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CONTINUOUS LIQUID CHROMATOGRAPHY*

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SUMMARY

On the basis of preliminary investigations, automatic equipment has been developed for continuous liquid chromatography. It consists of eight column sections, and four liquid streams can be introduced and four streams can be withdrawn simultaneously. By modifying the programme-disc of the switching valve, different chromatographic techniques can be accomplished.

In one mode of operation, a continuous countercurrent moving bed process can be simulated by shifting the positions of the liquid inlets and outlets along the fixed bed of adsorbents. In comparison with the fixed bed system, continuous separation, higher capacity and a much lower solvent circulation can be achieved in the simulated moving bed technique.

In addition, by changing the programme-disc, different elution techniques, flow programming and stepwise elution can be carried out and the semi-continuous separation of multicomponent mixtures can be achieved.

INTRODUCTION

For the application of chromatographic methods to preparative work, especially on a production scale and in the scaling up of the widely used fixed bed batch chromatographic techniques using large-diameter packed beds, considerable effort has been put into the development of continuous chromatographic processes.

Depending on the state of the mobile phase, various continuous processes and equipment have been developed in both gas and liquid chromatography. These processes differ in the method of circulating the gas and liquid, respectively, and in the design of the equipment, but of course they aim to put into practice the same principles of operation and can be discussed theoretically on a common basis.

In gas chromatography, various equipment with different designs and capacities has been introduced for continuous moving bed separation and descriptions have been given of the moving bed process[1–6].

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In order to eliminate the disadvantages of the moving bed processes connected with the mechanical and operating difficulties and adsorbent attrition, rotating circular column techniques and equipment have been developed. The common feature of these techniques is that the packing is contained in a circular column or in columns in series arranged in a cylindrical form and the column is rotated along fixed inlet and outlet ports[7–9]. Laboratory rotating equipment consisting of 100 columns arranged in the form of a circle was developed for the separation of multicomponent mixtures, but in this arrangement the columns are necessarily batch-operated[10,11].

In liquid chromatography, continuous moving bed processes have also been developed, on the one hand for the separation of petroleum fractions and on the other for use in production-scale ion-exchange processes (treatment of sugar syrups, recovery of copper and uranium, etc.)[12–14]. In this field, high-capacity industrial units are being operated. The application of the rotating circular column technique to continuous liquid chromatography has also been described[15].

As early as the 1950s, reports were made of the development of a continuous chromatographic apparatus suitable for the separation of complex mixtures[16,17]. The principle of the apparatus is as follows. A bed of adsorbent is contained between two concentric cylinders in the shape of a cylindrical annulus, and solution is applied continuously to the top of the bed while the column is slowly rotated under the inlet port. A head of eluting solvent is maintained above the fixed bed. As the solution and solvent move down the column, the sample components move with different velocities and appear continuously at different distances around the circumference of the column. Through the exit orifices, the separated components are received in separate collectors. Developments have since been reported based essentially on the above principle, giving details of the construction and applications of an apparatus for continuous liquid–solid chromatography[18,19].

The disadvantages of the moving bed processes were overcome in a continuous adsorption process developed by Universal Oil Products (UOP) for industrial-scale separation[20–22]. The system employs a fixed bed and the movement of solids past fixed points of liquid feed and withdrawal is simulated by moving the positions of the feed and withdrawal along a stationary bed. In this operation, the functional zones (adsorption, rectification, desorption) are shifted stepwise along the fixed adsorbent bed. It follows that as the heights of the bed sections shifted in a step will decrease, the nearer a true continuous countercurrent system is simulated.

The efficiency and economic advantages of the simulated moving bed system have been successfully demonstrated in several commercial units of tens of thousands of tons capacity. The simulated moving bed system has been applied on an industrial scale for separating normal paraffins from other hydrocarbons on molecular sieves (Molex process), for separating olefins from paraffins (Olex process) and for recovering *p*-xylene from mixtures with other C_8 hydrocarbons (Parex process).

In the simulated moving bed technique, the known disadvantages of the moving bed techniques, *i.e.*, mechanical difficulties of moving the solid, adsorbent attrition, expansion of the bed, uneven flow, channelling, low efficiency, etc., are eliminated and a continuous countercurrent separation can be accomplished.

In comparison with the fixed bed batch adsorption process, the continuous system requires much less adsorbent, and the desorbent circulation necessary is about half of that required for the batch system[20].

PRELIMINARY INVESTIGATIONS

In view of the above advantages of the simulated moving bed technique, it is surprising that no indication has been given of the development and application of equipment based on the above principle for laboratory or small-scale separations.

Our investigations were aimed at the development of equipment suitable for preparative work and the continuous separation of mixtures on a smaller scale, rendering possible high-pressure, high-performance liquid chromatography, versatile enough to accomplish different chromatographic separations.

Our first laboratory equipment consisted of a column system containing twelve glass tubes of 300 mm length and 14 mm I.D. connected elliptically to each other by metal fittings[23]. Each adjoining part was supplied with liquid inlet and outlet ports connected to a central distributing (switching) valve. To this switching valve, two inlet (feed and eluent) and two withdrawal lines were also connected. By rotating the switching valve, the inlet and withdrawal lines were shifted periodically by one column section. In this way, the functional zones were periodically shifted in the direction of the fluid flow around the column system and continuous countercurrent adsorption was simulated.

In comparison with the UOP system, the main alteration was that a carrier flow in the column system was not applied, thus eliminating the need for a circulating pump and the difficulties connected with the control of the liquid flows through the different bed sections. The required flows were achieved by conducting the liquid stream through pressure-compensating sections[24].

Having made hydrodynamic measurements with this equipment, the continuous recovery of benzene from gasoline was investigated using silica as adsorbent.

EQUIPMENT FOR CONTINUOUS LIQUID CHROMATOGRAPHY

On the basis of the preliminary investigations and model experiments, automatic equipment was developed for use at higher pressures and for varied applications. In the design of this equipment, the essential starting point was that in addition to continuous separations by the simulated moving bed technique, it should be suitable for use with chromatographic techniques and for the separation of multicomponent mixtures.

In both the UOP system and our first laboratory equipment, the individual column sections are directly connected to each other and the necessary liquid flows can be achieved only by careful regulation of the pressure pattern. In order to eliminate this drawback, our later equipment consisted of column sections connected to each other through the switching valve.

The equipment is shown in Fig. 1. The columns are located in a circular form around the central switching valve, and the liquid pumps can be seen on the right and the receivers on the left. In the upper rack, the mechanical device for rotating the switching valve and the timer are enclosed. Switching over the columns can also be actuated manually by a push-button. On the front panel are located pressure gauges that indicate the pressures of the inlet streams.

The main component of the equipment is the switching valve, which contains a rotary PTFE disc, shown diagrammatically in Fig. 2. To the central bore and to

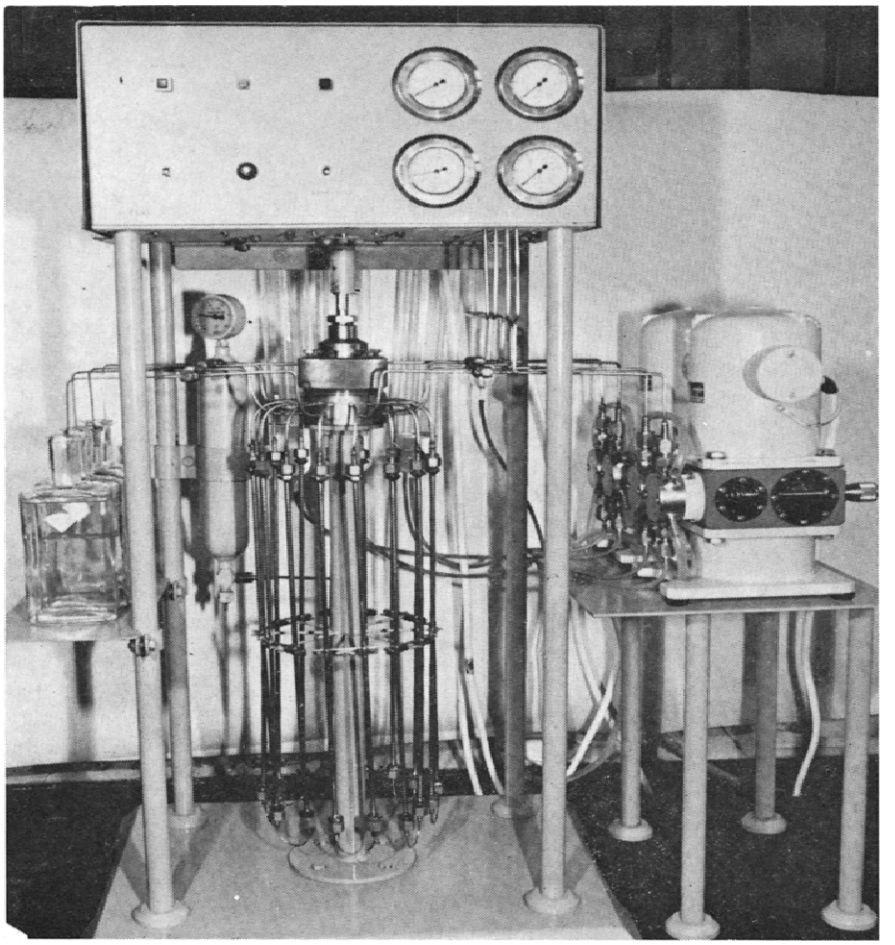

Fig. 1. Photograph of the continuous chromatographic equipment.

the seven concentric channels formed in the bottom of the housing, four inlet and four outlet lines are connected. The connecting lines to the columns are joined to 16 bores formed on the external concentric channel. These bores are connected with the appropriate inlet and outlet channels through the bore of the rotary disc. In order to prevent mixing of the liquid streams in the inlet and outlet channels, the rotary disc is pressed down on to the bottom of the housing by a spring. Above the rotary disc and connected to it by bolts, a second rotating disc is placed, the stem of which is joined to the electromechanical rotating device. This device turns the rotating disc and the PTFE disc through 45° in a clockwise direction following an electrical signal from the timer. Owing to this rotation, the inlet and outlet points of the liquid streams are connected to the next column section through the bores of the rotary disc. By turning the valve round, each column is again at its starting position.

The switching programme can be achieved by preparing appropriate bores in the rotary disc based on preliminary batch experiments. By changing the rotary disc, various column switchings and separation techniques can be accomplished.

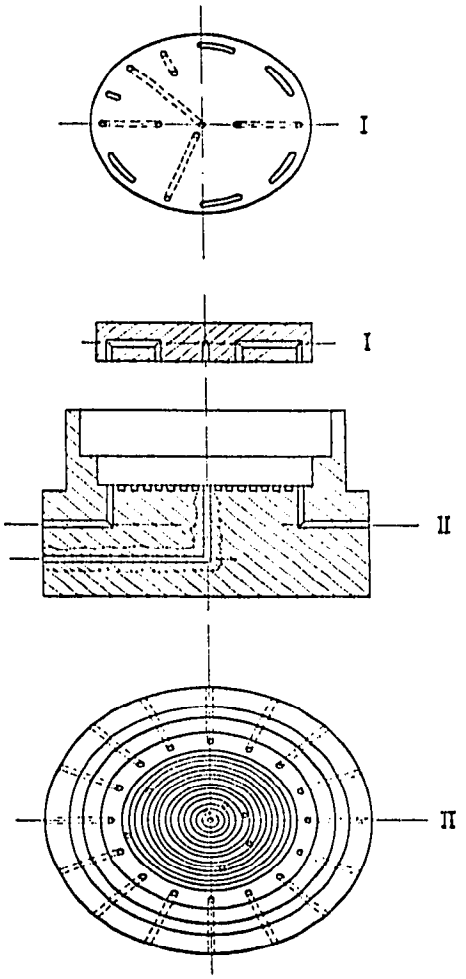

Fig. 2. Schematic diagram of the switching valve. I, Rotary PTFE disc; II, valve housing.

The functional diagram of the equipment is shown in Fig. 3. Eight U-shaped columns are connected to the switching valve. The connecting lines are made of small-bore tubing so as to reduce the dead volume, and the columns and tubing are made of stainless steel. The experiments were carried out with columns of 3 and 6 mm I.D., 50 and 100 cm in length. Larger diameter columns (up to 30 mm) can also be applied, as the liquid permeability of the switching valve is about 20 l/h in each line.

The feed system consists of four liquid pumps and four reservoirs. In addition to the mixture to be separated, three different solvents can be introduced, *i.e.*, stepwise elution or displacement techniques can also be carried out. The liquids are introduced with piston-type twin pumps (made by the Research Institute for High Pressure, Hungary), and damping devices in the inlet lines can also be applied. The collection system consists of four withdrawal lines and four collection vessels (glass) and four products can be withdrawn simultaneously.

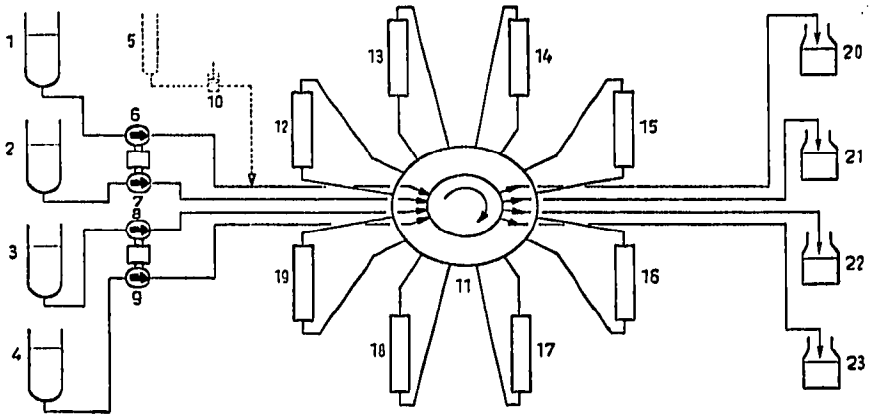

Fig. 3. Functional diagram of the continuous chromatographic equipment.
1–5, Liquid reservoirs; 6–10, pumps; 11, switching valve; 12–19, columns; 20–23, collection vessels.

The equipment in its present form can be operated at pressures up to 35 atm. With a modified switching valve and high-pressure pumps, higher pressures as used in high-performance liquid chromatography might be achieved. The pressure limit of the given equipment precluded the use of high-efficiency, small-sized packings.

The number of column sections can be increased by using a modified switching valve. In the simulated moving bed system, in order to approach more nearly to a true continuous countercurrent system, it is expedient to have a large number of short column sections; in the present equipment, 16 column sections at the most can be operated.

CONTINUOUS COUNTER-CURRENT SEPARATION WITH A SIMULATED MOVING BED

The fundamental difference between a batch and a continuous counter-current adsorption process lies in the application of a reflux operation and the involvement of a rectification zone. While in a batch system only a short section of the bed is in operation, in a continuous counter-current system the whole bed is being operated. In order to understand this better, we can consider the operation of a real moving bed system. The diagram of such an operation is shown in Fig. 4.

The solid adsorbent in the column moves downwards with a constant velocity counter-current to the upward-flowing liquid stream. In the middle of the column a mixture A + B is introduced. In the adsorption zone above the feed inlet, the more strongly adsorbed component B is completely adsorbed (when the advancing velocity of the adsorption zone for B is not greater than the moving velocity of the adsorbent), while component A (together with the eluent) can be withdrawn as a product at the top of the adsorption zone. The adsorbent moving downwards from the feed inlet also contains adsorbed component A in addition to component B, according to the adsorption equilibria. In order to desorb all adsorbed material, a solvent E (eluent) is introduced at the bottom of the column. This solvent flows upwards and gradually desorbs the adsorbed material. Also, component B desorbed in this way flows partly upwards in the column and displaces the adsorbed component A. In the rectification

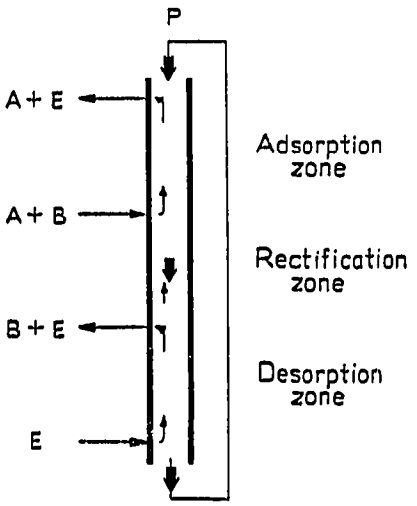

Fig. 4. Principle of moving bed operation. A, Weakly adsorbed component; B, strongly adsorbed component; E, desorbent; P, packing.

zone below the feed inlet, the concentration of component A is gradually decreasing and at a given height there is only component B in the adsorbed phase. At this stage, the product containing B + E can be withdrawn. Component A desorbed in the rectification zone, together with some component B and solvent E, enters the adsorption zone and finally all of component A passes into the top product.

Virtually the same operation is carried out in a simulated moving bed system when the movement of the solid is being simulated by shifting the positions of the inlets and outlets.

A continuous counter-current process furnishes two products. By withdrawing a side-product from the rectification zone below the feed inlet, it is possible to get a third product, but this will always consist of a mixture of the components according to the adsorption equilibria.

In order to accomplish the simulated moving bed technique, two inlets (mixture to be separated and eluent) and two outlets (light and heavy products) are required. As regards to the scheme shown in Fig. 3, only two inlet and two outlet lines are being operated in this particular case. The switching diagram of the columns is shown in Fig. 5.

In order to study the simulated moving bed operation, the separation of a model mixture containing benzene (component A) and naphthalene (component B) in *n*-hexane was investigated. The aim of these investigations was to demonstrate the feasibility of the simulated moving bed operation and to compare it with the batch operation. The experiments were carried out using eight columns of 50 cm length and 6 mm I.D., dry-packed with a 63–80 μm sieve fraction of alumina, activated at 120° for 2 h. *n*-Hexane (technical grade) was used as the solvent (E). The feed and products were analyzed by gas chromatography.

The feed mixture is introduced into column 7. Columns 7 and 8 connected in

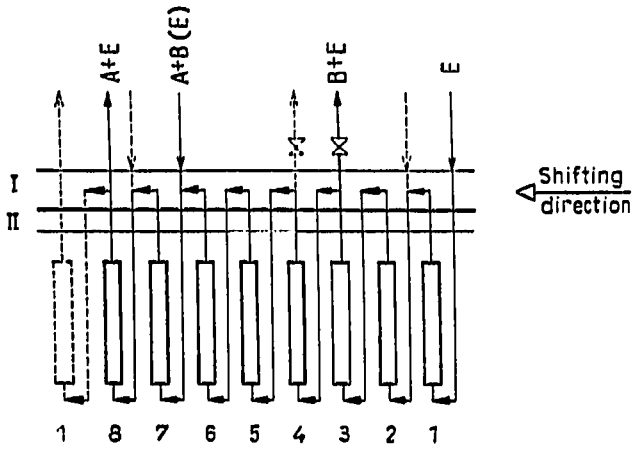

Fig. 5. Switching diagram of the columns in simulated moving bed operation. I, Rotary PTFE disc; II, valve housing; 1–8, columns; A and B, feed components; E, solvent.

series represent the adsorption zone, and the effluent from column 8 consists of benzene + *n*-hexane and does not contain naphthalene.

The eluent is introduced into column 1 and in this functional period columns 1, 2 and 3 connected in series represent the desorption zone. The effluent from column 3 consists of *n*-hexane and naphthalene. The effluent take-off is controlled by a valve in the outlet line so that part of the *n*-hexane + naphthalene stream is directed into column 4. Columns 4, 5 and 6 connected in series represent the rectification zone, in which the displacement of the adsorbed benzene occurs. The effluent from column 6 is introduced into column 7 together with the feed.

In Fig. 5, the broken lines show the switching diagram of the next period. By turning the switching valve through 45°, the positions of the inlet and outlet lines are shifted clockwise by one column and the operation is carried on. In this way, the functional zones advance continuously in the column system. On the basis of batch experiments, the cycle time was fixed at 10 min for the separation of the above mixture.

The results of the continuous operation are given in Table I. In order to give a direct comparison, the results of a batch separation carried out with the above model mixture are also given in Table I. To evaluate these processes, the maximum load of adsorbent and the amount of solvent necessary to regenerate the adsorbent were compared.

The results of the experiments shown in Table I indicate that in batch operation the maximum load of the adsorbent is 70% and the amount of solvent necessary is 257% of that in the continuous simulated moving bed system.

For this evaluation, it should be noted that our equipment consisted of relatively long and few column sections, which means that only a rough approximation of the continuous countercurrent operation is achieved. Also, no attempt was made to optimize the operating parameters. By increasing the number and decreasing the length of the column sections and also by optimizing the operating conditions, the maximum load of the adsorbent can be increased and solvent circulation can be

TABLE I

COMPARISON OF BATCHWISE AND CONTINUOUS SIMULATED MOVING BED OPERATION

Feed: benzene–naphthalene–*n*-hexane (3:4:93, w/w). Solvent: *n*-hexane (technical grade).

Operating conditions	*Batch operation*	*Continuous operation*
Columns		
Length (cm)	50	8 × 50
I.D. (mm)	6	6
Packing	Al_2O_3	Al_2O_3
Particle size (μm)	63–80	63–80
Characteristics		
Adsorbent load (g adsorbate/g adsorbent, h)	0.0241	0.0344
Relative load (%)	70	100
Solvent circulation (ml/g adsorbate)	265	103
Relative solvent circulation (%)	257	100
Effluent concentration (with time)	Strongly fluctuating	Slightly fluctuating

decreased. In addition, the difference between the characteristics of batch and continuous operation depends considerably on the separation factor (relative retention) of the components to be separated and also on the adsorbability of the solvent used.

MULTICOMPONENT SEPARATIONS

The equipment shown in Figs. 1 and 3 is suitable for use in other chromatographic techniques and for the simultaneous recovery of more than two products (up to four at present). For this purpose, only the rotary disc needs to be replaced with a new disc with appropriate bores.

FLOW PROGRAMMING

A simple chromatographic process is the separation of the sample mixture into four products using one solvent. The switching diagram of the columns in this technique is shown in Fig. 6. The mixture to be separated, consisting of components A, B, C and D, is introduced into the solvent stream entering column 5. Sample introduction is achieved with a sampling device (broken line in Fig. 3) according to a programme. As shown in Fig. 6, in the given layout two columns connected in series represent one functional zone and switching is accomplished by shifting the inlet and outlet streams by two columns (90° rotation). As the cycle time is fixed and increasing amounts of solvent are needed in order to elute the more strongly adsorbed components, the flow-rates of the solvent streams (E_1–E_4) are different and fixed at appropriate values so as to ensure complete desorption of the given component during the cycle time. The flow-rate of stream E_1 is set so as to ensure complete elution of component A from columns 5 and 6, while components B + C + D are retained partially separated on the packing. After switching over, the E_2 stream is directed on to columns 5 and 6 for elution of component B. Components C and D will be

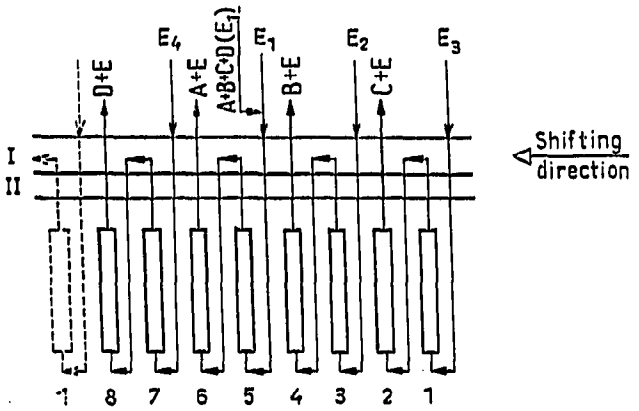

Fig. 6. Switching diagram of the columns for flow programming. I, Rotary PTFE disc; II, valve housing; 1–8, columns; A, B, C and D, sample components; E_1–E_4, solvent.

eluted by solvent streams E_3 and E_4, respectively. The column purged with stream E_4 does not contain any adsorbed component and in the next cycle the sample mixture can again be introduced.

From the above scheme, it can be seen that in fact elution by solvent flow programming is carried out. In comparison with the flow programming accomplished in one column, this system has the following advantages: (1) liquid pumps need not be programmed, each pump delivers fixed amounts; (2) liquid introductions (except the sample mixture) and product withdrawals are carried out continuously and each separated component can be collected continuously in a separate receiver; and (3) four column sections are in operation simultaneously and high capacities can be achieved.

The application of the equipment in order to accomplish the separation described in connection with Fig. 6 is illustrated by the following example. The separation of C_{16}–C_{22} saturated and unsaturated fatty acid methyl esters was investigated on Kieselgel coated with silver nitrate using ethyl acetate–*n*-hexane (5:95, v/v) as

TABLE II

SEPARATION OF FATTY ACID METHYL ESTERS BY FLOW PROGRAMMING

Eight columns, 50 cm × 10 mm I.D. Packing: $AgNO_3$–Kieselgel, 63–80 μm. Switching: 12 min. Feed: 5 ml/h of C_{16}–C_{22} fatty acid methyl esters (seed extract). Solvents: E_1–E_4, ethyl acetate–*n*-hexane (5:95, v/v).

Property	*Solvent*				
	E_1	E_2	E_3	E_4	ΣE
Flow-rate (ml/h)	740	250	690	1890	3770
Product	A	B	C	D	
Product compositions (wt.-%): (solvent free)					
C_{16}–C_{22}	79.5	19.5	—	—	
C_{16}–$C_{18:1}$	20.5	78.3	4.2	—	
$C_{18:2}$	—	2.2	92.2	4.9	
$C_{18:3}$	—	—	3.6	95.1	

solvent. The operating conditions and product compositions are given in Table II. The analysis of the products was carried out by gas chromatography (20% DEGS on Chromosorb W) and by analytical liquid chromatography (Waters ALC 201, silver nitrate–Kieselgel packing). It can be seen from the results that a fairly high throughput capacity can be achieved with the equipment.

STEPWISE ELUTION

The separation of components with widely different retention characteristics generally requires a long time and gives poor efficiency when one solvent is used. For the separation of such samples, in order to enhance the desorption of the heavier components several solvents or solvent mixtures of increasing polarity, *i.e.*, stepwise elution or gradient elution, are applied.

Our equipment is suitable for carrying out stepwise elution in a continuous manner. In Fig. 7, the switching diagram of the columns is shown for obtaining three pure products. As in Fig. 6, switching is accomplished by two columns in series. The sample mixture, consisting of components A, B, C and D, is introduced into solvent stream E_1 entering column 5. Solvent streams E_1–E_3 consist of solvent or solvent mixtures of increasing polarity (strength). The strength of these solvents is chosen so that during the given cycle time solvent E_1 should desorb components A + B (weakly adsorbed), solvent E_2 desorbs component C and solvent E_3 desorbs component D (strongly adsorbed). The solvent stream E_4 in Fig. 6, introduced on to column 7, serves to purge the more polar solvent E_3, *i.e.*, to regenerate the packing before introduction of a new sample.

In comparison with the usual stepwise elution technique, there is a further advantage in our system that in addition to changing the polarity of the solvent, the optimum flow-rates of the individual solvents can be selected, *i.e.*, simultaneous flow programming can be accomplished.

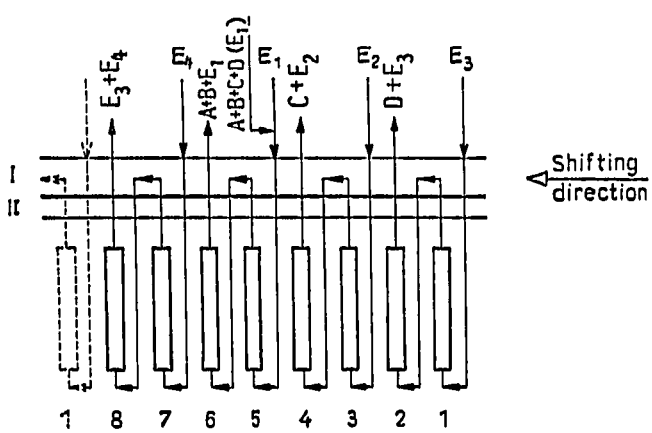

Fig. 7. Switching diagram of the columns for stepwise elution. I, Rotary PTFE disc; II, valve housing; 1–8, columns; A, B, C and D, sample components; E_1–E_4, solvents.

TABLE III

SEPARATION OF FATTY ACID METHYL ESTERS BY STEPWISE ELUTION AND FLOW PROGRAMMING

Eight columns, 50 cm × 10 mm I.D. Packing: $AgNO_3$–Kieselgel, 63–80 μm. Switching: 12 min. Feed: 5 ml/h of C_{16}–C_{22} fatty acid methyl esters (seed extract). Solvents: E_1 and E_4, ethyl acetate–*n*-hexane (5:95, v/v); E_2, ethyl acetate–*n*-hexane (10:90, v/v); E_3, ethyl acetate–*n*-hexane (15:85, v/v).

Property	*Solvent*				
	E_1	E_2	E_3	E_4	ΣE
Flow-rate (ml/h)	990	490	550	670	2700
Product	A + B	C	D	–	
Product compositions (wt.-%):					
C_{16}–C_{22}, $C_{16:1}$–$C_{18:1}$	96.3	3.8	–	–	
$C_{18:2}$	3.7	93.5	4.2	–	
$C_{18:3}$	–	2.7	95.8	–	

Using the above technique, we investigated the separation of a sample mixture containing C_{16}–C_{22} fatty acid methyl esters. The operating conditions and product compositions are given in Table III. On the basis of the results, it can be seen that in the separation of a given amount of sample mixture by stepwise elution, the solvent circulation is about 40% lower than in the case of a single solvent.

In the techniques applied to multicomponent separations, continuous countercurrent contact cannot be used as the introduction of the feed is accomplished periodically and hence batchwise adsorption and desorption take place in the individual columns. It follows that the operation of the equipment in these cases can be regarded as a system containing multiple fixed bed columns. By means of the switching valve, however, the appropriate coupling and efficient utilization of the columns can be easily accomplished and the equipment is suitable for the semi-continuous separation of mixtures on a preparative scale.

The system and the techniques outlined above were investigated using adsorbent packings. Obviously, the equipment can also be applied to other chromatographic techniques, for instance in ion-exchange or gel permeation chromatography. In ion-exchange chromatography, the simulated moving bed technique seems to be suitable for the separation of ionic compounds from the non-ionic components of a mixture. In gel permeation chromatography, several applications can be foreseen for the simulated moving bed as well as for multicomponent separations.

Further applications are currently being investigated and will be described elsewhere.

In addition to preparative separations, the equipment seems to be suitable for accomplishing continuous analysis by liquid chromatography with analytical columns. In the analysis of samples when only one component or a few components are to be monitored while the other, heavier, components should be displaced with a more polar solvent, the sample introduction can be accomplished with short cycles and the components to be detected can be eluted and introduced into a detector with short time delays, while the regeneration of the packings in the individual columns is being carried out continuously and after the complete cycle each column is again ready for sample introduction.

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