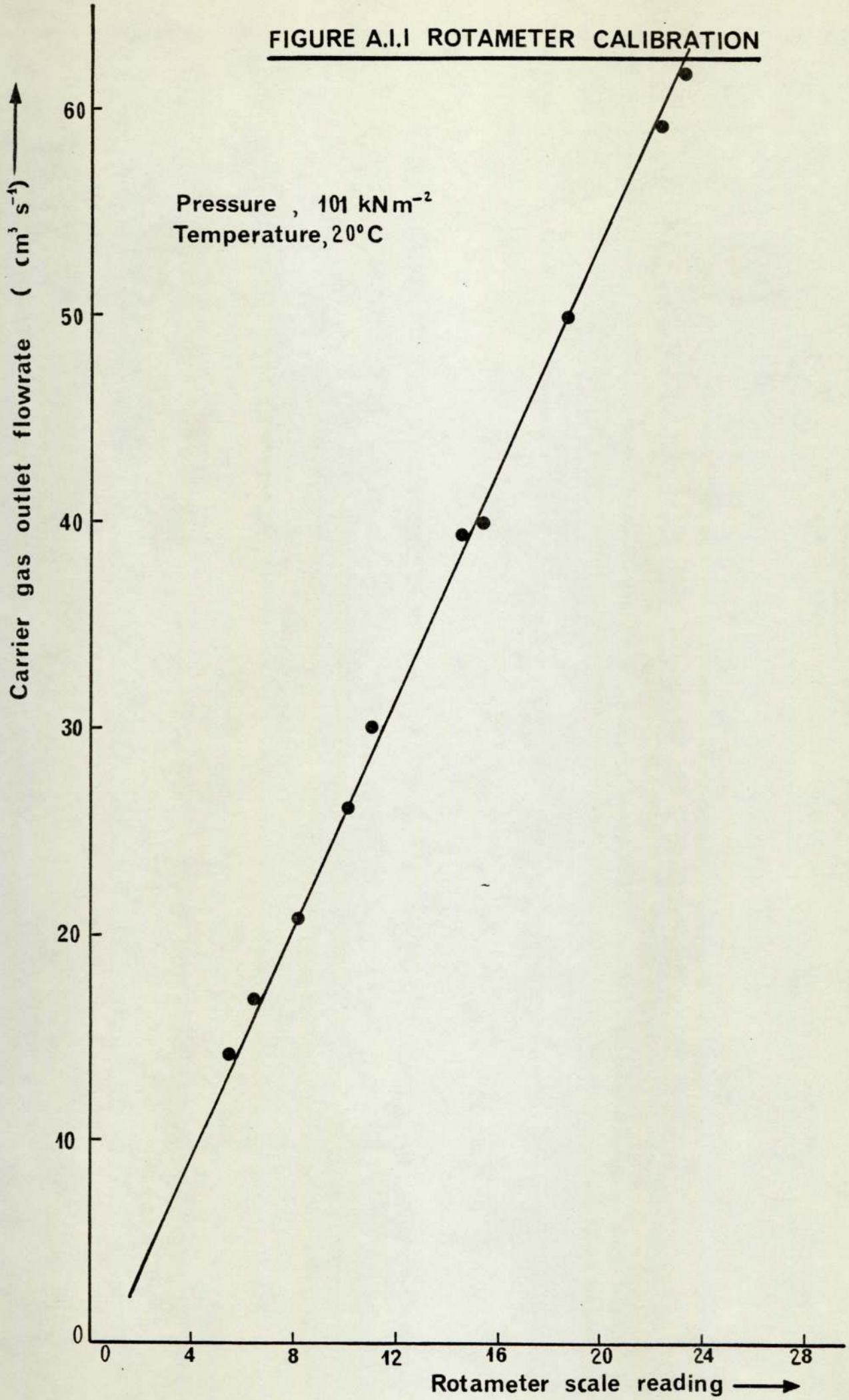


FIGURE A.1.2 ROTAMETER CALIBRATION

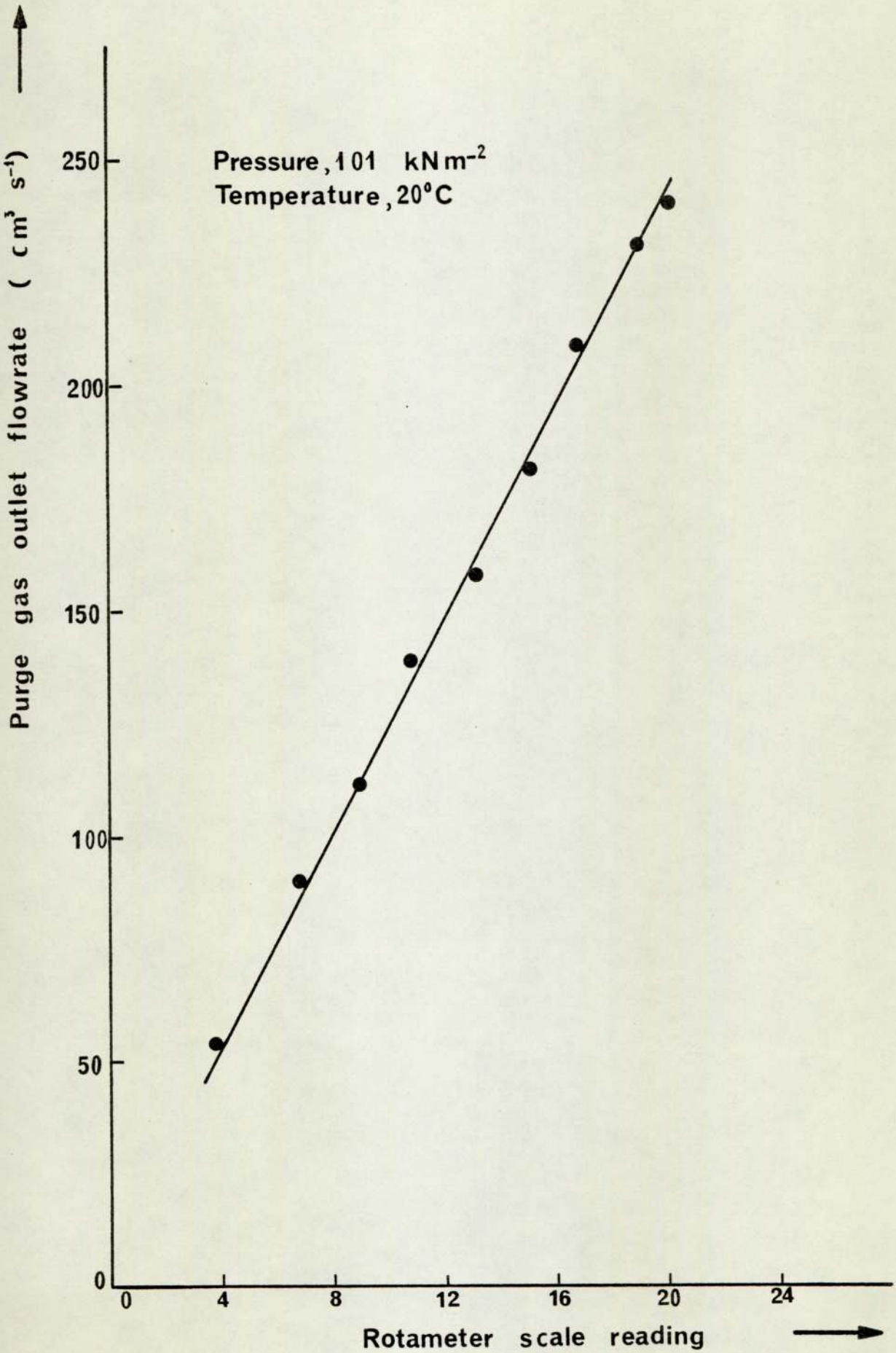
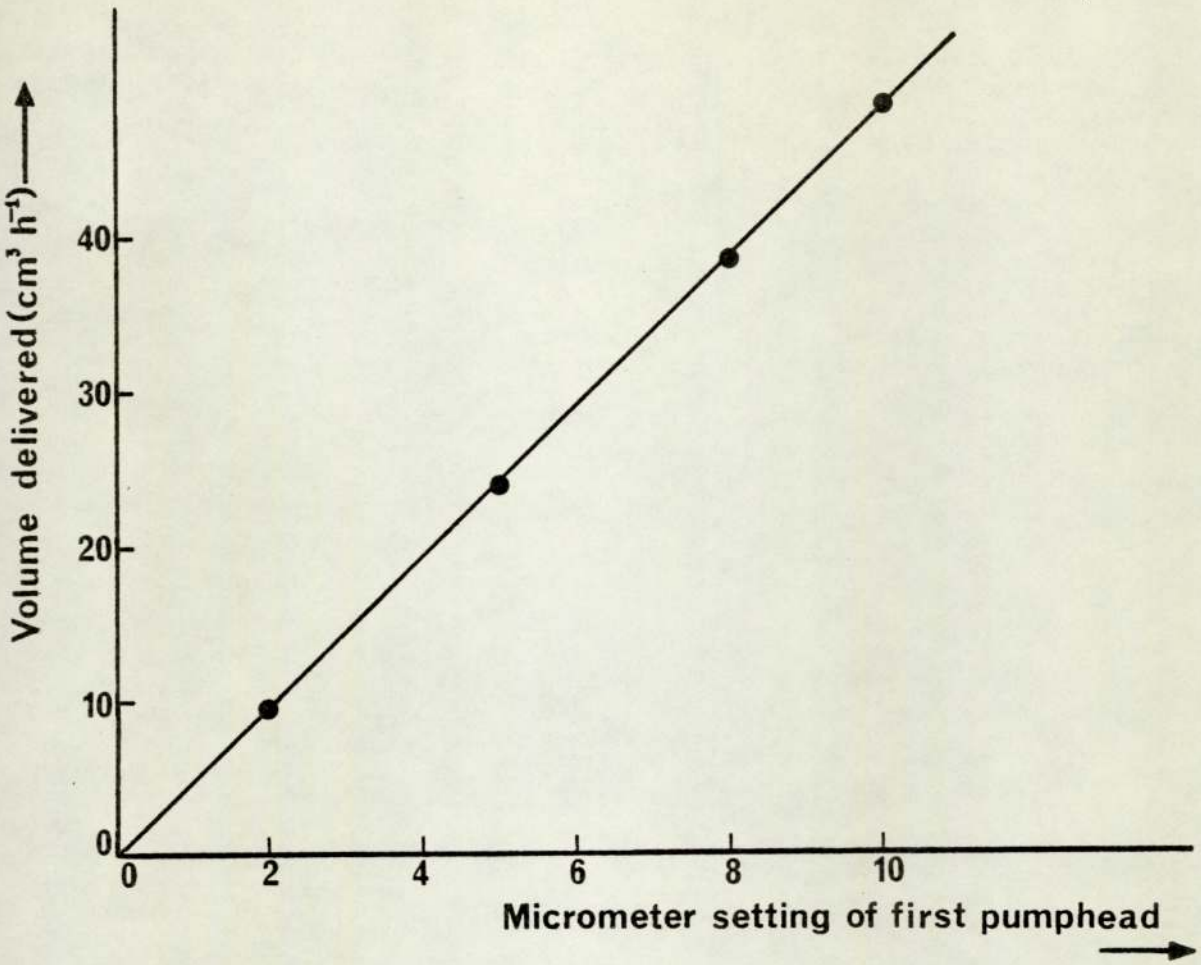
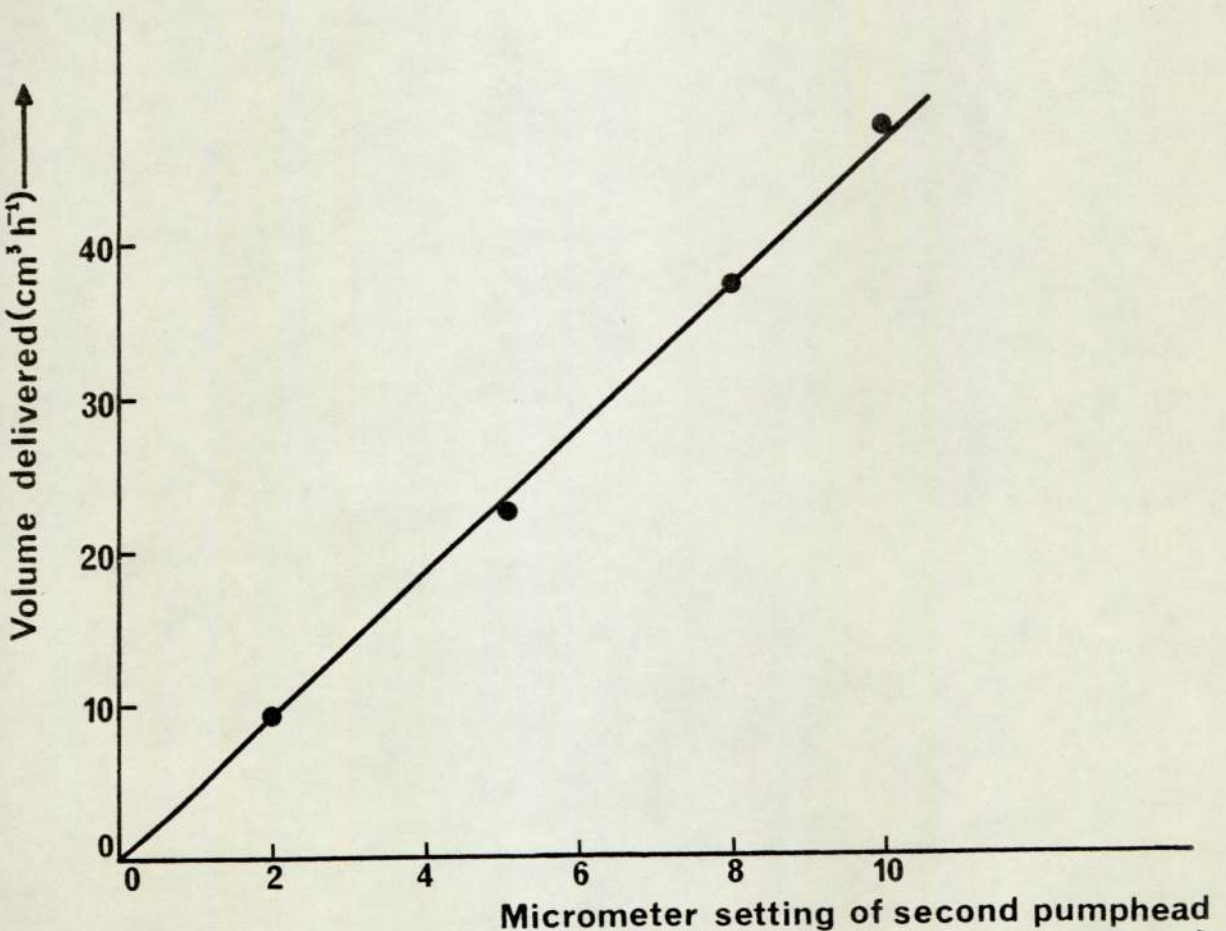


FIGURE A.1.3 CALIBRATION OF MICROPUMP





APPENDIX 2

Calculations for the Determination of Thermodynamic Data

A.2.1 CALCULATION OF VAPOUR PRESSURES

The vapour pressure data required in our studies were determined by an equation of the form:

$$\log P^\circ = A^* + B^*/T \qquad (A.2.1)$$

where, P° : vapour pressure in N m^{-2}

T : temperature in °K

A^*, B^*: constants calculated by a least square analysis the available vapour pressure data given in the literature (158, 175, 187).

The determined A*, B* constants for some of the solutes used in this work are listed in the following Table.

TABLE A.2.1 THE VALUES OF THE CONSTANTS IN EQUATION A.2.1

SOLUTE	A*	B* x 10^{-3}
acetic acid	10.43	-2.12
propionic acid	10.98	-2.46
palmitic acid	11.00	-3.77
oleic acid	12.08	-4.46
ethyl acetate	10.50	-1.92
methyl propionate	10.45	-1.92
methyl chloroacetate	11.02	-2.40
ethyl acetoacetate	10.88	-2.65
camphene	10.59	-2.40
cis-citral	10.87	-2.93

In addition the Antoine equation was often employed for vapour pressure determinations, when its constants values Ai, Bi, Ci could be found in the literature (188,189).

$$\log P^\circ = Ai - \frac{Bi}{t+Ci}$$

hence, P° : vapour pressure in mmHg

t : temperature in °C

Vapour pressure data may also be predicted by the equation,

$$\log P^\circ = -0.2185\ A'/T + B'$$

where,

P° : vapour pressure in mmHg

T : temperature in °K

A' : the molar heat of vaporization in cal mol^{-1}

B' : a constant

and the values A' and B' for various solutes are given in Reference (190).

Unfortunately, the determined vapour pressure data by the latest equation found sometimes to deviate from the available in literature data (158,175). Therefore, this method was discarded in favour of the previous ones.

A.2.2 CALCULATION OF CRITICAL CONSTANTS

Experimental data on the critical constants of substances are rare in the literature, and with the continual creation of new compounds this situation is likely to remain. To overcome this problem several empirical equations have been developed to calculate critical constants from other physical properties. Some of these equations were used in this work to estimate the critical properties of some fatty acid compounds, required for the determination of second virial coefficients (Appendix A.2.3), and the results are summarized in Table A.2.2. Comparing the calculated critical values with the experimental values, available in the literature (190), a very good agreement was obtained (see Table A.2.2).

A.2.2.1 CRITICAL TEMPERATURE (T_c)

The temperature at which the molecular kinetic energy of translation equals the maximum potential energy of attraction is termed the critical temperature (T_c). Above the critical temperature the liquid state is impossible for a single component, and compression results only in a highly compressed gas, retaining all the properties of the gaseous state.

The best over-all methods of calculating T_c, appear to be those of Riedel, Lydersen and Eduljee.

a. Lydersen method (191)

The critical temperature is determined from the following equation:

$$\frac{T_b}{T_c} = 0.567 + \Sigma\Delta T - (\Sigma\Delta T)^2$$

where T_b, is the boiling point of the compound in °K

and $\Sigma\Delta T$, is the summation of Lydersen atomic and structural contributions, some of which are listed below:

$\Delta T_{CH_3,CH_2}$	= 0.020	ΔT_{Cl}	= 0.017
ΔT_{CH}	= 0.012	$\Delta T_{c=o}$	= 0.040
ΔT_{c}	= 0.000	ΔT_{COOH}	= 0.085

b. Riedel method (191)

Similar to the previous method, T_c is given now by the equation

$$\frac{T_b}{T_c} = 0.574 + \Sigma\Delta T$$

and the Riedel additive contributions are as follows:

$\Delta T_{CH_3,CH_2}$	= 0.016	ΔT_{Cl}	= 0.013
ΔT_{CH}	= 0.013	$\Delta T_{c=o}$	= 0.046
ΔT_{C}	= 0.003	ΔT_{COOH}	= 0.070

c. Eduljee method (191)

This method uses the equation,

$$\frac{T_b}{T_c} = \frac{\Sigma\Delta T}{100}$$

and the following atomic and structural contributions,

ΔT_C = -55.32 $\Delta T_{C=O}$ = 31.63

ΔT_H = 28.52 ΔT_{COOH} = 35.94

ΔT_{Cl} = 29.89

A.2.2.2 CRITICAL PRESSURE (P_c)

The pressure required to liquefy a gas at its critical temperature is known as the critical pressure, P_c.

a. Lydersen method (192)

For the P_c determinations this method uses the correlation,

$$P_c = \frac{M}{(0.34 + \Sigma\Delta P)^2}$$

where M : molecular weight

P_c : critical pressure in atm. absolute

$\Sigma\Delta P$: the summation of atomic and structural contributions

and $\Delta P_{CH_3,CH_2}$ = 0.227 ΔP_C = 0.210 $\Delta P_{C=O}$ = 0.29

ΔP_{CH} = 0.210 ΔP_{Cl} = 0.320 ΔP_{COOH} = 0.40

b. Eduljee method (192)

Eduljee's approach for P_c determinations is,

$$P_c = \frac{10^4.M}{(\Sigma\Delta P)^2}$$

ΔP_C = -9.35 ΔP_{Cl} = 48.00

ΔP_H = 16.20 ΔP_{COOH} = 57.70

A.2.2.3 CRITICAL VOLUME (V_c)

Critical temperature and pressures fix the critical state at which there is no distinction between the gaseous and liquid states. The volume at the critical state is called the critical volume, V_c.

a. Lydersen method (192)

V_c is estimated by the following correlation,

$$V_c = 40 + \Sigma\Delta V$$

where, V_c : critical volume in $cm^3 mol^{-1}$

and

$\Delta V_{CH_3,CH_2} = 55$	$\Delta V_{Cl} = 49$	$\Delta V_{C=O} = 60$
$\Delta V_{CH} = 51$	$\Delta V_{C} = 41$	$\Delta V_{COOH} = 80$

TABLE A.2.2 CRITICAL PROPERTIES OF SOME FATTY ACID COMPOUNDS

CHEMICAL NAME	CRITICAL TEMPERATURE °C			CRITICAL PRESSURE kN m^{-2}			CRITICAL VOLUME cm^3 mol^{-1}		
	Eduljee method	Lydersen method	Experimental data (190)	Eduljee method	Lydersen method	Experimental data (190)	Eduljee method	Lydersen method	Experimental data (190)
Acetic acid	318.6	319.3	321.6	6,474	6,505	5,786	-	175.0	171.1
Propionic acid	336.9	339.6	339.0	5,208	5,259	5,370	-	230.0	231.5
Ethyl acetate	254.8	255.0	250.1	-	4,012	3,830	-	285.0	286.1
Ethyl caproate	329.5	340.3	-	-	2,543	-	-	505.0	-
Ethyl caprylate	355.3	375.0	-	-	2,148	-	-	615.0	-
Ethyl chloroacetate	341.6	342.4	-	-	3,790	-	-	334.0	-
Methyl propionate	257.8	258.4	257.4	-	4,012	3,982	-	285.0	282.4
Methyl chloracetate	338.4	338.1	-	-	4,387	-	-	279.0	-
Ethyl acetoacetate	355.0*	370.0	-	-	3,273	-	-	400.0	-

* Riedel method

A.2.3 CALCULATION OF THE SECOND VIRIAL COEFFICIENTS

A.2.3.1 PURE VAPOURS

a. Nitrogen

The second virial coefficients (B_{22}) of nitrogen may be determined by the following empirical equations.

1. Adlard equation (47)

$$B_{22} = 50.46 - \frac{1344.5}{0.08206\ T} - \frac{4.2\ 10^7}{T^3}$$

2. Pitzer and Curl equation (47)

$$\frac{P_c.B_{22}}{R.Tc} = B^*_o\ (T_R) + W.B^*_1\ (T_R)$$

where,

P_c, T_c : critical constants

T_R : reduced temperature, T/T_c

W : accentric factor, defined by

$$W = -\log P_{R\ /T_R = 0.7} - 1.000$$

B^*_o, B^*_1 : reduced virial coefficients functions, expressed as follows

$$B^*_o = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3}$$

$$B^*_1 = 0.073 + \frac{0.46}{T_R} - \frac{0.50}{T_R^2} - \frac{0.097}{T_R^3} - \frac{0.0073}{T_R^8}$$

The latest equation generally applies to pure, non-polar gases and has been considered by many authors as a very good correlation.

Particular for the B_{22} determinations of nitrogen both the Adlard and Pitzer-Curl equations provide data which are in good agreement with the available experimental data (193). For the simplicity of calculations Adlard's method was employed in this work and the results of calculations are summarized in Table A.2.3.

TABLE A.2.3 SECOND VIRIAL COEFFICIENTS OF NITROGEN

Temperature	B_{22}
°C	$cm^3\ mol^{-1}$
24.0	-6.15
60.5	0.20
74.0	2.24
90.0	4.46
100.0	5.74
120.0	8.10
140.0	10.20
160.0	12.11
180.0	13.85
200.0	15.43

b. fatty acid compounds

O'Connell and Prausnitz Equation (172,194)

This equation is an extension of the Pitzer-Curl equation to polar fluids, given as follows.

$$\frac{B_{11} \cdot P_c}{R \cdot T_c} = B_o^* (T_R) + W_H \cdot B_1^* (T_R) + f (\mu_R, T_R) - n \cdot f_a (T_R)$$

where,

W_H : the accentric factor of the polar component's homomorph. The homomorph of a polar molecule is defined as that hydrocarbon which has the same number and bonding arrangement of atoms other than hydrogen (a non-polar molecule of about the same size and shape).

B_o^*, B_1^* : functions of T_R, defined as in the Pitzer-Curl equation.

μ_R : the reduced dipole moment, defined by

$$\mu_R = \frac{10^5 \cdot \mu^2 \cdot P_c}{T_c^2}$$

where μ : the dipole moment of component in Debye units

P_c : the critical pressure in atmospheres

T_c : the critical temperature in degrees Kelvin

$$f_\mu (\mu_R, T_R) = -5.237220 + 5.665807 + 5.665807 (\ln \mu_R) - 2.133816 (\ln \mu_R)^2 +$$

$$+ \frac{1}{T_R} [5.769770 - 6.181427 (\ln \mu_R) + 2.283270 (\ln \mu_R)^2 -$$

$$- 0.2649074 (\ln \mu_R)^3]$$

for $\mu_R > 4$, and $f (\mu_R, T_R) = 0$ for $\mu_R < 4$ (molecules of very low polarity)

n : the association constant, is an empirically determined quantity which reflects the tendency of a component to associate with itself to form dimers

$f_a(T_R)$: the association function, given by

$$f_a(T_R) = \exp [6.6\ (0.7-T_R)]$$

Using the above method the second virial coefficients of some fatty acid compounds (B_{11}) were determined, and the results are summarized in Table A.2.4. The calculated B_{12} values have been found in very good agreement with available literature experimental values (193), as is shown in Fig. A.2.1.

Finally it should be noted that the major sources used to obtain the required parameters for the solution of the O'Connell-Prausnitz equation were: (189,190,194,195).

A.2.3.2 VAPOUR MIXTURES

The second, cross virial coefficient (B_{12}) of a vapour mixture consisting of a polar and a non-polar gas may be determined by the Pitzer-Curl equation, using the O'Connell-Prausnitz mixing rules (172):

$$\frac{P_{c12} \cdot B_{12}}{R \cdot T_{c12}} = B_o^* (T_R) + W_{12} \cdot B_1^* (T_R)$$

where,

$$T_{c12} = (T_{c1} \cdot T_{c2})^{1/2}$$

$$W_{12} = 1/2\ (W_1 + W_{H2})$$

$$P_{c12} = \frac{4\ T_{c12} \left[\frac{P_{c1} \cdot V_{c1}}{T_{c1}} + \frac{P_{c2} \cdot V_{c2}}{T_{c2}}\right]}{\left(V_{c1}^{1/3} + V_{c2}^{1/3}\right)^3}$$

The above method was used to predict second, cross virial coefficients for ethyl acetate-nitrogen and methyl chrloracetate-nitrogen mixtures, and the determined B_{12} values are given in Table 4.6. Note, that in order for the accentric factor, W_1, of nitrogen to be obtained, the following empirical equation (190) was employed:

$$\log P = 5.76381 - \frac{853.522}{T} + \frac{54372.3}{T^2} - \frac{1783500}{T^3}$$

which is valid for nitrogen, when P is greater than 101.33 kN m^{-2} (1 atm.).

FIGURE A.21 Comparison of the predicted O'Connell-Prausnitz equation B data with the available literature experimental data for ethyl acetate

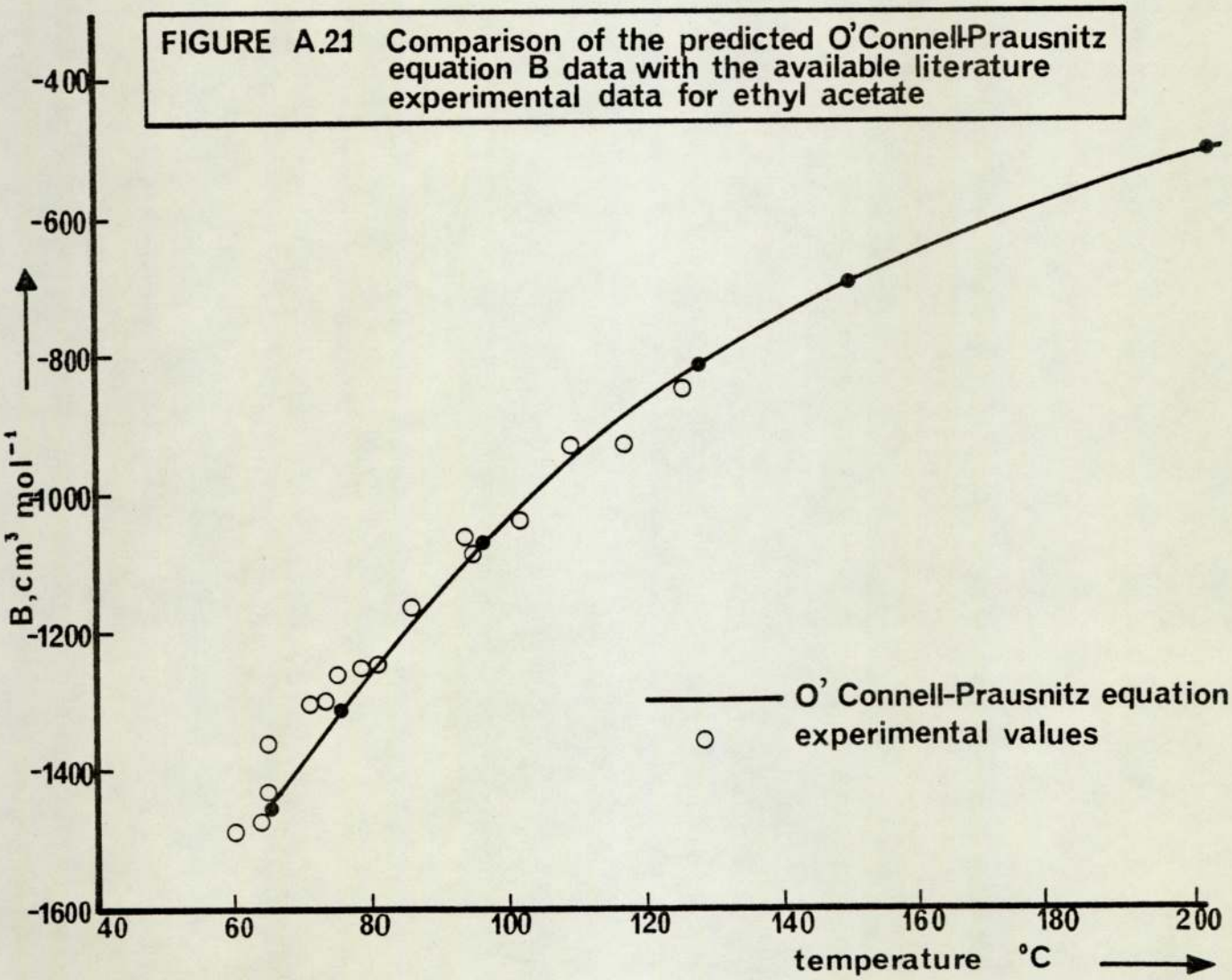


TABLE A.2.4 : SECOND VIRIAL COEFFICIENTS OF ETHYL ACETATE, METHYL PROPIONATE AND METHYL CHLOROACETATE

TEMPER	B_{11} ethyl acetate	TEMPER	B_{11} methyl propionate	TEMPER	B_{11} methyl chloroacetate
°C	$cm^3\ mol^{-1}$	°C	$cm^3\ mol^{-1}$	°C	$cm^3\ mol^{-1}$
57.5	-1587	67.0	-1507	92.2	-2210
60.5	-1528	77.7	-1352	94.5	-2157
64.8	-1461	98.9	-1104	96.5	-2121
67.5	-1430	130.8	- 842	97.8	-2069
74.5	-1329	152.1	- 718	101.5	-2024
75.4	-1313	205.2	- 517	105.0	-1954
79.0	-1263	-	-	107.7	-1910
81.7	-1230	-	-	118.0	-1735
96.6	-1073	-	-	130.3	-1557
128.2	- 821	-	-	154.7	-1269
149.4	- 696	-	-	191.4	- 964
202.2	- 500	-	-	215.8	- 819

APPENDIX 3

Experimental Details of Separation Runs

TABLE A.3.1.1 RECORDED DATA FOR RUN 60-21-29-130

RUN DESCRIPTION

System : 50/50 V/V-"ARKLONE" P/ "GENKLENE" P

Temper.
- Oven : 60°C
- Purge in : 80°C
- Carrier in : 61°C

Ambient conditions
- Pressure : 101 kNm^{-2}
- Temper. : 20°C*

Gmc/L' : 28.9

Switching rate : 130 s

Feedrate : 21 $cm^3 h^{-1}$

Separating section
- Pin : 198 kN m^{-2}
- Pout : 184 kN m^{-2}
- Ga : 4.2 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 158 kN m^{-2}
- Sa : 188.3 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 31 $cm^3 s^{-1}$
Bridge current : 115 mA
Bridge voltage : 18 V
Sensitivity : 9.7

Sampling valve

Temperature : ambient
Pressure in Sample loop : ambient
Sample volume : 0.26 cm^3 (corrected to N.T.P)

F-11

Pressure H_2 : 236 kN m^{-2}
Pressure O_2 : 270 kN m^{-2}
Flow N_2 : 0.42 $cm^3 s^{-1}$
Sensitivity : 1×10^4
Column temper : 55°C
Chromat. Column Specific. : 121.9 cm long and 0.3 cm in O-D stainless steel column packed with 16.67% of F.F.A.P. on 500-353 µm chromosorb W, AW-DMCS

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 4, 80 sec after sequencing action, on the 3rd cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I $\times 10^6$ g cm^{-3}	Product II $\times 10^6$ g cm^{-3}
7,8	122	14420	<20	330.8	<0.4
8,9	183	13590	<20	353.8	<0.4
9,10	244	12130	<20	303.8	<0.4
10,11	305	10670	190	265.4	3.8
11,12	366	2940	10570	73.1	211.5
12,1	427	<60	18980	<1.5	380.8
1,2	488	256	22140	7.7	442.3
2,3	549	<60	18740	<1.5	373.1
3,4	610	<60	956	<1.5	19.2
4,5	671	<60	<20	<1.5	<0.4
5,6	0	10440	<20	257.7	<0.4
6,7	61	14760	<20	400.0	<0.4

NOTE: * As ambient temperature was considered the temperature near the measuring and controlling devices of the gas streams of the SCCR-2 unit

TABLE A.3.1.1 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 4 , 120 sec after sequencing action, on the 4th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
8,9	183	14540	<20	384.6	<0.4
9,10	244	11270	<20	280.8	<0.4
10,11	305	8536	<20	211.5	<0.4
11,12	366	7765	4520	192.3	88.5
12,1	427	161	11440	3.8	226.9
1,2	488	<60	19760	<1.5	396.1
2,3	549	<60	18330	<1.5	365.4
3,4	610	<60	<20	<1.5	<0.4
4,5	671	<60	<20	<1.5	<0.4
5,6	0	11700	<20	292.3	<0.4
6,7	61	15740	<20	442.3	<0.4
7,8	122	13780	<20	361.5	<0.4

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 8 , 80 sec after sequencing action, on the 7th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
3,4	366	<60	7981	<1.5	159.6
4,5	427	<60	14750	<1.5	296.1
5,6	488	<60	20620	<1.5	411.5
6,7	549	<60	21070	<1.5	423.1
7,8	61o	<60	<20	<1.5	<0.4
8,9	671	<60	<20	<1.5	<0.4
9,10	0	11310	<20	280.8	<0.4
10,11	61	10250	<20	253.8	<0.4
11,12	122	10430	<20	257.7	<0.4
12,1	183	12050	<20	303.8	<0.4
1,2	244	11940	<20	300.0	<0.4
2,3	305	5910	<20	146.1	<0.4

TABLE A.3.1.2 RECORDED DATA FOR RUN 60-21-38-130

RUN DESCRIPTION

System : 50/50 V/V "ARKLONE" P/ "GENKLENE" P

Temper.
- Oven : 60°C
- Purge in : 80°C
- Carrier in : 63°C

Ambient conditions
- Pressure : 100 kNm^{-2}
- Temper. : 20°C

Gmc/L' : 38.1

Switching rate : 130 s

Feedrate : 21 $cm^3 h^{-1}$

Separating section
- Pin : 198 kNm^{-2}
- Pout : 179 kNm^{-2}
- Ga : 5.5 $cm^3 s^{-1}$

Purge section
- Pin : 184 $kN\ m^{-2}$
- Pout : 156 $kN\ m^{-2}$
- Sa : 188.3 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 3.1 $cm^3 s^{-1}$
Bridge current : 120 mA
Bridge voltage : 17V
Sensitivity : 9.7

Sampling valve

Temperature : ambient
Pressure in Sample loop : ambient
Sample volume : 0.26 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 236 $kN\ m^{-2}$
Pressure O_2 : 270 $kN\ m^{-2}$
Flow N_2 : 0.40 $cm^3 s^{-1}$
Sensitivity : 1×10^4
Column temper : 55°C
Chromat. Column Specific. : As in the run 60-21-29-130 (see Table A.3.1.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 80 sec after sequencing action, on the 5th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I $\times 10^6 g\ cm^{-3}$	Product II $\times 10^6 g\ cm^{-3}$
6,7	427	<30	13470	<0.7	269.2
7,8	488	<30	17010	<0.7	340.4
8,9	549	<30	20680	<0.7	415.4
9,10	610	<30	<20	<0.7	<0.4
10,11	671	<30	<20	<0.7	<0.4
11,12	0	11890	<20	300.0	<0.4
12,1	61	10050	<20	248.1	<0.4
1,2	122	11300	<20	280.8	<0.4
2,3	183	13130	<20	338.5	<0.4
3,4	244	10080	<20	250.0	<0.4
4,5	305	13400	<20	346.1	<0.4
5,6	366	1981	9922	50.0	196.1

TABLE A.3.1.2 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 10 , 120 sec after sequencing action , on the 7th cycle					
Isolated columns	Distance of sample point from product II outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $x10^{6}$ $9cm^{-3}$	Product II $x10^{6}$ $9cm^{-3}$
11,12	0	12200	<20	307.7	<0.4
12,1	61	9486	<20	234.6	<0.4
1,2	122	12140	<20	307.7	<0.4
2,3	183	11520	<20	288.5	<0.4
3,4	244	14720	<20	396.1	<0.4
4,5	305	10620	3493	261.5	69.2
5,6	366	<30	10630	<0.7	211.5
6,7	427	<30	13820	<0.7	276.9
7,8	488	<30	17650	<0.7	353.8
8,9	549	<30	20540	<0.7	411.5
9,10	610	<30	<20	<0.7	<0.4
10,11	671	<30	<20	<0.7	<0.4

TABLE A.3.1.3 RECORDED DATA FOR RUN 60-21-43-130

RUN DESCRIPTION

System: 50/50 V/V
"Arklone" P/"Genklene" P

Temper.
- Oven : 60°C
- Purge in: 80°C
- Carrier in: 62°C

Ambient conditions
- Pressure : 102 kNm^{-2}
- Temper. : 21°C

Gmc/L' : 43.1

Switching rate : 130 s

Feedrate : 21 $cm^3 s^{-1}$

Separating section
- Pin : 198 kNm^{-2}
- Pout : 181 kNm^{-2}
- Ga : 6.2 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 153 kN m^{-2}
- Sa : 211.7 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 3.1 $cm^3 s^{-1}$
Bridge current: 120 mA
Bridge voltage: 17 V
Sensitivity : 9.7

Sampling valve

Temperature : ambient
Pressure in Sample loop : ambient
Sample volume: 0.26 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 236 kN m^{-2}
Pressure O_2 : 270 kN m^{-2}
Flow N_2 : 0.41 $cm^3 s^{-1}$
Sensitivity : 1 x 10^4
Column temper: 55°C
Chromat. Column Specific. : As in the run 60-21-29-130 (see Table A.3.1.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 4 , 80 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I, x10^6g cm^{-3}	Product II x10^6g cm^{-3}
1,2	488	<40	20710	<1.0	415.4
2,3	549	<40	16490	<1.0	330.8
3,4	610	<40	581	<1.0	11.5
4,5	671	<40	<20	<1.0	<0.4
5,6	0	6274	<20	157.7	<0.4
6,7	61	13640	<20	353.8	<0.4
7,8	122	12960	<20	334.6	<0.4
8,9	183	10260	<20	253.8	<0.4
9,10	244	10500	<20	257.7	<0.4
10,11	305	10490	1824	257.7	34.6
11,12	366	2556	11340	61.5	226.9
12,1	427	<40	19790	<1.0	396.1

TABLE A.3.1.3 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 4 , 120 sec after sequencing action, on the 5th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
1,2	488	<40	23930	<1.0	476.9
2,3	549	<40	19660	<1.0	392.3
3,4	610	<40	<20	<1.0	<0.4
4,5	671	<40	<20	<1.0	<0.4
5,6	0	8266	<20	203.8	<0.4
6,7	61	12390	<20	315.4	<0.4
7,8	122	15010	<20	407.7	<0.4
8,9	183	12870	<20	330.8	<0.4
9,10	244	11790	<20	296.1	<0.4
10,11	305	9016	5120	223.1	100.0
11,12	366	<40	12940	<1.0	257.7
12,1	427	<40	22490	<1.0	450.0

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 10 , 80 sec after sequencing action, on the 6th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
2,3	183	12560	<20	323.1	<0.4
3,4	244	14920	<20	403.8	<0.4
4,5	305	14890	<20	403.8	<0.4
5,6	366	4061	12350	100.0	246.1
6,7	427	<40	15990	<1.0	319.2
7.8	488	<40	20810	<1.0	415.4
8,9	549	<40	23650	<1.0	473.1
9,10	610	<40	<20	<1.0	<0.4
10,11	671	<40	<20	<1.0	<0.4
11,12	0	11950	<20	303.8	<0.4
12,1	61	12160	<20	307.7	<0.4
1,2	122	11890	<20	300.0	<0.4

TABLE A.3.1.4 RECORDED DATA FOR RUN 60-21-58-130

RUN DESCRIPTION

System: 50/50 V/V
"Arklone" P/"Genklene" P

Temper.
- Oven : 60°C
- Purge in : 80°C
- Carrier in: 62°C

Ambient conditions
- Pressure : 101 kNm^{-2}
- Temper. : 19°C

Gmc/L' : 58.4

Switching rate : 130 s

Feedrate : 21 $cm^3 s^{-1}$

Separating section
- Pin : 198 kNm^{-2}
- Pout : 177 kNm^{-2}
- Ga : 8.33 $cm^3 s^{-1}$

Purge section
- Pin : 184 kNm^{-2}
- Pout : 153 kNm^{-2}
- Sa : 211.7 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 3.1 $cm^3 s^{-1}$
Bridge current: 120 mA
Bridge voltage: 17V
Sensitivity : 9.7

Sampling valve

Temperature : ambient
Pressure in Sample loop : ambient
Sample volume: 0.26 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 236 kN m^{-2}
Pressure O_2 : 270 kN m^{-2}
Flow N_2 : 0.41 $cm^3 s^{-1}$
Sensitivity : 1×10^4
Column temper: 55°C
Chromat. Column Specific. { As in the run 60-21-29-130 (see Table A.3.1.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 80 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I $\times 10^6 g\ cm^{-3}$	Product II $\times 10^6 g\ cm^{-3}$
11,12	0	10660	<20	265.4	<0.4
12,1	61	10630	<20	261.5	<0.4
1,2	122	11460	<20	284.6	<0.4
2,3	183	9840	<20	242.3	<0.4
3,4	244	13780	<20	353.8	<0.4
4,5	305	15010	3776	407.7	84.6
5,6	366	904	14930	23.1	326.9
6,7	427	<20	21560	<0.5	476.9
7,8	488	<20	26920	<0.5	592.3
8,9	549	<20	28560	<0.5	630.8
9,10	610	<20	<20	<0.5	<0.4
10,11	671	<20	<20	<0.5	<0.4

TABLE A.3.1.4 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 10 , 120 sec after sequencing action, on the 8th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
5,6	366	<20	16170	<0.5	357.7
6,7	427	<20	24690	<0.5	542.3
7,8	488	<20	27470	<0.5	607.7
8,9	549	<20	28480	<0.5	630.8
9,10	610	<20	<20	<0.5	<0.4
10,11	671	<20	<20	<0.5	<0.4
11,12	0	8085	<20	200.0	<0.4
12,1	61	12230	<20	300.0	<0.4
1,2	122	9791	<20	242.3	<0.4
2,3	183	8250	<20	203.8	<0.4
3,4	244	11920	<20	292.3	<0.4
4,5	305	10380	8482	257.7	184.6

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 8 , 80 sec after sequencing action, on the 9th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
12,1	183	11270	<20	276.9	<0.4
1,2	244	13100	<20	323.1	<0.4
2,3	305	5645	3383	138.5	76.9
3,4	366	<20	14120	<0.5	311.5
4,5	427	<20	21520	<0.5	473.1
5,6	488	<20	27480	<0.5	607.7
6,7	549	<20	29150	<0.5	650.0
7,8	610	<20	800	<0.5	19.2
8,9	671	<20	<20	<0.5	<0.4
9,10	0	10700	<20	265.4	<0.4
10,11	61	9745	<20	238.5	<0.4
11,12	122	9875	<20	246.1	<0.4

TABLE A.3.1.4 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 8 , 120 sec after sequencing action, on the 11th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
6,7	549	<20	29180	<0.5	657.7
7,8	610	<20	<20	<0.5	<0.4
8,9	671	<20	<20	<0.5	<0.4
9,10	0	9404	<20	230.8	<0.4
10,11	61	10830	<20	265.4	<0.4
11,12	122	10670	<20	265.4	<0.4
12,1	183	13010	<20	319.2	<0.4
1,2	244	11580	<20	288.5	<0.4
2,3	305	2127	7637	53.8	169.2
3,4	366	<20	15880	<0.5	350.0
4,5	427	<20	24050	<0.5	526.9
5,6	488	<20	28680	<0.5	638.5

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 4 , 80 sec after sequencing action, on the 15th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
6,7	61	16730	<20	484.6	<0.4
7,8	122	14670	≤20	396.1	<0.4
8,9	183	12080	<20	307.7	<0.4
9,10	244	13160	<20	342.3	<0.4
10,11	305	11060	5178	273.1	103.8
11,12	366	2339	14540	57.7	288.5
12,1	427	<20	25310	<0.5	507.7
1,2	488	<20	30050	<0.5	601.9
2,3	549	<20	30150	<0.5	603.8
3,4	610	<20	1244	<0.5	23.1
4,5	671	<20	<20	<0.5	<0.4
5,6	0	8364	<20	207.7	<0.4

TABLE A.3.1.4 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 4 , 120 sec after sequencing action , on the 16th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
6,7	61	16600	<20	480.8	<0.4
7,8	122	14290	<20	380.8	<0.4
8,9	183	14040	<20	369.2	<0.4
9,10	244	11160	<20	276.9	<0.4
10,11	305	8626	8999	211.5	180.8
11,12	366	<20	16560	<0.5	330.8
12,1	427	<20	27630	<0.5	553.8
1,2	488	<20	30340	<0.5	607.7
2,3	549	<20	29040	<0.5	581.5
3,4	610	<20	<20	<0.5	<0.4
4,5	671	<20	<20	<0.5	<0.4
5,6	0	13960	<20	369.2	<0.4

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 4 , 40 sec after sequencing action , on the 17th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
6,7	61	14950	<20	407.7	<0.4
7,8	122	12030	<20	303.8	<0.4
8,9	183	13800	<20	361.5	<0.4
9,10	244	12080	<20	307.7	<0.4
10,11	305	12240	<20	309.6	<0.4
11,12	366	5482	12720	134.6	253.8
12,1	427	<20	22140	<0.5	442.3
1,2	488	<20	29270	<0.5	586.1
2,3	549	<20	30850	<0.5	618.1
3,4	610	<20	4397	<0.5	88.5
4,5	671	<20	<20	<0.5	<0.4
5,6	0	450	<20	15.4	<0.4

TABLE A.3.1.5 RECORDED DATA FOR RUN 60-21-44-60

RUN DESCRIPTION

System: 50/50 V/V
"Arklone" P/"Genklene" P

Temper.
- Oven : 60°C
- Purge in: 80°C
- Carrier in: 62°C

Ambient conditions
- Pressure :101 kNm^{-2}
- Temper. :21°C

Gmc/L' : 43.8

Switching rate : 60s

Feedrate : 21 cm^3s^{-1}

Separating section
- Pin : 198 kNm^{-2}
- Pout : 167 kNm^{-2}
- Ga : 13.3 cm^3s^{-1}

Purge section
- Pin : 184 $kN\ m^{-2}$
- Pout : 158 $kN\ m^{-2}$
- Sa : 188 cm^3s^{-1}

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 3.1 cm^3s^{-1}
Bridge current: 120 mA
Bridge voltage: 17V
Sensitivity : 9.7

Sampling valve

Temperature :ambient
Pressure in Sample loop :ambient
Sample volume: 0.26 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 236 $kN\ m^{-2}$
Pressure O_2 : 270 $kN\ m^{-2}$
Flow N_2 : 0.41 cm^3s^{-1}
Sensitivity : 1×10^4
Column temper: 55°C
Chromat. Column Specific. As in the run 60-21-29-130 (See Table A.3.1.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 8 , 50 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I $\times 10^6 g\ cm^{-3}$	Product II $\times 10^6 g\ cm^{-3}$
8,9	671	<40	<40	< 1.0	<0.8
9,10	0	5650	<40	138.5	<0.8
10,11	61	6999	<40	173.1	<0.8
11,12	122	5763	<40	144.2	<0.8
12,1	183	6631	<40	165.4	<0.8
1,2	244	10010	<40	246.1	<0.8
2,3	305	5103	<40	126.9	<0.8
3,4	366	693	828	19.2	15.4
4,5	427	<40	4544	<1.0	88.5
5,6	488	<40	6438	<1.0	126.9
6,7	549	<40	7241	<1.0	142.3
7,8	610	<40	<40	<1.0	<0.8

TABLE A.3.1.5 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 12 , 50 sec after sequencing action , on the 7th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
9,10	488	<40	5599	<1.0	111.5
10,11	549	<40	4585	<1.0	92.3
11,12	610	<40	<40	<1.0	<0.8
12,1	671	<40	<40	<1.0	<0.8
1,2	0	5789	<40	142.3	<0.8
2,3	61	3848	<40	96.1	<0.8
3,4	122	7342	<40	180.8	<0.8
4,5	183	7021	<40	173.1	<0.8
5,6	244	10340	<40	246.1	<0.8
6,7	305	4621	370	115.4	7.7
7,8	366	195	2098	7.7	42.3
8,9	427	<40	3271	<1.0	65.4

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 10 , 50 sec after sequencing action , on the 8th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
1,2	122	4942	< 40	123.1	< 0.8
2,3	183	9120	< 40	226.9	< 0.8
3,4	244	8047	< 40	196.1	< 0.8
4,5	305	4951	< 40	123.1	0.8
5,6	366	173	2242	5.8	42.3
6,7	427	<40	2974	<1.0	57.7
7,8	488	<40	3238	<1.0	63.5
8,9	549	<40	4320	<1.0	84.6
9,10	610	<40	< 40	<1.0	<0.8
10,11	671	<40	< 40	<1.0	<0.8
11,12	0	7789	< 40	192.3	<0.8
12,1	61	4538	< 40	111.5	<0.8

TABLE A.3.1.6 RECORDED DATA FOR RUN 60-21-43-80

RUN DESCRIPTION

System: 50/50 V/V
"Arklone" P/"Genklene" P

Temper.
- Oven : 60°C
- Purge in: 80°C
- Carrier in: 63°C

Ambient conditions
- Pressure : 100 kN m^{-2}
- Temper. : 20°C

Gmc/L' : 43.3

Switching rate : 80s

Feedrate : 21 $cm^3 h^{-1}$

Separating section
- Pin : 198 kN m^{-2}
- Pout : 172 kN m^{-2}
- Ga : 10 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 159 kN m^{-2}
- Sa : 190 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 3.1 $cm^3 s^{-1}$
Bridge current: 115 mA
Bridge voltage: 18 V
Sensitivity : 9.7

Sampling valve

Temperature : ambient
Pressure in Sample loop : ambient
Sample volume: 0.26 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 236 kN m^{-2}
Pressure O_2 : 270 kN m^{-2}
Flow N_2 : 0.42 $cm^3 s^{-1}$
Sensitivity : 1×10^4
Column temper: 55°C
Chromat. Column Specific. : As in the run 60-21-29-130 (see Table A.3.1.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 4 , 60 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I $\times 10^6$ g cm^{-3}	Product II $\times 10^6$ g cm^{-3}
1,2	488	293	10980	3.8	219.2
2,3	549	<60	9723	<1.5	192.3
3,4	610	<60	1478	<1.5	30.8
4,5	671	<60	<30	<1.5	<0.6
5,6	0	10750	<30	265.4	<0.6
6,7	61	10090	<30	250.0	<0.6
7,8	122	12680	<30	326.9	<0.6
8,9	183	12600	<30	323.1	<0.6
9,10	244	10390	<30	257.7	<0.6
10,11	305	7789	752	192.3	11.5
11,12	366	2802	5576	69.2	111.5
12,1	427	<60	9371	<1.5	188.5

TABLE A.3.1.6 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 10 , 60 sec after sequencing action, on the 8th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
9,10	610	<60	<30	<1.5	<0.6
10,11	671	<60	<30	<1.5	<0.6
11,12	0	9959	<30	246.1	<0.6
12,1	61	8014	<30	196.1	<0.6
1,2	122	8697	<30	215.4	<0.6
2,3	183	9530	<30	234.6	<0.6
3,4	244	10140	<30	250.0	<0.6
4,5	305	11720	<30	292.3	<0.6
5,6	366	1827	6534	46.1	130.8
6,7	427	<60	8635	<1.5	173.1
7,8	488	<60	8254	<1.5	165.4
8,9	549	<60	9612	<1.5	192.3

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 8 , 60 sec after sequencing action, on the 10th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
1,2	244	11240	<30	276.9	<0.6
2,3	305	5678	<30	142.3	<0.6
3,4	366	455	2548	13.5	50.0
4,5	427	< 60	7200	<1.5	142.3
5,6	488	< 60	10880	<1.5	219.2
6,7	549	< 60	10370	<1.5	207.7
7,8	610	<60	<30	<1.5	<0.6
8,9	671	<60	<30	<1.5	<0.6
9,10	0	7470	<30	184.6	<0.6
10,11	61	7424	<30	184.6	<0.6
11,12	122	7536	<30	184.6	<0.6
12,1	183	10200	<30	250.0	<0.6

TABLE A.3.1.6 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 8 , 60 sec after sequencing action , on the 11th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
1,2	244	11240	<30	280.8	<0.6
2,3	305	5238	<30	128.8	<0.6
3,4	366	401	2321	11.5	46.1
4,5	427	<60	6795	<1.5	134.6
5,6	488	<60	10440	<1.5	207.7
6,7	549	<60	10370	<1.5	207.7
7,8	610	<60	<30	<1.5	<0.6
8,9	671	<60	<30	<1.5	<0.6
9,10	0	7187	<30	176.9	<0.6
10,11	61	9382	<30	230.8	<0.6
11,12	122	6904	<30	169.2	<0.6
12,1	183	9029	<30	223.1	<0.6

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 8 , 30 sec after sequencing action , on the 12th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
3,4	366	1802	607	46.1	11.5
4,5	427	<60	5300	<1.5	105.8
5,6	488	<60	9078	<1.5	180.8
6,7	549	<60	9812	<1.5	196.1
7,8	610	<60	1661	<1.5	34.6
8,9	671	<60	<30	<1.5	<0.6
9,10	0	<60	<30	<1.5	<0.6
10,11	61	9835	<30	242.3	<0.6
11,12	122	8057	<30	200.0	<0.6
12,1	183	6010	<30	150.0	<0.6
1,2	244	8957	<30	223.1	<0.6
2,3	305	6435	<30	157.7	<0.6

TABLE A.3.1.7 RECORDED DATA FOR RUN 60-21-42-100

RUN DESCRIPTION

System: 50/50 V/V "Arklone" P/"Genklene" P

Temper.
- Oven :60°C
- Purge in :80°C
- Carrier in: 63°C

Ambient conditions
- Pressure :101 kN m^{-2}
- Temper. :21°C

Gmc/L' : 42.1

Switching rate :100 s

Feedrate :21 $cm^3 h^{-1}$

Separating section
- Pin :198 kN m^{-2}
- Pout :177 kN m^{-2}
- Ga :7.9 $cm^3 s^{-1}$

Purge section
- Pin :184 kN m^{-2}
- Pout :157 kN m^{-2}
- Sa :188 $cm^3 h^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 3.1 $cm^3 s^{-1}$
Bridge current: 115 mA
Bridge voltage: 18 V
Sensitivity : 9.7

Sampling valve

Temperature : ambient
Pressure in Sample loop : ambient
Sample volume: 0.26 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 236 kN m^{-2}
Pressure O_2 : 270 kN m^{-2}
Flow N_2 : 0.42 $cm^3 s^{-1}$
Sensitivity : 1×10^4
Column temper: 55°C
Chromat. Column Specific. { As in the run 60-21-29-130 (see Table A.3.1.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 70 sec after sequencing action, on the 6th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I, x10⁴g cm^{-3}	Product II x10⁴g cm^{-3}
5,6	366	581	8461	15.4	169.2
6,7	427	<40	10440	<1.0	207.7
7,8	488	<40	12460	<1.0	251.9
8,9	549	<40	15500	<1.0	311.5
9,10	610	<40	<20	<1.0	<0.4
10,11	671	<40	<20	<1.0	<0.4
11,12	0	8437	<20	207.7	<0.4
12,1	61	8097	<20	200.0	<0.4
1,2	122	9915	<20	244.2	<0.4
2,3	183	9332	<20	230.8	<0.4
3,4	244	9170	<20	226.9	<0.4
4,5	305	8322	<20	203.8	<0.4

TABLE A.3.1.7 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 12 , 70 sec after sequencing action, on the 9th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
6,7	305	5120	1528	126.9	28.8
7,8	366	<40	6169	<1.0	123.1
8,9	427	<40	11050	<1.0	221.1
9,10	488	<40	9849	<1.0	196.1
10,11	549	<40	13200	<1.0	265.4
11,12	610	<40	<20	<1.0	<0.4
12,1	671	<40	<20	<1.0	<0.4
1,2	0	5650	<20	138.5	<0.4
2,3	61	10490	<20	259.6	<0.4
3,4	122	10630	<20	261.5	<0.4
4,5	183	12340	<20	311.5	<0.4
5,6	244	10850	<20	265.4	<0.4

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 4 , 70 sec after sequencing action, on the 11th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
1,2	488	<40	12400	<1.0	248.1
2,3	549	<40	9736	<1.0	194.2
3,4	610	<40	<20	<1.0	<0.4
4,5	671	<40	<20	<1.0	<0.4
5,6	0	7182	<20	176.9	<0.4
6,7	61	9886	<20	246.1	<0.4
7,8	122	8058	<20	200.0	<0.4
8,9	183	10200	<20	251.9	<0.4
9,10	244	7895	<20	196.2	<0.4
10,11	305	7002	1522	173.1	28.8
11,12	366	1576	7590	42.3	188.5
12,1	427	<40	14100	<1.0	282.7

TABLE A.3.1.8 RECORDED DATA FOR RUN 55-21-42-160

RUN DESCRIPTION

System: 50/50 V/V
"Arklone" P/"Genklene" P

Temper.
- Oven: 55°C
- Purge in: 75°C
- Carrier in: 57°C

Ambient conditions
- Pressure: 102 kN m^{-2}
- Temper.: 19°C

Gmc/L′: 42.3

Switching rate: 160 s

Feedrate: 21 $cm^3 s^{-1}$

Separating section
- Pin: 198 kN m^{-2}
- Pout: 181 kN m^{-2}
- Ga: 5.0 $cm^3 s^{-1}$

Purge section
- Pin: 184 kN m^{-2}
- Pout: 163 kN m^{-2}
- Sa: 173 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow: 3.1 $cm^3 s^{-1}$
Bridge current: 115 mA
Bridge voltage: 17 V
Sensitivity: 9.7

Sampling valve

Temperature: ambient
Pressure in Sample loop: ambient
Sample volume: 0.26 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2: 236 kN m^{-2}
Pressure O_2: 270 kN m^{-2}
Flow N_2: 0.38 $cm^3 s^{-1}$
Sensitivity: 1 x 10^4
Column temper: 55°C
Chromat. Column Specific: As in the run 60-21-29-130 (see Table A.3.1.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10, 100 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10⁶g cm^{-3}	Product II x10⁶g cm^{-3}
6,7	427	<20	21120	<0.5	423.1
7,8	488	<20	23890	<0.5	476.9
8,9	549	<20	25680	<0.5	515.4
9,10	610	<20	<50	<0.5	<1.0
10,11	671	<20	<50	<0.5	<1.0
11,12	0	7930	<50	196.1	<1.0
12,1	61	8178	<50	203.8	<1.0
1,2	122	8304	<50	205.8	<1.0
2,3	183	10250	<50	251.9	<1.0
3,4	244	14150	<50	373.1	<1.0
4,5	305	12180	3928	307.7	76.9
5,6	366	186	14310	5.8	286.5

TABLE A.3.1.8 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 10 , 100 sec after sequencing action, on the 7th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ g cm^{-3}	Product II $\times 10^6$ g cm^{-3}
4,5	305	11800	3605	296.1	73.1
5,6	366	172	13880	5.8	276.9
6,7	427	<20	20700	<0.5	413.5
7,8	488	<20	24010	<0.5	480.8
9,10	610	<20	<50	<0.5	<1.0
10,11	671	<20	<50	<0.5	<1.0
11,12	0	9183	<50	226.9	<1.0
12,1	61	9417	<50	230.8	<1.0
1,2	122	8265	<50	205.8	<1.0
2,3	183	8481	<50	211.5	<1.0
3,4	244	14730	<50	396.1	<1.0
8,9	549	<20	26460	<0.5	530.8

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 8 , 100 sec after sequencing action, on the 10th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ g cm^{-3}	Product II $\times 10^6$ g cm^{-3}
5,6	488	<20	25560	<0.5	511.5
6,7	549	<20	21240	<0.5	423.1
7,8	610	<20	<50	<0.5	<1.0
8,9	671	<20	<50	<0.5	<1.0
9,10	0	12600	<50	323.1	<1.0
10,11	61	12030	<50	303.8	<1.0
11,12	122	11630	<50	292.3	<1.0
12,1	183	10590	<50	261.5	<1.0
1,2	244	11400	<50	284.6	<1.0
2,3	305	5071	2801	126.9	53.8
3,4	366	<20	13630	<0.5	273.1
4,5	427	<20	21210	<0.5	423.1

TABLE A.3.1.9 RECORDED DATA FOR RUN 65.21-43-160

RUN DESCRIPTION

System: 50/50 V/V
"Arklone" P/"Genklene" P

Temper.
- Oven : 65°C
- Purge in : 80°C
- Carrier in: 67°C

Ambient conditions
- Pressure : 101 kN m^{-2}
- Temper. : 20°C

Gmc/L' : 42.8

Switching rate : 160s

Feedrate : 21 $cm^3 s^{-1}$

Separating section
- Pin : 198 kN m^{-2}
- Pout : 184 kN m^{-2}
- Ga : 5.0 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 160 kN m^{-2}
- Sa : 171.7 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 3.1 $cm^3 s^{-1}$
Bridge current: 115 mA
Bridge voltage: 17V
Sensitivity : 9.6

Sampling valve

Temperature : ambient
Pressure in Sample loop : ambient
Sample volume: 0.26 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 236 kN m^{-2}
Pressure O_2 : 270 kN m^{-2}
Flow N_2 : 0.38 $cm^3 s^{-1}$
Sensitivity : 1 x 10^4
Column temper: 55°C
Chromat. Column Specific. : As in the run 60-21-29-130 (see Table A.3.1.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 8, 100 sec after sequencing action, on the 3rd cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10^6g cm^{-3}	Product II x10^6g cm^{-3}
2,3	305	6479	1637	161.5	30.8
3,4	366	<20	15560	<0.5	311.5
4,5	427	<20	21820	<0.5	434.6
5,6	488	<20	25660	<0.5	515.4
6,7	549	<20	27070	<0.5	542.3
7,8	610	<20	<50	<0.5	<1.0
8,9	671	<20	<50	<0.5	<1.0
9,10	0	13290	<50	342.3	<1.0
10,11	61	13140	<50	338.5	<1.0
11,12	122	12290	<50	311.5	<1.0
12,1	183	12230	<50	307.7	<1.0
1,2	244	14110	<50	373.1	<1.0

TABLE A.3.1.9 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 9 , 100 sec after sequencing action, on the 4th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^{4}$ 9cm^{-3}	Product II $\times 10^{4}$ 9cm^{-3}
2,3	183	13020	<50	334.6	<1.0
3,4	244	14360	<50	380.8	<1.0
4,5	305	14540	1203	384.6	23.1
5,6	366	171	13020	5.8	257.7
6,7	427	<20	17620	<0.5	353.8
7,8	488	<20	21090	<0.5	423.1
8,9	549	<20	22860	<0.5	457.7
9,10	610	<20	<50	<0.5	<1.0
10,11	671	<20	<50	<0.5	<1.0
11,12	0	10990	<50	273.1	<1.0
12,1	61	11990	<50	303.8	<1.0
1,2	122	13450	<50	350.0	<1.0

TABLE A.3.2.1 RECORDED DATA FOR RUN 105-21-378-300

RUN DESCRIPTION

System: 50/50 V/V methyl chloroacetate/ethyl acetate

Temper.
- Oven : 105°C
- Purge in : 135°C
- Carrier in: 108°C

Ambient conditions
- Pressure :100 kN m^{-2}
- Temper. :26°C

Gmc/L′ : 377.8

Switching rate : 300s

Feedrate : 21 $cm^3 s^{-1}$

Separating section
- Pin : 198 kNm^{-2}
- Pout : 146 kN m^{-2}
- Ga : 21.3 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 136 kN m^{-2}
- Sa : 232 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 2.1 $cm^3 s^{-1}$
Bridge current: 115 mA
Bridge voltage: 17.5V
Sensitivity : 9.1

Sampling valve

Temperature : 150°C
Pressure in Sample loop : ambient
Sample volume: 0.38 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 239 kN m^{-2}
Pressure O_2 : 274 kN m^{-2}
Flow N_2 : 0.77 $cm^3 s^{-1}$
Sensitivity : 50 x 10^2
Column temper: 150°C
Chromat. Column Specific: 2m long and 0-6 cm in O-D stainless steel column packed with, 18% of F.F.A.P. on 250-177 µm chromosorb W, AW-DMCS

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 8 , 150 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10^4g cm^{-3}	Product II x10^4g cm^{-3}
7,8	610	<50	<100	<0.2	<0.2
8,9	671	<50	<100	<0.2	<0.2
9,10	0	5895	<100	27.6	<0.2
10,11	61	19850	<100	89.5	<0.2
11,12	122	22520	<100	100.0	<0.2
12,1	183	23660	<100	105.3	<0.2
1,2	244	27170	<100	121.1	<0.2
2,3	305	30500	11170	135.5	25.0
3,4	366	26610	15700	118.4	34.2
4,5	427	20080	19920	89.5	43.4
5,6	488	1748	20220	7.9	44.7
6,7	549	<50	21430	<0.2	47.4

TABLE A.3.2.1 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 10 , 150 sec after sequencing action , on the 5th cycle					
Isolated columns	Distance of sample point from product II outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $\times 10^6$ 9cm^{-3}	Product II $\times 10^6$ 9cm^{-3}
9,10	610	< 50	<100	< 0.2	< 0.2
10,11	671	< 50	<100	< 0.2	< 0.2
11,12	0	11940	<100	54.0	< 0.2
12,1	61	19270	<100	85.5	< 0.2
1,2	122	21230	<100	94.7	< 0.2
2,3	183	25190	<100	113.2	< 0.2
3,4	244	27640	250	123.7	< 0.2
4,5	305	31810	14670	141.3	32.9
5,6	366	29810	22290	132.9	48.7
6,7	427	21110	23450	94.7	51.3
7,8	488	3701	23650	17.1	52.1
8,9	549	<50	27860	<0.2	61.1

TABLE A.3.2.2 RECORDED DATA FOR RUN 105-21-413-300

RUN DESCRIPTION

System: 50/50 V/V methyl chloroacetate/ethyl lactate

Temper.
- Oven : 105°C
- Purge in : 135°C
- Carrier in: 108°C

Ambient conditions
- Pressure : 102 kNm^{-2}
- Temper. : 25°C

Gmc/L′ : 413.3

Switching rate : 300s

Feedrate : 21 cm^{3}s^{-1}

Separating section
- Pin : 205 kNm^{-2}
- Pout : 144 kNm^{-2}
- Ga : 23 cm^{3}s^{-1}

Purge section
- Pin : 198 kNm^{-2}
- Pout : 143 kNm^{-2}
- Sa : 248 cm^{3}s^{-1}

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 2.1 cm^{3}s^{-1}
Bridge current: 115 mA
Bridge voltage: 17.5 V
Sensitivity : 9.1

Sampling valve

Temperature : 150°C
Pressure in Sample loop : ambient
Sample volume: 0.37 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 239 kN m^{-2}
Pressure O_2 : 274 kN m^{-2}
Flow N_2 : 0.77 cm^{3}s^{-1}
Sensitivity : 20 x 10^2
Column temper: 150°C
Chromat. Column Specific. : As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 8 , 200 sec after sequencing action, on the 3rd cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10^{5}g cm^{-3}	Product II x10^{5}g cm^{-3}
3,4	366	5911	8405	27.0	18.9
4,5	427	<50	20480	<0.2	46.0
5,6	488	<50	20910	<0.2	47.3
6,7	549	<50	16960	<0.2	37.8
7,8	610	<50	<100	<0.2	<0.2
8,9	671	<50	<100	<0.2	<0.2
9,10	0	13680	<100	63.5	<0.2
10,11	61	16760	<100	77.0	<0.2
11,12	122	18860	<100	86.5	<0.2
12,1	183	21200	<100	97.3	<0.2
1,2	244	23610	5720	108.1	5.9
2,3	305	21940	7609	101.3	17.6

TABLE A.3.2.3 RECORDED DATA FOR RUN 105-21-444-300

RUN DESCRIPTION

System: 50/50 - methyl chloroacetate-ethyl lactate

Temper.
- Oven : 150°C
- Purge in : 135°C
- Carrier in: 108°C

Ambient conditions
- Pressure :102 kNm^{-2}
- Temper. :28°C

Gmc/L´ : 444.0

Switching rate : 300 s

Feedrate : 21 $cm^3 s^{-1}$

Separating section
- Pin : 205kN m^{-2}
- Pout : 146 kNm^{-2}
- Ga : 25 $cm^3 s^{-1}$

Purge section
- Pin : 191 kNm^{-2}
- Pout : 139 kNm^{-2}
- Sa : 245 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 $cm^3 s^{-1}$
Bridge current: 110 mA
Bridge voltage: 17 V
Sensitivity : 9.1

Sampling valve

Temperature : 145°C
Pressure in Sample loop : ambient
Sample volume: 0.38 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 239 kN m^{-2}
Pressure O_2 : 274 kN m^{-2}
Flow N_2 : 0.77 $cm^3 s^{-1}$
Sensitivity : 20 x 10^2
Column temper: 150°C
Chromat. Column Specific. { As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 8 , 150 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10^4g cm^{-3}	Product II x10^4g cm^{-3}
2,3	305	53160	45340	94.7	39.5
3,4	366	16400	46120	28.9	40.8
4,5	427	<50	62750	<0.2	56.6
5,6	488	<50	79860	<0.2	69.7
6,7	549	<50	82690	<0.2	72.4
7,8	610	<50	<100	<0.2	<0.2
8,9	671	<50	<100	<0.2	<0.2
9,10	0	17560	<100	31.6	<0.2
10,11	61	45170	9981	80.3	9.2
11,12	122	45420	12130	80.8	10.5
12,1	183	44450	19320	80.3	17.1
1,2	244	49350	22010	88.2	19.7

TABLE A.3.2.3 CONTINUED

CONCENTRATION PROFILE ANALYSIS					
The samples were taken from column 10 , 150 sec after sequencing action, on the 5th cycle					
Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std)	
		Product I	Product II	Product I $x10^6$ 9cm^{-3}	Product II $x10^6$ 9cm^{-3}
3,4	244	46950	20870	84.2	18.4
4,5	305	56190	43280	100.0	38.2
5,6	366	22740	50910	39.5	44.7
6,7	427	<50	80520	<0.2	69.7
7,8	488	<50	82230	<0.2	72.4
8,9	549	<50	84920	<0.2	74.2
9,10	610	<50	<100	<0.2	<0.2
10,11	671	<50	<100	<0.2	<0.2
11,12	0	40570	6722	72.4	5.8
12,1	61	45970	7610	84.2	6.6
1,2	122	46030	9980	84.2	9.2
2,3	183	52240	15290	93.4	13.2

TABLE A.3.2.4 RECORDED DATA FOR RUN 110-38-273-200

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate/ethyl lactate

Temper.
- Oven : 110°C
- Purge in : 120°C
- Carrier in: 113°C

Ambient conditions
- Pressure : 100 kNm^{-2}
- Temper. : 29°C

Gmc/L′ : 273.0

Switching rate : 200 s

Feedrate : 38 cm^{3}s^{-1}

Separating section
- Pin : 198 kN m^{-2}
- Pout : 143 kN m^{-2}
- Ga : 23.0 cm^{3}s^{-1}

Purge section
- Pin : 184 kN m^{-2}
- Pout : 143 kN m^{-2}
- Sa : 197 cm^{3}s^{-1}

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 cm^{3}s^{-1}
Bridge current: 130 mA
Bridge voltage: 19 V
Sensitivity : 10.0

Sampling valve

Temperature :125°C
Pressure in Sample loop :ambient
Sample volume: 0.35 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 cm^{3}s^{-1}
Sensitivity : 20 x 10^2
Column temper: 125°C
Chromat. Column Specific. { As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column sequencing action, on the 4th cycle 10 , 150 sec after

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I, x10^{6}g cm^{-3}	Product II x10^{6}g cm^{-3}
11,12	0	38890	<100	120.0	<0.1
12,1	61	50000	<100	152.0	<0.1
1,2	122	57510	<100	157.7	<0.1
2,3	183	79260	<100	240.0	<0.1
3,4	244	94270	<100	282.9	<0.1
4,5	305	96040	41880	288.6	57.1
5,6	366	88280	59930	265.7	80.0
6,7	427	80080	62010	242.9	82.9
7,8	488	69440	63570	211.4	85.7
8,9	549	32060	58120	97.1	77.1
9,10	610	<100	<100	<0.3	<0.1
10,11	671	<100	<100	<0.3	<0.1

TABLE A.3.2.5 RECORDED DATA FOR RUN 110-40-313-200

RUN DESCRIPTION	
System:	50/50 V/V methyl chloroacetate/ethyl lactate
Temper.	Oven : 110°C Purge in : 120°C Carrier in : 112°C
Ambient conditions	Pressure : 100 kN m^{-2} Temper. : 28°C
Gmc/L´	: 313.5
Switching rate	: 200 s
Feedrate	: 40 $cm^3 s^{-1}$
Separating section	Pin : 205 kN m^{-2} Pout : 136 kN m^{-2} Ga : 26.3 $cm^3 s^{-1}$
Purge section	Pin : 184 kN m^{-2} Pout : 150 kN m^{-2} Sa : 195 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION	
Katharometer	
Gas flow	: 5.0 $cm^3 s^{-1}$
Bridge current	: 130 mA
Bridge voltage	: 19 V
Sensitivity	: 10.0
Sampling valve	
Temperature	: 117°C
Pressure in	ambient
Sample loop	: 0.35 cm^3
Sample volume: (corrected to N.T.P.)	
F-11	
Pressure H_2	: 308 kN m^{-2}
Pressure O_2	: 308 kN m^{-2}
Flow N_2	: 1.2 $cm^3 s^{-1}$
Sensitivity	: 20 x 10^2
Column temper:	125°C
Chromat. Column Specific.	As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 150 sec after sequencing action, on the 7th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10^6g cm^{-3}	Product II x10^6g cm^{-3}
11,12	0	60280	<100	182.9	<0.1
12,1	61	65780	<100	200.0	<0.1
1,2	122	72060	<100	220.0	<0.1
2,3	183	84040	<100	255.7	<0.1
3,4	244	96990	<100	291.4	<0.1
4,5	305	93130	60860	280.0	81.4
5,6	366	84760	69700	257.1	92.9
6,7	427	69320	66630	211.4	88.6
7,8	488	53130	68430	161.4	91.4
8,9	549	3329	48240	10.0	65.7
9,10	610	<100	<100	<0.3	<0.1
10,11	671	<100	<100	<0.3	<0.1

TABLE A.3.2.6 RECORDED DATA FOR RUN 110-40-351-200

RUN DESCRIPTION		
System: 50/50 V/V - methyl chloroacetate ethyl lactate		
Temper.	Oven	:110°C
	Purge in	:120°C
	Carrier in	:112°C
Ambient conditions	Pressure	:102 kN m^{-2}
	Temper.	:30°C
Gmc/L′		: 350.6
Switching rate		:200 s
Feedrate		:40 $cm^3 s^{-1}$
Separating section	Pin	:212 kN m^{-2}
	Pout	:137 kN m^{-2}
	Ga	:30.0 $cm^3 s^{-1}$
Purge section	Pin	:184 kN m^{-2}
	Pout	:150 kN m^{-2}
	Sa	:183 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION	
Katharometer	
Gas flow	: 5.0 $cm^3 s^{-1}$
Bridge current	:130 mA
Bridge voltage	:19 V
Sensitivity	:10.0
Sampling valve	
Temperature	: 114°C
Pressure in Sample loop	: ambient
Sample volume: (corrected to N.T.P.)	0.34 cm^3
F-11	
Pressure H_2	:308 kN m^{-2}
Pressure O_2	:308 kN m^{-2}
Flow N_2	:1.2 $cm^3 s^{-1}$
Sensitivity	:20 x 10^2
Column temper:	:125°C
Chromat. Column Specific.	As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 150 sec after sequencing action, on the 5th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I, x10⁶g cm^{-3}	Product II x10⁶g cm^{-3}
11,12	0	61910	<100	194.1	<0.1
12,1	61	63270	<100	197.1	<0.1
1,2	122	67380	<100	211.8	<0.1
2,3	183	72230	<100	226.5	<0.1
3,4	244	99810	<100	308.8	<0.1
4,5	305	80650	58450	252.9	80.9
5,6	366	69510	65130	217.6	89.7
6,7	427	45180	57400	141.2	79.4
7,8	488	18030	61490	55.9	85.3
8,9	549	<100	48500	<0.3	67.6
9,10	610	<100	<100	<0.3	<0.1
10,11	671	<100	<100	<0.3	<0.1

TABLE A.3.2.7 RECORDED DATA FOR RUN 110-37-365-200

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate/ethyl lactate

Temper.
- Oven : 110°C
- Purge in : 120°C
- Carrier in : 112°C

Ambient conditions
- Pressure : 101 kN m^{-2}
- Temper. : 30°C

Gmc/L' : 365.1

Switching rate : 200 s

Feedrate : 37 $cm^3 h^{-1}$

Separating section
- Pin : 239 kN m^{-2}
- Pout : 150 kN m^{-2}
- Ga : 35.0 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 151 kN m^{-2}
- Sa : 183 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 $cm^3 s^{-1}$
Bridge current : 130 mA
Bridge voltage : 19 V
Sensitivity : 10.0

Sampling valve

Temperature : 115°C
Pressure in Sample loop : ambient
Sample volume : 0.34 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 $cm^3 s^{-1}$
Sensitivity : 20 x 10^2
Column temper : 125°C
Chromat. Column Specific. : As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 150 sec after sequencing action, on the 5th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I, x10⁶g cm^{-3}	Product II x10⁶g cm^{-3}
11,12	0	33610	<100	105.9	<0.1
12,1	61	39310	<100	123.5	<0.1
1,2	122	51310	<100	160.3	<0.1
2,3	183	64200	<100	201.5	<0.1
3,4	244	49810	31270	155.9	44.1
4,5	305	47100	50880	147.1	70.6
5,6	366	11180	48510	35.3	67.6
6,7	427	<50	72360	<0.2	100.0
7,8	488	<50	61670	<0.2	85.3
8,9	549	<50	34160	<0.2	47.1
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1

TABLE A.3.2.8 RECORDED DATA FOR RUN 110-40-425-200

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate/ethyl lactate

Temper.
- Oven : 110°C
- Purge in : 120°C
- Carrier in: 112°C

Ambient conditions
- Pressure : 100kN m^{-2}
- Temper. : 29°C

Gmc/L' : 424.8

Switching rate : 200 s

Feedrate : 40 $cm^3 s^{-1}$

Separating section
- Pin : 260 kN m^{-2}
- Pout : 148 kN m^{-2}
- Ga : 43.3 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 156 kN m^{-2}
- Sa : 170 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 $cm^3 s^{-1}$
Bridge current: 130 mA
Bridge voltage: 19 V
Sensitivity : 10.0

Sampling valve

Temperature : 113°C
Pressure in Sample loop : ambient
Sample volume: 0.34 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 $cm^3 s^{-1}$
Sensitivity : 20 x 10^2
Column temper: 125°C
Chromat. Column Specific: As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 150 sec after sequencing action, on the 6th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I, x10⁶g cm^{-3}	Product II x10⁶g cm^{-3}
2,3	183	35350	18350	111.8	26.5
3,4	244	30440	31020	97.1	44.1
4,5	305	33090	39480	104.4	55.9
5,6	366	8400	42030	26.5	58.8
6,7	427	<50	54490	<0.2	76.5
7,8	488	<50	44680	<0.2	61.8
8,9	549	<50	<100	<0.2	<0.1
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1
11,12	0	38830	<100	123.5	<0.1
12,1	61	33670	<100	105.9	<0.1
1,2	122	62250	<100	194.1	<0.1

TABLE A.3.2.9 RECORDED DATA FOR RUN 110-36-366-250

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate/ethyl lactate

Temper.
- Oven : 110°C
- Purge in: 120°C
- Carrier in: 112°C

Ambient conditions
- Pressure :101 kN m^{-2}
- Temper. :28°C

Gmc/L′ : 366.0

Switching rate :250 s

Feedrate :36 $cm^3 s^{-1}$

Separating section
- Pin :232 kN m^{-2}
- Pout :157 kN m^{-2}
- Ga :28.3 $cm^3 s^{-1}$

Purge section
- Pin :184 kN m^{-2}
- Pout :151 kN m^{-2}
- Sa :165 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 $cm^3 s^{-1}$
Bridge current: 130 mA
Bridge voltage: 19 V
Sensitivity : 10.0

Sampling valve

Temperature :112°C
Pressure in Sample loop :ambient
Sample volume: 0.34 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 $cm^3 s^{-1}$
Sensitivity : 20 x 10^2
Column temper: 125°C
Chromat. Column Specific. { As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 150 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10⁶g cm^{-3}	Product II x10⁶g cm^{-3}
11,12	0	34130	<100	105.9	<0.1
12,1	61	32110	<100	100.0	<0.1
1,2	122	54190	<100	169.1	<0.1
2,3	183	43071	<100	135.3	<0.1
3,4	244	39930	26730	126.5	38.2
4,5	305	28190	41240	88.2	57.3
5,6	366	8919	48240	29.4	66.2
6,7	427	<50	72060	<0.2	100.0
7,8	488	<50	68520	<0.2	94.1
8,9	549	<50	6180	<0.2	8.8
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1

TABLE A.3.2.10 RECORDED DATA FOR RUN 110-41-367-300

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate/ethyl lactate

Temper.
- Oven: 110°C
- Purge in: 120°C
- Carrier in: 112°C

Ambient conditions
- Pressure: 101 kNm^{-2}
- Temper.: 28°C

Gmc/L': 367.3

Switching rate: 300 s

Feedrate: 41 cm^3s^{-1}

Separating section
- Pin: 232 kN m^{-2}
- Pout: 163 kN m^{-2}
- Ga: 23.3 cm^3s^{-1}

Purge section
- Pin: 184 kN m^{-2}
- Pout: 151 kN m^{-2}
- Sa: 165 cm^3s^{-1}

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 cm^3s^{-1}
Bridge current: 130 mA
Bridge voltage: 19 V
Sensitivity : 10.0

Sampling valve

Temperature : 109°C
Pressure in Sample loop : ambient
Sample volume: 0.34 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 cm^3s^{-1}
Sensitivity : 20 x 10^2
Column temper: 125°C
Chromat. Column Specific. { As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 200 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10^6g cm^{-3}	Product II x10^6g cm^{-3}
1,2	122	72560	<100	226.5	<0.1
2,3	183	82950	<100	260.3	<0.1
3,4	244	50940	20800	160.3	29.4
4,5	305	37760	50390	119.1	70.6
5,6	366	13880	61580	44.1	85.3
6,7	427	<50	95700	<0.2	129.4
7,8	488	<50	97060	<0.2	132.3
8,9	549	<50	7188	<0.2	11.8
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1
11,12	0	36550	<100	114.7	<0.1
12,1	61	64740	<100	202.9	<0.1

TABLE A.3.2.11 RECORDED DATA FOR RUN 110-40-375-350

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate/ethyl lactate

Temper.
- Oven : 110°C
- Purge in : 120°C
- Carrier in: 112°C

Ambient conditions
- Pressure : 102 kN m^{-2}
- Temper. : 26°C

Gmc/L' : 375.5

Switching rate : 350 s

Feedrate : 40 $cm^3 s^{-1}$

Separating section
- Pin : 232 kN m^{-2}
- Pout : 163 kN m^{-2}
- Ga : 20 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 155 kN m^{-2}
- Sa : 162 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 $cm^3 s^{-1}$
Bridge current: 130 mA
Bridge voltage: 19 V
Sensitivity : 10.0

Sampling valve

Temperature :113°C
Pressure in Sample loop :ambient
Sample volume: 0.34 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 $cm^3 s^{-1}$
Sensitivity : 20 x 10^2
Column temper: 125°C
Chromat. Column Specific. { As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 200 sec after sequencing action, on the 5th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10⁶g cm^{-3}	Product II x10⁶g cm^{-3}
2,3	183	38840	18300	123.5	25.0
3,4	244	33750	32180	105.9	44.1
4,5	305	31210	50940	97.1	70.6
5,6	366	9337	75400	29.4	102.9
6,7	427	<50	100800	<0.2	138.2
7,8	488	<50	84280	<0.2	114.7
8,9	549	<50	<100	<0.2	<0.1
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1
11,12	0	33320	<100	102.9	<0.1
12,1	61	44510	<100	138.2	<0.1
1,2	122	47140	<100	147.1	<0.1

TABLE A.3.2.12 RECORDED DATA FOR RUN 110-60-374-200

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate-ethyl lactate

Temper.
- Oven :110°C
- Purge in :120°C
- Carrier in: 112°C

Ambient conditions
- Pressure :101 kN m^{-2}
- Temper. :25°C

Gmc/L' : 374.5

Switching rate :200 s

Feedrate :60 $cm^3 s^{-1}$

Separating section
- Pin :239 kN m^{-2}
- Pout :148 kN m^{-2}
- Ga :35.3 $cm^3 s^{-1}$

Purge section
- Pin :184 kN m^{-2}
- Pout :150 kN m^{-2}
- Sa :183 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 $cm^3 s^{-1}$
Bridge current: 120 mA
Bridge voltage: 19 V
Sensitivity : 9.6

Sampling valve

Temperature :103°C
Pressure in Sample loop :ambient
Sample volume: 0.33 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 $cm^3 s^{-1}$
Sensitivity : 20 x 10^2
Column temper: 125°C
Chromat. Column Specific: As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 150 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I, x10^6g cm^{-3}	Product II x10^6g cm^{-3}
2,3	183	80700	<100	260.6	<0.1
3,4	244	82410	<100	265.1	<0.1
4,5	305	88300	95905	281.8	133.3
5,6	366	67050	84740	216.7	119.7
6,7	427	44960	123200	145.4	172.7
7,8	488	9643	88260	30.3	125.8
8,9	549	<50	132500	<0.2	184.8
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1
11,12	0	52110	<100	168.2	<0.1
12,1	61	64770	<100	209.1	<0.1
1,2	122	75730	<100	242.4	<0.1

TABLE A.3.2.13 RECORDED DATA FOR RUN 110-80-427-200

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate/ethyl lactate

Temper.
- Oven : 110°C
- Purge in : 120°C
- Carrier in: 112°C

Ambient conditions
- Pressure : 101 kNm^{-2}
- Temper. : 25°C

Gmc/L' : 427.3

Switching rate : 200 s

Feedrate : 80 cm^3h^{-1}

Separating section
- Pin : 253 $kN\ m^{-2}$
- Pout : 143 $kN\ m^{-2}$
- Ga : 41.7 cm^3s^{-1}

Purge section
- Pin : 184 $kN\ m^{-2}$
- Pout : 150 $kN\ m^{-2}$
- Sa : 183 cm^3s^{-1}

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 cm^3s^{-1}
Bridge current: 120 mA
Bridge voltage: 19 V
Sensitivity : 9.6

Sampling valve

Temperature : 112°C
Pressure in Sample loop : ambient
Sample volume: 0.34 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 $kN\ m^{-2}$
Pressure O_2 : 308 $kN\ m^{-2}$
Flow N_2 : 1.2 cm^3s^{-1}
Sensitivity : 20×10^2
Column temper: 125°C
Chromat. Column Specific: As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 150 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I, $\times 10^6 g\ cm^{-3}$	Product II $\times 10^6 g\ cm^{-3}$
3,4	244	75330	<100	235.3	<0.1
4,5	305	79680	82800	250.0	113.2
5,6	366	74950	85660	235.3	117.6
6,7	427	55180	103000	173.5	132.7
7,8	488	40520	90370	126.5	122.1
8,9	549	<50	68290	<0.2	94.1
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1
11,12	0	58490	<100	182.3	<0.1
12,1	61	67280	<100	210.3	<0.1
1,2	122	88310	<100	276.5	<0.1
2,3	183	95480	<100	295.6	<0.1

TABLE A.3.2.14 RECORDED DATA FOR RUN 120.40-346-200

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate/ethyl lactate

Temper.
- Oven : 120°C
- Purge in : 125°C
- Carrier in: 122°C

Ambient conditions
- Pressure : 100 kN m^{-2}
- Temper. : 30°C

Gmc/L' : 345.8

Switching rate : 200 s

Feedrate : 40 $cm^3 h^{-1}$

Separating section
- Pin : 212 kN m^{-2}
- Pout : 136 kN m^{-2}
- Ga : 29.2 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 150 kN m^{-2}
- Sa : 182 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 $cm^3 s^{-1}$
Bridge current: 120 mA
Bridge voltage: 19 V
Sensitivity : 9.6

Sampling valve

Temperature : 111°C
Pressure in Sample loop : ambient
Sample volume: 0.34 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 $cm^3 s^{-1}$
Sensitivity : 20 x 10^2
Column temper: 125°C
Chromat. Column Specific. : As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 150 sec after sequencing action, on the 7th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10^6g cm^{-3}	Product II x10^6g cm^{-3}
4,5	305	30340	110300	97.1	150.0
5,6	366	<50	100800	<0.2	136.8
6,7	427	<50	82540	<0.2	113.2
7,8	488	<50	<100	<0.2	<0.1
8,9	549	<50	<100	<0.2	<0.1
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1
11,12	0	16010	7342	50.0	10.3
12,1	61	13790	47030	44.1	64.7
1,2	122	18000	50000	55.9	69.1
2,3	183	24350	62450	76.5	85.3
3,4	244	22060	76440	70.6	105.9

TABLE A.3.2.15 RECORDED DATA FOR RUN 120-38-241-200

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate-ethyl lactate

Temper.
- Oven : 120°C
- Purge in : 125°C
- Carrier in: 122°C

Ambient conditions
- Pressure : 100 kN m^{-2}
- Temper. : 29°C

Gmc/L' : 241.2

Switching rate : 200 s

Feedrate 38 $cm^3 s^{-1}$

Separating section
- Pin : 198 kN m^{-2}
- Pout : 143 kN m^{-2}
- Ga : 19.8 $cm^3 s^{-1}$

Purge section
- Pin : 184 kN m^{-2}
- Pout : 147 kN m^{-2}
- Sa : 180 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 $cm^3 s^{-1}$
Bridge current: 120 mA
Bridge voltage: 19 V
Sensitivity : 9.6

Sampling valve

Temperature : 107°C
Pressure in Sample loop : ambient
Sample volume: 0.34 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 $cm^3 s^{-1}$
Sensitivity : 20 x 10^2
Column temper: 125°C
Chromat. Column Specific: As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 150 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10⁶g cm^{-3}	Product II x10⁶g cm^{-3}
11,12	0	57030	<100	179.4	<0.1
12,1	61	61020	<100	191.2	<0.1
1,2	122	92880	<100	288.2	<0.1
2,3	183	91850	<100	285.3	<0.1
3,4	244	77960	73190	244.1	100.0
4,5	305	46520	85150	145.6	116.2
5,6	366	<50	96100	<0.2	130.9
6,7	427	<50	109900	<0.2	150.0
7,8	488	<50	96250	<0.2	130.9
8,9	549	<50	5700	<0.2	8.8
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1

TABLE A.3.2.16 RECORDED DATA FOR RUN 110-38-248-200

RUN DESCRIPTION

System: 50/50 V/V - methyl chloroacetate/ethyl lactate

Temper.
- Oven: 110°C
- Purge in: 120°C
- Carrier in: 112°C

Ambient conditions
- Pressure: 101 kNm^{-2}
- Temper.: 27°C*

Gmc/L´: 248.0

Switching rate: 200 s

Feedrate: 38 $cm^3 h^{-1}$

Separating section
- Pin: 198 kN m^{-2}
- Pout: 150 kN m^{-2}
- Ga: 20.8 $cm^3 s^{-1}$

Purge section
- Pin: 184 kN m^{-2}
- Pout: 143 kN m^{-2}
- Sa: 197 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow: 5.0 $cm^3 s^{-1}$
Bridge current: 130 mA
Bridge voltage: 19 V
Sensitivity: 10.0

Sampling valve

Temperature: 120°C
Pressure in Sample loop: ambient
Sample volume: 0.35 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2: 308 kN m^{-2}
Pressure O_2: 308 kN m^{-2}
Flow N_2: 1.2 $cm^3 s^{-1}$
Sensitivity: 20 x 10^2
Column temper: 125°C
Chromat. Column Specific.: As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10, 150 sec after sequencing action, on the 5th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10^6g cm^{-3}	Product II x10^6g cm^{-3}
3,4	244	83910	<100	255.7	<0.1
4,5	305	95630	37970	288.6	51.4
5,6	366	89920	57180	271.4	77.1
6,7	427	81960	53260	248.6	71.4
7,8	488	74010	55710	225.7	77.1
8,9	549	19570	50330	60.0	68.6
9,10	610	<100	<100	<0.3	<0.1
10,11	671	<100	<100	<0.3	<0.1
11,12	0	17390	<100	54.3	<0.1
12,1	61	27390	<100	84.3	<0.1
1,2	122	40890	<100	125.7	<0.1
2,3	183	56000	<100	171.4	<0.1

NOTE * As ambient temperature was considered the temperature near the measuring and controlling devices of the gas streams of the SCCR-2 unit

TABLE A.3.2.17 RECORDED DATA FOR RUN 130-40-182-150

RUN DESCRIPTION

System : 50/50 V/V - methyl chloroacetate-ethyl lactate

Temper.
- Oven : 130°C
- Purge in : 135°C
- Carrier in : 132°C

Ambient conditions
- Pressure : 102 kNm^{-2}
- Temper. : 27°C

Gmc/L' : 182.1

Switching rate : 150 s

Feedrate : 40 $cm^3 s^{-1}$

Separating section
- Pin : 212 kN m^{-2}
- Pout : 145 kN m^{-2}
- Ga : 20 $cm^3 s^{-1}$

Purge section
- Pin : 198 kN m^{-2}
- Pout : 160 kN m^{-2}
- Sa : 163.3 $cm^3 s^{-1}$

ANALYSIS DESCRIPTION

Katharometer

Gas flow : 5.0 $cm^3 s^{-1}$
Bridge current : 120 mA
Bridge voltage : 19 V
Sensitivity : 9.6

Sampling valve

Temperature : 110°C
Pressure in Sample loop : ambient
Sample volume : 0.34 cm^3 (corrected to N.T.P.)

F-11

Pressure H_2 : 308 kN m^{-2}
Pressure O_2 : 308 kN m^{-2}
Flow N_2 : 1.2 $cm^3 s^{-1}$
Sensitivity : 20 x 10^2
Column temper : 125°C
Chromat. Column Specific. : As in the run 105-21-378-300 (see Table A.3.2.1)

CONCENTRATION PROFILE ANALYSIS

The samples were taken from column 10 , 100 sec after sequencing action, on the 4th cycle

Isolated columns	Distance of sample point from product I outlet (cm)	Integrator units		Concentration (std.)	
		Product I	Product II	Product I x10^5g cm^{-3}	Product II x10^5g cm^{-3}
4,5	305	66420	96670	205.9	130.9
5,6	366	56430	130100	176.5	179.4
6,7	427	10390	134580	33.8	183.8
7,8	488	<50	71430	<0.2	97.1
8,9	549	<50	38490	<0.2	52.9
9,10	610	<50	<100	<0.2	<0.1
10,11	671	<50	<100	<0.2	<0.1
11,12	0	85180	<100	264.7	<0.1
12,1	61	70170	<100	220.6	<0.1
1,2	122	60160	47300	188.2	64.7
2,3	183	35500	60300	111.8	82.3
3,4	244	39590	88350	126.5	120.6