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IN SITU LOADING AND RELOADING OF GAS CHROMATOGRAPHIC COLUMNS WITH STATIONARY LIQUIDS

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SUMMARY

The supercritical *in situ* loading technique is shown to be a promising method for loading columns that are difficult to pack, such as small-bore columns packed with small particles and capillary packed columns. The applicability of the method is shown for gas chromatographic columns of normal dimensions, for small-bore columns packed with small particles for use in high-pressure gas chromatography and for capillary columns.

The percentage loading can be varied and predicted. The range of polarities of stationary liquids that can be loaded with *n*-pentane as solvent is satisfactory. This range can probably be extended by using acetone as solvent. The loading and reloading of columns with different stationary liquids is shown to be possible. The method is relatively fast: about 4 h are needed for the complete procedure.

INTRODUCTION

Since the early days of gas chromatography (GC), packed columns have been prepared nearly universally by coating support particles, usually 100–200 μm in diameter, in batch operation with stationary liquid and afterwards packing these coated particles in tubes with vibration. This method is satisfactory for columns with an I.D. of 2 mm and more, using particles of 100–200 μm. However, in attempts to increase the efficiency of packed columns, column types with different dimensions have been proposed. Among these, micropacked columns[1,2] and packed capillaries[3], showing an increased permeability and lower theoretical plate height owing to a column diameter to particle diameter ratio of about 5 and lower. Another type are the microparticulate columns[4,5] in which particles with a diameters significantly below 100 μm are used. The preparation of such columns starting with liquid loaded particles presents difficulties, or at least does not allow to obtain columns with an optimal packing structure. Reasons are the poor

flow characteristics of coated particles in the packing of small-bore columns and the impossibility of using loaded packings in the drawing of packed capillaries and in the slurry packing of columns with particles in the range 10–100 μm which are required in microparticulate columns. A method for the *in situ* loading of columns would therefore be valuable, significantly facilitating the preparation of a packed column with an optimal geometric structure. It would also be possible to load such an optimally packed column, once prepared, with different loading percentages or various stationary liquids.

An *in situ* loading method should fulfil the following requirements:

(i) the stationary liquid should be distributed evenly over the available surface area in the column;

(ii) the method should be applicable to stationary liquids that differ widely in polarity and maximal working temperature (molecular weight);

(iii) the amount of stationary liquid deposited in the column should be predictable to some extent and be adjustable over a wide range;

(iv) for application to high-pressure gas chromatography (HPGC) columns the method should be compatible with low permeability.

Requirement (i) is connected with the efficiency of the column. It indicates on the one hand that a given amount of stationary liquid should be distributed as uniformly as possible in the pore system of the particles rather than forming different pools. This requirement is connected with the wettability of the surface by the stationary liquid. When a suitable combination of surface characteristics and nature of the stationary liquid is chosen, it can be assumed that the equilibrium state of distribution will be reached after proper conditioning of the column (by surface migration and microdistillation), irrespective of the packing and loading procedures. A failure to reach this situation would be reflected in an increased liquid phase mass transfer contribution to the theoretical plate height.

On the other hand, each particle in the column should be loaded with an amount of stationary liquid proportional to its surface area, irrespective of the radial and axial position of the particle in the column. As will become clear in this paper, this is the major problem with *in situ* loading. Failure to reach this situation affects the efficiency significantly through various mechanisms:

(a) Radial profiles in the degree of loading density will lead to different migration rates of retained compounds for different radial positions. Depending on the rate of radial mass exchange, this will contribute a profile term to the theoretical plate height which will be mathematically highly analogous to the flow profile contribution as discussed by Littlewood[6] and Sie and Rijnders[7].

A plate height contribution proportional to the flow velocity and inversely proportional to the radial dispersion coefficient will be the result. This effect can be disastrous in columns with normal column to particle diameter ratios (HPGC), detrimental in micropacked columns and of minor importance in most packed capillaries, and Halasz and co-workers[8,9] succeeded in loading these latter columns by the static evaporation method, which did not work during this study with normal packed columns.

(b) Longitudinal profiles will have a detrimental effect in all kinds of columns. It is known that coupling of columns with different phase ratios generally leads to a decrease in efficiency that is sometimes very significant. Without any detailed study

we suspect, however, that the demands for columns with normal column to particle diameter ratios are not as stringent as for the radial distribution.

(c) Uneven distribution of stationary liquid over various particles will lead to unnecessarily large film thickness in certain parts of the column. This will also increase the plate height via an increased resistance to mass transfer in the liquid phase. This effect will be important in all types of columns.

Requirement (ii) makes the method proposed by Petsev and Kostova[10,11] less attractive. They evaporated the stationary liquid and transported this vapour towards the column by means of a gas flow. Obviously, only relatively volatile liquids can be handled in this way. Also, requirement (i) is not fulfilled, as a longitudinal gradient in the loading density was observed. Moreover, contrary to requirement (iii), only small amounts of liquid could be deposited on the support.

The method proposed by Sie and Van den Hoed[12] is also not very satisfactory. In this method the column is filled completely with a solution of the stationary liquid in a more volatile solvent. The solution is removed from the interparticle space by a slow gas stream. Subsequently the solvent is evaporated from the pores of the particles. The "fingering" during the gas displacement leads to an uneven distribution of the stationary liquid, and columns of acceptable efficiency can only be obtained with this method when the stationary liquid is allowed to redistribute during about a week. This last expedient is, of course, only effective for volatile stationary liquids and requirement (ii) is not fulfilled.

We investigated different methods for depositing stationary liquids on the support in the column. The method of Sie and Van den Hoed[12] was also included, although it is not applicable to most stationary liquids in GC, because we had some hope that the redistribution step in GC could be omitted as the faster radial mass transfer in GC makes an uneven distribution of liquid less significant than in liquid chromatography. Also, the conditions in narrow-bore GC columns could facilitate the attainment of homogeneity during the preparation of columns.

EXPERIMENTAL

Apparatus

Accurate control of temperature and pressure is crucial for the supercritical coating method, and this was achieved in the system shown in Fig. 1. Essentially it consists of a liquid chromatograph to which the column to be loaded is connected. The liquid chromatograph is equipped with a microparticulate column as restrictor.

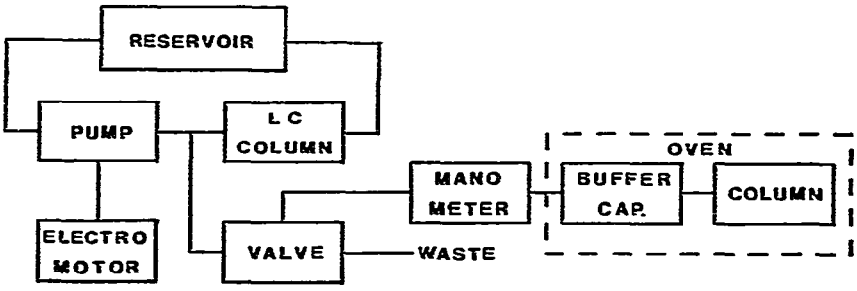

Fig. 1. Apparatus used in supercritical column loading.

The system was constructed from a reciprocating pump (Orlita, Giessen, G.F.R.; Type AE-10-44), a Bourdon-type manometer (Wika, Klingenberg, G. F. R.), a high-pressure injection valve (Valco, HPSV, CV-6-UHPA), a buffer capillary (2 m × 1.1 mm I.D.) and a temperature-programmable oven (Packard Becker, Delft, The Netherlands; Type 1452D) which contained the buffer capillary and the column to be loaded. The flow control knob of the Orlita pump was connected by string with the axis of a variable-speed electromotor. Except when stated otherwise, copper columns of I.D. 4 mm and length 1 m were used in all experiments.

Columns of the usual dimension were tested on a Hewlett-Packard Model 5750 gas chromatograph with flame-ionization detection. The stainless-steel capillary column (30 m × 0.5 mm I.D.) was tested on a Packard 427 gas chromatograph and the small-bore column (1.5 m × 1.1 mm I.D.) packed with small particles was tested on a home-made high-pressure gas chromatograph described earlier[5].

Chemicals and materials

In the preparation of GC columns of normal dimensions, Chromosorb G AW DMCS ($\bar{d}_p = 150\ \mu m$) (Johns-Manville, Denver, Colo., U.S.A.) was used, and Spherosil XOC-005 ($\bar{d}_p = 45\ \mu m$) (Rhône Poulenc, Paris, France) for the HPGC column.

OV-3, OV-7 and squalane (Merck, Darmstadt, G.F.R.) were used as stationary liquids and *n*-pentane (J. T. Baker, Deventer, The Netherlands) as the solvent.

The carrier gas was nitrogen (Hoek-Loos, Amsterdam, The Netherlands).

The sample compounds used for characterizing the columns were methane (J. T. Baker, Phillipsburg, N.J., U.S.A.), *n*-heptane and *n*-octane (Merck, GC quality) and toluene (Merck).

Procedures

The column tubes were packed with the solid support in the normal way. The columns were filled with solution of stationary liquid by pushing the solution by gas pressure into the evacuated column. One end was closed and the other end was connected with the buffer capillary, and the column and buffer capillary were placed into the oven and a flow of *n*-pentane through the liquid chromatographic column was established. The desired pressure in the column to be loaded was adjusted by varying the flow-rate. Then the temperature programme of the oven was started. For the packed GC column of normal dimensions and the capillary column the temperature rise was 2°/min. The HPGC column was coated with a temperature programme of 1°/min. After the desired temperature had been reached, decompression was started. A gradual decrease in the flow-rate setting of the liquid pump led to a gradual decrease in the pressure. The normal GC columns and the capillary column were decompressed at a rate of 5 bar/min and the HPGC column at 2 bar/min.

The plate height of the columns was calculated according to the equation

$$H = \frac{L}{5.54} \cdot \left(\frac{W_{0.5}}{t_R}\right)^2$$

where L = length of the column, t_R = retention time, $W_{0.5}$ = peak width at half-height and H = theoretical plate height.

The capacity factor (κ_i) of a component i was determined from its retention time and that of an unretarded component (methane). The injection volume was 20 μl headspace and the temperature was 100°.

Amounts of stationary liquid in a loaded column were estimated from the equation

$$m_x = \frac{\kappa_{ix}}{\kappa_{ir}} \frac{V_{mx}}{V_{mr}} m_r$$

where:

m_x = mass of stationary liquid in column x;
m_r = mass of stationary liquid in a reference column r loaded in the classical way;
κ_{ix}, κ_{ir} = capacity factors observed for compound i in columns x and r, respectively;
V_{mx}, V_{mr} = gas phase volumes in columns x and r, respectively.

RESULTS AND DISCUSSION

We examined the applicability of several *in situ* loading techniques, especially with narrow-bore columns packed with small particles, as used in HPGC.

Coating by solvent evaporation

First we tested the so-called static coating technique, as used in capillary GC, for its applicability to packed columns. This method appears to be relatively simple and would allow the calculation of the percentage loading from the volume of the solution in the column and its concentration. A column packed with solid support by the balanced density slurry method[13] was completely filled with a solution of the stationary liquid and closed at one end. Then the solvent was evaporated in two different ways. The first method consisted in connecting the open end of the column with a vacuum pump and evaporating the solvent. As this method could possibly lead to the formation of bubbles, another method of evaporation, originally used by Golay[14] for capillaries, was also tried. The column, open end first, was fed at a steady, slow rate into a tubular oven.

Unfortunately, the efficiency of columns prepared by these methods were very poor for retarded compounds, while the theoretical plate number for the unretarded compounds remained at the high values observed for the uncoated columns. This indicates poor homogeneity of the stationary liquid distribution. An explanation of these results can readily be given as follows. For the evaporation of the solvent, heat must be supplied to the column packing. At normal temperatures the heat of evaporation of common solvents is high ($H^{20}_{vap} = 26{,}280$ J/mole for *n*-pentane[15]). The only way in which this heat can be transported is through the column wall. This will result in a steep radial temperature gradient within the column and it can be expected that evaporation will take place predominantly close to the wall. A net transport of stationary liquid towards the wall will occur during the evaporation and the result will be that it is distributed non-homogeneously over the column cross-section, most of it being deposited near or on the column wall. Attempts to diminish the influence of this effect by carrying out both evaporation methods very slowly were unsuccessful.

In order to overcome this problem, we tried to localize the stationary liquid solution within the particles by expelling the solution from the interparticle space before evaporation. A number of procedures which could possibly lead to the removal of the solution from the interparticle space were tested. First it was tried to expel the solution by means of a slow stream of gas[12]. In accordance with the finding and reasoning of Sie and Van den Hoed, we found that the volume of the solution displaced from the column was lower than that of the interparticle space, and that the columns obtained after evaporation of the remaining solution were also poor for retained compounds. This behaviour has also been explained[12]. The boundary plane of gas and liquid during the displacement will show "fingering". Once such a finger has reached the end of the column, the remaining solution cannot be pushed out by the gas pressure because of the large difference in viscosity between liquid solution and gas and because of the capillary forces holding the remaining solution in position. After evaporation, a non-homogeneously loaded column will result. Next, the removal of the interparticle solution from the column was attempted by means of a modification of the mercury plug method introduced by Schomburg and Husmann[16] for the coating of capillary columns. It was expected that pushing a plug of mercury through the column would remove the solution from the interparticle space while leaving the solution in the intraparticle space in position. A minimum absolute pressure, p_m, will be required below which mercury would be pushed out from the interstitial pores by the capillary pressure, according to[17]

$$p_m(\text{bar}) = \frac{12.4}{d_{pore}(\mu\text{m})}$$

where d_{pore} is the pore diameter. We therefore carried out the experiment at an absolute pressure of 35 bar, corresponding to a minimum diameter of accessible pores of 0.35 μm. The differential pressure over the column was 0.2 bar. The experiment failed because the mercury plug disintegrated. This again can be attributed to the fact that "a straight interface perpendicular to the direction of flow will be unstable from the viewpoint of viscosity as well as capillary"[12].

The last attempt to remove the interparticle solution consisted in overcoming the capillary forces by gravitation. As the interparticle voids are much larger than the intraparticle pores, it should be possible to remove the interparticle solution, while leaving the solution in the pores of the particles in position. Equalizing the diameter of the interparticle voids to about half of the particle diameter and expressing the capillary forces as a pressure, we obtain

$$p_{cap} = \frac{4\gamma}{d_p}$$

where γ is the surface tension, d_p is the particle diameter and p_{cap} is the capillary pressure. The gravitational forces are a function of the height of the liquid column, which should be considered. Equating this height to the diameter of a particle, and expressing the gravitational force also as a pressure, we obtain

$$p_{grav} = d_p \varrho g$$

where ϱ is the density and g is the gravitation constant.

As gravitational pressure must overcome the capillary pressure, the following condition should be met:

$$g > \frac{4\gamma}{d_p^2 \varrho}$$

For 30-μm particles and *n*-hexane as a solvent, the gravitation must be of the order of $1.5 \cdot 10^4$ m/sec^2 or higher.

We tried to effect the removal of the interparticle solution by rotating the whole column by means of a drilling machine, but did not succeed in obtaining enough gravitation for a 1.5-m column. Also for practical reasons (the rotation is a dangerous operation) we therefore abandoned this method, although it may be useful for much shorter columns which would fit into a laboratory centrifuge.

Supercritical loading

Because direct evaporation of the solvent from a completely filled column was not successful and it was also not possible to expel the interparticle solution, we examined closely the process of evaporation[18,19] of the solvent.

The potential energy of attraction between molecules is responsible for the existence of the liquid state. This potential energy is counterbalanced to some extent by the kinetic energy of the molecules. The molecules escaping from the liquid, causing the vapour pressure, are those of higher than average velocity and energy. When evaporation takes place, therefore, the average energy of the remaining molecules in the liquid is reduced, and energy must be supplied to the system in order to maintain the temperature. This corresponds to the internal energy of vaporization. As the temperature is raised in a liquid–gas system, the kinetic energy of the molecules increases but there is little effect on the cohesive forces responsible for the internal energy of vaporization. The temperature at which the average kinetic energy becomes equal to the average potential energy is the critical temperature. The heat of vaporization decreases when the temperature is increased to become zero at the critical temperature. Fig. 2 shows ΔH_{vap} as a function of temperature for *n*-pentane[15]. Thus, if we go from the liquid state to the vapour state via the supercritical region, the energy necessary for the "evaporation" is gradually supplied to the system while it is heated. There is no sudden increase in heat flow with its resulting inhomogeneity, as occurs with evaporation in the gas–liquid region. The above can be visualized in a p–T diagram, and such a diagram is shown for *n*-pentane in Fig. 3 on the basis of experimental data[15].

The critical point at which there is no longer any distinction between gas and liquid is at $T = T_c = 196.6°$ and $P = P_c = 33.7$ bar. In the normal evaporation process, one goes from L_1, which lies above the vapour pressure curve and therefore corresponds to liquid, to G_1 in the gas region. When evaporation takes place, *e.g.*, at the boiling point at 1 bar, 357 J are needed for every gram of *n*-pentane. On the other hand, if one first pressurizes the system to a value above the critical pressure (L_2) and then heats it to a temperature above the critical temperature, one reaches a point (F_2) in which no distinction can be made between gas and liquid, the fluidum state. After decompression (F_2) and cooling (G_1), a phase transition has been effected without discontinuity. Thus, at some point between L_1 and G_1, a stationary liquid dissolved in the liquid must have segregated from it in a phase transition.

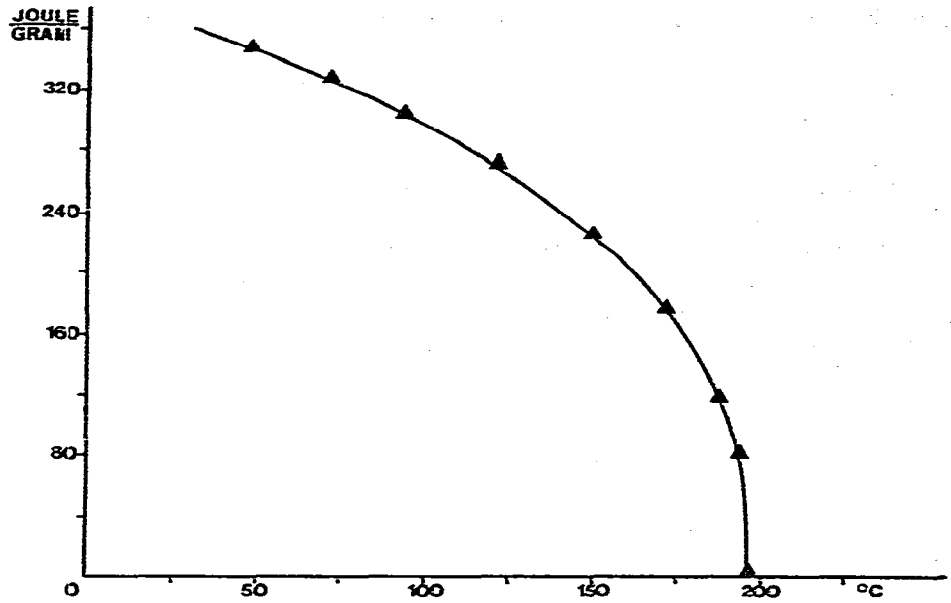

Fig. 2. Heat of vaporization of *n*-pentane at different temperatures.

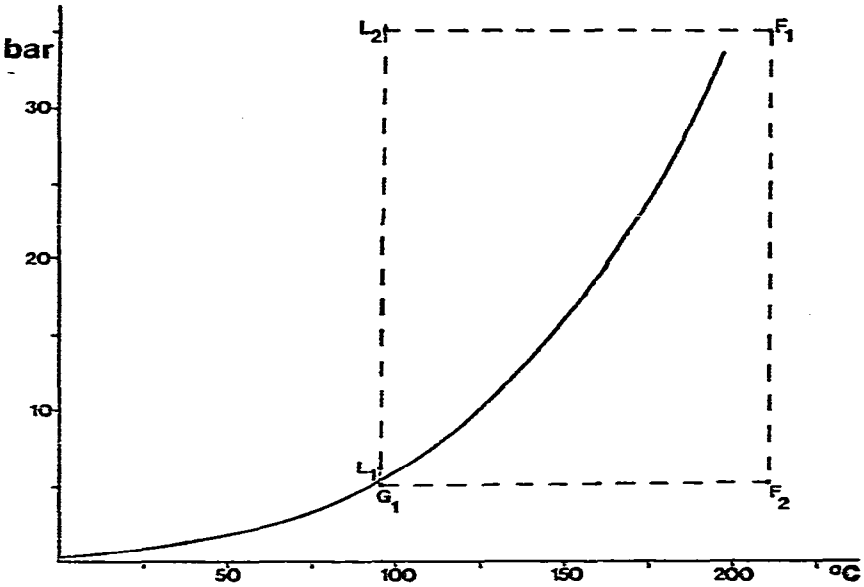

Fig. 3. Vapour pressure curve for *n*-pentane. For case of drawing L_1 and G_1 are placed at 5 bar.

During the pressurization step only an increase in molecular interactions will occur and segregation in this step is highly improbable. During the heating step, the liquid will expand. This expansion is strongly dependent on the value of the reduced pressure, $p_r = p/p_c$, the ratio of the pressure and the critical pressure of the

mixture. For high reduced pressures the expansion is relatively small, and for low reduced pressures it is large. In the former instance segregation of the stationary liquid cannot be expected during the heating step, because the molecular interactions responsible for the solubility of the stationary liquid in the "solvent" will remain very large, as the density remains high. In the second instance, however, heating at a low reduced pressure, the density of the "solvent" is decreased to such an extent that segregation of the stationary liquid will occur. In the decompression step, the expansion of the solvent will continue. Also, the molecular interactions will diminish further in magnitude and if the stationary liquid was not already segregated from the solvent in the heating step, it will segregate in this step. Either expansion process, isobaric heating or isothermal decompression, therefore can bring about the deposition of the stationary liquid on the support.

In the former instance, which occurs if the pressure is initially brought to a relatively low value, we shall speak about thermal deposition; in the latter, which occurs if the pressure is initially relatively high, we shall speak about decompression deposition.

As follows from the above, the location of the critical point of the mixture of solvent and stationary liquid is important. This is not known for the mixtures we used and calculation is hardly possible[19,20]. However, comparison of critical point positions of mixtures given in the literature[18–20] suggests that the critical temperature is only slightly increased compared with that of the pure solvent, but that the increase in the critical pressure can be considerable. This is also supported by our own experiments on thermal deposition.

Columns obtained by slow decompression (a, b, c and d) showed a large variation in homogeneity of the stationary liquid distribution, as can be concluded from the data pertaining to the minimal value and increase of the theoretical plate height with velocity in Table I, which also show a large variation. If the pressure in the system during the heating step was lower than 67 bar, the homogeneity was poor. The homogeneity of columns heated at higher pressures, however, is the same as that of columns loaded and packed in the normal way.

TABLE I

INFLUENCE OF THE CONDITIONS OF THE SUPERCRITICAL LOADING TECHNIQUE

Column dimensions: 1 m × 4 mm I.D. Support: Chromosorb G AW DMCS (150 μm). Solvent: *n*-pentane. Stationary liquid: OV-3. T = final temperature (°C). p = initial pressure (bar). $\Delta p/\Delta t$ = decompression rate (bar/min). m_{T1} = amount of stationary liquid present in the column at initial temperature (grams). m_l = calculated amount of stationary liquid present in the column after the loading procedure (grams). % = loading percentage [(mass of stationary liquid)/(mass of support)]. $\Delta H/\Delta v$ = slope of the rising part of the H–v curve (msec). H_{min} = theoretical plate height at the minimum of the H–v curve (mm).

Column	T	p	$\Delta p/\Delta t$	m_{T1}	m_{T1}/m_l	%	$\Delta H/\Delta v$	H_{min}
a	243	34	5	0.744	1.81	4.7	20.1	1.10
b	243	51	5	0.871	1.89	5.3	18.2	0.73
c	243	67	5	0.755	2.42	3.5	12.5	0.59
d	243	100	5	0.751	2.06	4.2	12.8	0.70
e	243	73	∞	0.762	2.18	4.1	12.9	0.80
f	243	200	5	0.618	1.99	3.4	—	—
g	243	200	15	0.615	6.53	1.1	—	—

This result can be explained by the existence of two different mechanisms of the stationary liquid deposition when this occurs in the heating step.

In the first mechanism, the pressure is below the critical point of the mixture. At a certain temperature the solution starts to boil, *i.e.*, a new phase develops which is rich in the volatile compound, the solvent. The stationary liquid remains in solution initially but is finally deposited either by liquid–liquid phase demixing or by complete evaporation of the solvent from this phase. The process is essentially the same as the static evaporation loading method described before for normal temperatures, although the heat of vaporization is substantially lower.

In the second mechanism, the pressure is higher than the critical pressure of the mixture. On heating, the solubility of the stationary liquid becomes so low that it segregates as a new phase, *i.e.*, the new phase is rich in the non-volatile compound. In literature[19,20] the process is called retrograde condensation of the second kind. The deposition of the stationary liquid on the support occurs homogeneously, as can be derived from the results in Table I.

That in these instances deposition of the stationary liquid occurs in the heating step is also supported by the observation that after heating to 243° [T_r (ratio of temperature and critical temperature) = 1.1] at a pressure of 73 bar ($p_r = 2.2$), fast and slow decompression gave columns with about the same loading percentage (columns a, b, c and d *versus* e). This indicates that the phase segregation took place in the heating step, as in other instances the rate of decompression had a marked influence on the percentage loading.

A number of these columns obtained by thermal deposition were cut into two equal parts in order to determine the longitudinal homogeneity. No significant difference in the capacity factors for the two halves could be measured.

In decompression deposition, which occurs when the pressure is raised, two processes can also be distinguished. If the temperature is below the critical temperature of the mixture, boiling starts as soon as the pressure drops below the vapour pressure of the mixture. On the other hand, if the temperature is higher than the critical temperature of the mixture during decompression, a process which is known as retrograde condensation of the first kind[19,20] occurs. During the expansion the solubility of the stationary liquid decreases, until at a certain pressure, or within a certain pressure range, it is deposited on the support.

That in these instances deposition takes place during the decompression step is supported by the data on rapidly decompressed columns. Columns heated to 243° ($T_r = 1.1$) at 200 bar ($p_r = 6$) and than rapidly decompressed showed a significantly lower loading than columns that were slowly decompressed (columns f and g in Table I).

The capacity factors in halved columns were measured in order to estimate the longitudinal homogeneity. Rapidly decompressed columns had a loading up to 20% higher in the closed end half than in the other half. This can be attributed to the slower rate of decompression in the closed end half, owing to the restriction of the half connected to the capillary. For slowly decompressed columns we did not observe a significant difference in the percentage loadings of the two halves, as estimated from the capacity factors.

Solvents for supercritical loading

Because of the limited solubility in *n*-pentane of a number of polar stationary liquids, other solvents were also examined for their suitability in supercritical loading procedures. The solvent must have low critical constants. In particular, the critical temperature should not be too high, because in the loading process a temperature of 1.1 times this value is reached and both the stationary liquid and the solvent may decompose. Chloroform was useless because decomposition took place during heating and hydrochloric acid was formed, which attacked the tube material. Acetone, with the critical point at 236° and 47 bar, appeared to be suitable for supercritical loading. OV-3 was loaded supercritically with acetone as a solvent at $T = 290°$ ($T_r = 1.1$) and $P = 140$ bar ($p_r = 3$) and a decompression rate of 5 bar/min.

The percentage loading was less than expected from the experiments with *n*-pentane as solvent. This may be attributed to the higher loading temperature intrinsic to the use of acetone. However, the adjustment of the starting concentration of the stationary liquid solution can be used to control the percentage loading.

Reloading of columns

A column was loaded and reloaded with three different stationary liquids (see Table II). The loading was carried out by the supercritical loading technique with *n*-pentane as solvent. The stationary liquid was washed from a loaded column by pumping 100 times the column volume of *n*-pentane at a low flow-rate through the column. The capacity factor of the washed columns differed only negligibly from that of an unloaded column.

TABLE II

CAPACITY FACTORS OF LOADED AND RELOADED COLUMNS

Column dimensions: 1 m × 4 mm I.D. Support: Chromosorb G AW DMCS (150 μm). Column temperature during chromatography: 100°.

Solute	*k*					
	Unloaded	*SE-30*	*Washed*	*OV-3*	*Washed*	*OV-7*
n-Heptane	0.029	1.61	0.033	1.66	0.046	1.73
n-Octane	0.041	3.19	0.069	3.27	0.088	3.44
Toluene	0.038	2.49	0.067	3.07	0.088	3.75

Variation of the degree of loading

A number of columns were loaded under the same circumstances ($T = 243°$, $P = 73$ bar) with different concentrations of stationary liquid in the loading solution. OV-3 was used as the stationary liquid and *n*-pentane as the solvent. As can be seen in Table III, the percentage loading can be varied in this way and is proportional to the concentration of stationary liquid. Thus, after one pilot experiment with a specific stationary liquid–solvent combination, the percentage loading can easily be controlled by adjusting the loading concentration.

TABLE III

DEPENDENCE OF PERCENTAGE LOADING ON CONCENTRATION OF THE LOADING SOLUTION

Column dimensions: 1 m × 4 mm I.D. Support: Chromosorb G AW DMCS (150 μm). Supercritical loading of OV-3 in *n*-pentane at $T = 243°$ and $P = 73$ bar, $\Delta p/\Delta t = -5$ bar/min and $\Delta T/\Delta t = 2°$/min.

Column	*Concentration of loading solution (g/ml)*	*Percentage loading (%)*
h	0.068	3.9
i	0.034	2.0
j	0.017	1.1

Application of the supercritical loading technique to HPGC columns and open-tubular columns

A 1.5-m × 1.1 mm I.D. stainless-steel capillary was slurry packed with Spherosil XOC-005 ($\bar{d}_p = 45$ μm)[13].

The column was then loaded with OV-3 by the supercritical loading method with *n*-pentane as solvent. To maintain homogeneous conditions throughout the column, the loading conditions were adapted to the needs of the relatively low permeability of columns packed with small particles. The temperature was increased at 1°/min to 243°, the pressure was held at 73 bar and the decompression rate was reduced to 2 bar/min. As can be seen from Table IV the efficiency of the column was satisfactory ($H = 0.181$ mm for *n*-hexane with $\kappa = 2.1$ in nitrogen at $T = 80°$).

Fig. 4 shows the separation of Dutch natural gas on the small-particle HPGC column. Because of the high sample capacity of this kind of column, the compromise between detection limit and resolution in the first part of the chro-

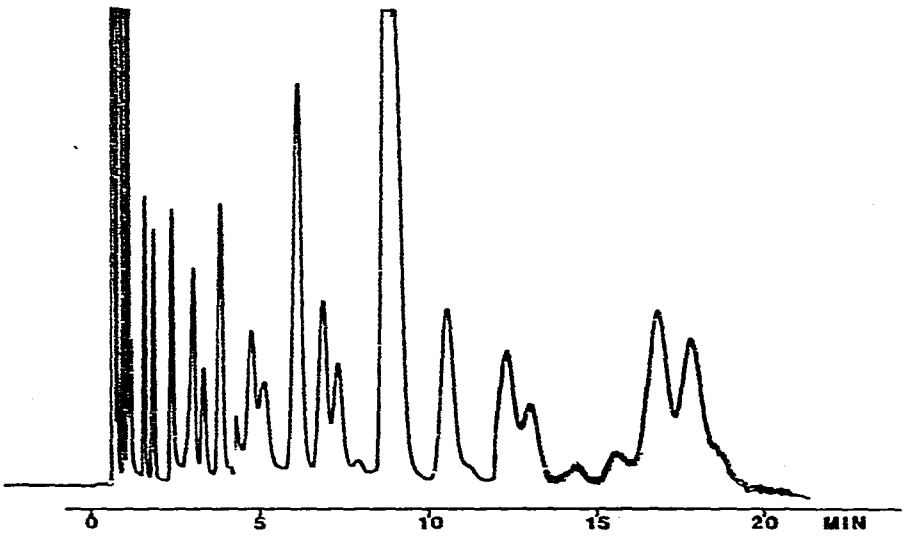

Fig. 4. Separation of Dutch natural gas on a microparticulate column coated using the supercritical loading technique. Column: 1.5 m × 1.1 mm I.D., packing Spherosil XOC-005 ($\bar{d}_p = 45$ μm), supercritically loaded with OV-3. Pressure drop, 15 bar; temperature, 22°.

matogram is very favourable. An amount of 100 μg of the gas mixture was injected, permitting the detection of very retarded trace compounds.

A stainless-steel capillary column (30 m $\times$ 0.5 mm I.D.) was also loaded with OV-3 using *n*-pentane as solvent ($\Delta T/\Delta t = 2°$/min, $\Delta p/\Delta t = -5$ bar/min) at the same temperature and pressure as with the microparticulate column. With nitrogen as carrier gas a theoretical plate height of 0.96 mm was obtained for *n*-decane ($\kappa = 5.3$) at 80°.

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