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A STUDY OF PACKED CAPILLARY COLUMNS

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SUMMARY

Separations in packed capillary columns have been investigated. Packed capillary columns possess advantages over both open-hole capillary columns and classical packed columns. The general efficiency of 10–15-m packed capillary columns ranges from 30,000 to 50,000 theoretical plates (HETP = 0.3–0.6 mm). The high efficiency of packed capillary columns is explained by a smoothing effect of the radial diffusion. A simple procedure was developed for preparing columns of this type. The analytical and physico-chemical applications of the packed capillary columns are discussed.

INTRODUCTION

Improvements of the resolution of chromatographic columns are determined to a considerable extent by the possibility of increasing the efficiency of the columns employed. It is known (*e.g.*, ref. 1) that the resolution (R) of two consecutive peaks is defined by the column packing selectivity (α; relative rention), the partition ratio of the second peak (K), the column efficiency (the number of theoretica plates, N, corresponding to the second peak), as well as the phase ratio (β) of the column:

$$R = \frac{\alpha - 1}{\alpha} \cdot \frac{K}{\beta + K} \sqrt{N} \qquad (1)$$

where $R = 4$ represents a 4σ separation between the two peaks*.

An increase in N permits the requirements to be reduced to a fixed phase selectivity and to improve the separation.

Theoretical investigations of the processes involved in separations on chromatographic columns showed that the column efficiency should increase when the path of radial diffusion is reduced, *i.e.*, with decreasing size of support particles and column diameter. Hence, since 1957, attention has been drawn to the use of capillary columns, *i.e.*, those of 0.2–1.0 mm I.D., in gas chromatography. Capillary chromatography was first mentioned by Martin[2] and then developed by Golay[3]. The columns were empty capillaries, the walls of which were coated with a stationary phase film. Further improvements of capillary columns yielded other types of small-diameter columns, as classified in Table I.

* In the present-day literature we assume $R = 1$ if the resolution of the two peaks corresponds to 4σ; in this case, the right-hand side of eqn. 1 should be divided by 4.

TABLE I

CLASSIFICATION OF CAPILLARY COLUMNS

Classification pattern	*Capillary columns*			
Location of packing in the column	*Surface film (wall coated)* Sorbent coats the column wall		*Packed* Column bulk is packed by a sorbent or a support coated by the sorbent	
Characteristics of packing	*Non-porous* Liquid film is coated on the non-porous column wall[2,3]	*Porous* Sorbent or solid support layer located on the column wall[4,5]	*Soft-packed* Column bulk is packed gently with sorbent. The volume of vacancies between sorbent particles is comparable with the particle volume[6]	*Dense-packed* Column is densely packed with sorbent[7,8]

Of particular interest are the columns with a packing which possess the advantages of both classical capillary and ordinary packed columns and provide many possibilities for the analysis of multicomponent mixtures (including isomers that are very difficult to separate), the determination of different physico-chemical characteristics and rapid analyses. Sorbent-packed capillary columns were prepared by Halász[6]. The tube, first packed with an active sorbent[6,9–13] or inert support[14] and then coated with stationary phase by the frontal method, is drawn on a Desty[15] device. Usually, the packing of such drawn capillaries is irregular. Long columns with comparatively high efficiencies can be prepared by this procedure, but supports with sufficient mechanical strength and thermal stability are required and in most instances cannot be coated with stationary phase in advance. Hence, in our opinion, the columns with densely packed sorbent (0.6–1.0 mm I.D.) are preferable. In this paper, such columns are referred to as packed capillary columns.

Carter[7] was the first to prepare columns of this type. The column (200 × 0.025–0.5 cm, stainless steel) was packed with microspherical glass (0.040 mm) and coated with the stationary phase (squalane) using the frontal method. The height equivalent to a theoretical plate (HETP) of the columns was within the range of 2–0.7 mm. Virus[8] prepared more efficient columns (HETP 0.36–0.39 mm). In this work, 100 × 0.05–0.1 cm metallic columns were packed with Chromosorb or Kieselguhr by means of a vibrator and coated with the stationary phase by the frontal method. Since 1963, capillary columns with previously prepared sorbent (column packing) have been used in gas chromatography. Vigdergaus and co-workers[16–21] and Berezkin and co-workers[22–30] studied and used such columns with previously prepared sorbents.

It should be noted that one can clearly distinguish two steps in the historical development of sorbent-packed capillary columns: (1) preparation and separation studies using short columns, and (2) the preparation and study of long columns. Short columns (usually from 1 to 5 m in length) possess high specific efficiencies (the number of theoretical plates per metre of the column is about 2000); however, the total efficiency of such columns is relatively small (not more than 10,000 theoretical plates).

It is reasonable to use these columns in rapid analyses. Long (more than 10 m) capillary columns with sorbent (column packing) were first prepared only recently[31,32]. The high total efficiency (up to 60,000 theoretical plates) provides possibilities for the study of multicomponent mixtures and mixtures that are very difficult to separate.

EXPERIMENTAL

Methods of preparing packed capillary columns

Short capillary columns (up to 5 m) can be packed with previously prepared sorbent by simply tapping them lightly by hand or by moving a mechanical vibrator along the column. The disadvantage of such methods is that they can only be used to pack short and medium-length columns. Short columns possess high specific efficiency, but their total efficiency is low. For preparing highly efficient columns, it is necessary to increase the column length to more than 10 m, retaining their high specific efficiency. Other disadvantages of these methods are the limitations imposed on the column material, *e.g.*, glass capillaries could not be used. However, glass columns have a number of advantages over metallic columns. Thus, some substances that come into contact with the metallic surface may be irreversibly sorbed or be decomposed[33–37], whereas a glass surface is essentially chemically inert (*e.g.*, with respect to diatomite). The packing of glass columns can be followed visually and the changes that occur in them can be observed. This facilitates considerably the handling of capillary columns. The availability of devices[15] for preparing capillaries of the required length and diameter is also an important advantage of glass capillary columns. The breakability of glass columns should not be regarded as a serious obstacle to their application.

Recently, methods have been developed for the preparation of packed capillary columns (of great length, including glass columns) which extend the possibilities of their application in gas chromatographic analysis. Cramers *et al.*[31] proposed a method for packing 15-m capillary columns with a sorbent using ultrasonic vibration and inert gas pressure. This enables to obtain highly efficient columns (up to 3000–35000 theoretical plates per metre), but requires the use of complex equipment.

A simpler device without the use of ultrasonic waves has been developed in our laboratory. The action of this device is based on two factors: column vibration and inert gas flow. However, the vibration is performed by means of low-frequency (50–100 Hz) electromechanical vibrators located at several positions along the column.

The device consists of a balloon with a compressed gas supply connected to it (via a reductor) with an electromechanically driven valve (this is used to apply periodical pressure in order to reduce the packing time, but it could be omitted) and stands with several vibrators (100-Hz electromagnetic relays), sorbent vessel and column holders. The relays are installed along a circle on a common base, so that the column is fastened over 5–10 coils (depending on its length). The column is arranged vertically and the coils are stretched. The upper end is joined to a sorbent vessel into which compressed gas is fed, while the lower end of the column is free. For rapid and qualitative packing, the sorbent should previously be sieved; 0.10–0.16- and 0.16–0.20-mm sorbent particles are used.

This device permits columns more than 20 m long and of 0.6–1.2 mm I.D. to be packed and provides good reproducibility of packing density, efficiency and reten-

TABLE II

REPRODUCIBILITY OF PACKING DENSITY, EFFICIENCY AND RETENTION INDICES

Column		*Packing*	*Packing weight per metre of column (g)*	*Minimum HETP (mm)*	*Retention indices*			
Length (m)	*I.D. (mm)*				*Benzene*	*2-Pentanone*	*1,4-Dioxane*	*1-Iodobutane*
14.5	0.8	5% Apiezon M on Chromosorb W (0.16–0.08 mm)	0.16	0.26	684	648	689	852
16.0	0.8		0.16	0.27	684	648	688	854
3.7	0.8		0.17	0.28	683	648	688	850
15.0	0.8		0.16	0.27	684	648	687	852
					Acetone	*Isopropanol*	*Ethyl acetate*	*Di-n-butyl ether*
13.8	0.9	15% Carbowax 4000 on Chromosorb P (0.16–0.20 mm)	0.24	0.35	797	888	878	989
10.0	0.9		0.25	0.37	796	886	878	990
5.0	0.9		0.25	0.38	796	887	877	988

tion indices (Table II). The sorbents were prepared using a well-known procedure. The experiments were carried out on a Tsvet-2 chromatograph with a flame ionization detector and linear temperature programming. The column efficiency was 3000 and in some instances 4000 theoretical plates per metre.

RESULTS AND DISCUSSION

Specificities of chromatographic separations in packed capillary columns

Packed capillary columns are columns of a special type. Owing to their small diameter and the presence of a packing, they hold an intermediate position and have the advantages of both open tubular capillary and ordinary packed columns. In spite of their high efficiency, open tubular capillary columns are less often employed than larger diameter columns[38]. This may be explained by the limited choice of stationary phases (generally non-polar liquid phases are used) and by the complex procedure for preparing reproducible columns. Two other important problems are associated with the use of classical capillary columns: they have a low capacity and a relatively large value of β (the ratio of the volumes of the gaseous and liquid phases in the column). The low capacity hinders direct sample introduction; the allowable sample amount is so small that sample introduction can be performed only with flow splitting. These small sample amounts lead to the need for increased detector sensitivity. The large β value also influences the separation. According to eqn. 1, an increase in β causes the separation to deteriorate, and is most pronounced in the separation of weakly sorbing substances.

These disadvantages are reduced when packed capillary columns are used. Such columns can be prepared with high reproducibility using packings of different polarities for both gas–liquid and gas–solid chromatography. The presence of sorbent (column packing) in the columns ensures a sufficiently high capacity. Table III gives

TABLE III

AMOUNT OF STATIONARY PHASE IN DIFFERENT COLUMNS

Column packing: 15% of squalane on Chezasorb (0.10–0.16 mm).

Type	*Length (m)*	*Internal diameter (mm)*	*Amount of liquid phase (g)*
Open tubular capillary	50	0.25	0.01
Packed capillary	15	0.8	1
Ordinary packed	2	3.0	3

approximate amounts of the stationary liquid phases (squalane) in different types of columns.

It can be seen from Table III that the amount of liquid phase in packed capillary columns is two orders of magnitude greater than in open tubular capillary columns. On the one hand, this permits sample introduction without a stream splitter, thus diminishing both errors in quantitative results and the need for a sensitive detector (*e.g.*, a microcatharometer can be used); on the other hand it improves the resolving power of the column on account of the decrease in β.

The advantages of packed capillary columns compared with ordinary packed columns are due to the small diameter of the columns, which gives high efficiency, the possibility of using efficient and expensive sorbents (because of the small amounts required) and carrier gases (the amount of carrier gas used even at high linear velocities is nearly an order of magnitude lower than in the ordinary columns), more stable temperature programming conditions (owing to a negligible thermal inertia of the column and low flow-rate of carrier gas), the creation of small-sized equipment with a compact thermostat (with rapid heating and cooling of the column) and, in some cases, lower resistance to carrier gas flow (thus one can employ long columns at the same inlet pressure).

Very little information is available on the study of the specificity of chromatographic separations on packed capillary columns, and the general features of separations in such columns are considered below.

The basic factor that limits the chromatographic separation is progressive broadening of the chromatographic zone upon its motion along the column packing. This may be influenced appreciably by flow dynamics, convective mixing and interphase mass transfer. The effects result in different velocities of the carrier gas and the components in various parts of the column cross-section, which is responsible for broadening of the chromatographic zone. Hence, in the study of the specificity of separation in chromatographic columns, it is important to establish the dependence of the variation in flow over the column cross-section upon different parameters (the column diameter in the above case). The effect of the column diameter on the broadening of chromatographic zones has been considered by many workers, but there is still no adequate explanation for the pattern of this dependence.

Giddings[39] suggested that the use of columns of smaller diameter should decrease zone broadening because of a smaller contribution of interchannel effects to the HETP, but with a decrease in column diameter the wall effects can increase[40].

A comparison of the efficiencies of packed columns of different diameters

TABLE IV

EFFECT OF COLUMN DIAMETER ON EFFICIENCY

Column packing: 5% squalane on Chromosorb W.

Component	*Carrier gas*	*2.3 m × 3 mm column*		*1.95 m × 1.2 mm column*		*2.16 m × 0.8 mm column*		*2 m × 0.5 mm column*	
		Min. HETP (mm)	*Optimal flow-rate* (cm/sec)*	*Min. HETP (mm)*	*Optimal flow-rate* (cm/sec)*	*Min. HETP (mm)*	*Optimal flow-rate* (cm/sec)*	*Min. HETP (mm)*	*Optimal flow-rate* (cm/sec)*
n-Pentane	Nitrogen	0.52	5	0.45	7	0.42	8	0.41	8
n-Hexane		0.54	6	0.46	6	0.44	8	0.45	8
n-Octane		0.60	6	0.50	6	0.49	7	0.50	7
n-Pentane	Helium	0.88	6	0.58	10	0.60	11	0.60	12
n-Hexane		0.78	8	0.62	12	0.58	11	0.58	12
n-Octane		0.72	8	0.60	10	0.55	10	0.55	12

* Average linear gas velocity.

(Table IV) employed in gas–liquid chromatography demonstrated that for columns of 0.5–1.2 mm diameter the minimum HETP value changes negligibly but increases for a 3-mm column. These results were obtained with nitrogen and helium as carrier gases. For all volatile substances investigated, the minimum HETP value increases on replacement of nitrogen with helium and the minimum of the curve HETP = f(u) (where u is the average linear carrier gas velocity) is shifted to higher linear velocities.

Of particular interest is the correlation between the gas-phase mass transfer term and the mass transfer term in the fixed phase on the efficiency of packed capillary columns. The results obtained showed that the resistance to mass transfer (the C term in the Van Deemter equation) decreases with decreasing column diameter (Table V). Hence, with a change in column diameter from 1.2 to 0.5 mm, the value of C decreases almost two-fold, while with a change in diameter from 3 to 0.5 mm, C decreases 2.5–3 times. These results and the dependence of C on the square of the column radius (Fig. 1) show that an increase in column diameter from 0.5 to 1.2 mm results in an even greater change in C than for the 1.2–3.0-mm range.

The gas phase and liquid phase resistances to mass transfer (C_G and C_L) in columns of different diameters were determined separately using the method proposed by Perrett and Purnell[41]. It can be seen from the results obtained for *n*-octane (Table VI)

TABLE V

THE RESISTANCE TO MASS TRANSFER TERM, C (sec), IN COLUMNS OF DIFFERENT DIAMETER

Column packing: 5% squalane on Chromosorb W (0.10–0.16 mm).

Component	*2.3 m × 3 mm column*		*1.95 m × 1.2 mm column*		*2.1 m × 0.8 mm column*		*2 m × 0.5 mm • column*	
	Nitrogen	*Helium*	*Nitrogen*	*Helium*	*Nitrogen*	*Helium*	*Nitrogen*	*Helium*
n-Pentane	0.018	0.012	0.010	0.008	0.009	0.007	0.006	0.005
n-Hexane	0.015	0.010	0.010	0.008	0.009	0.006	0.006	0.004
n-Octane	0.013	0.008	0.009	0.005	0.008	0.004	0.005	0.003

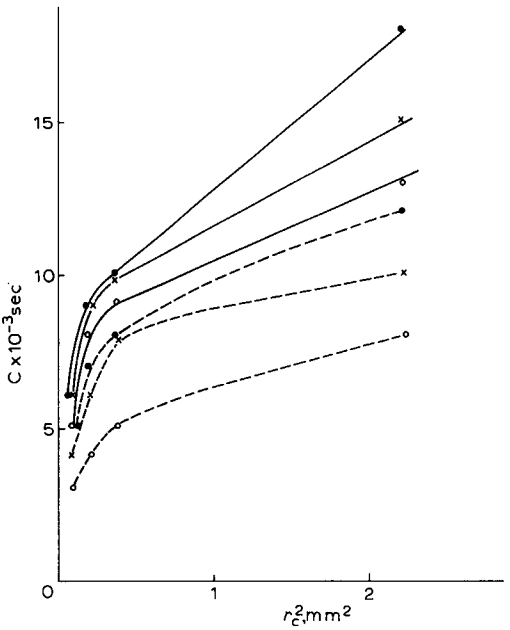

Fig. 1. The resistance to mass transfer term (C) *vs.* the square of the column radius (r^2). ●, *n*-Pentane; ×, *n*-hexane; ○, *n*-octane. Carrier gas: ———, nitrogen; — — —, helium.

that the column diameter has virtually no effect on C_L, while the change in C in columns of different diameters is due to the variations in C_G. When nitrogen is used as the carrier gas, the broadening of the chromatographic zone is determined by a gas-phase mass exchange, while in the case of helium in large-diameter columns (1.2–3 mm) such broadening is the resu t of gas-phase mass exchange, and in small-diameter columns (0.8–0.5 mm) it is the result of a liquid-phase mass transfer.

The higher efficiency of packed capillary columns compared with ordinary analytical columns can, in our opinion, be explained by the smoothing effect of radial diffusion.

TABLE VI

THE RESISTANCE TO MASS TRANSFER TERM, C (sec), FOR *n*-OCTANE IN COLUMNS OF DIFFERENT DIAMETER

Column packing: 5% squalane on Chromosorb W (0.10–0.16 mm).

Phase	*Carrier gas*	*Column*			
		2.3 m × 3 mm	*1.95 m × 1.2 mm*	*2.1 m × 0.8 mm*	*2 m × 0.5 mm*
In the gas phase (C_G)	Nitrogen	0.0110	0.0067	0.0059	0.0028
	Helium	0.0060	0.0027	0.0018	0.0007
In the liquid phase (C_L)		0.0020	0.0023	0.0021	0.0022
Total (C)	Nitrogen	0.013	0.0090	0.008	0.0050
	Helium	0.008	0.0050	0.004	0.0030

TABLE VII

CHARACTERISTICS OF MIXED COLUMN PACKING

Column No.	*Column packing composition (wt.%)*	
	Chromaton N-AW with 5% of squalane	*Chromaton N-AW without stationary phase*
1	5	95
2	50	50
3	100	0

In packed capillary columns, the sorption processes occur within a distance of 0.05–0.08 cm, so that the concentration of chromatographed substances in the columns is favourably levelled owing to diffusion. Hence the time of diffusion of the molecules of a substance being chromatographed over the column diameter is small and the distance passed by a zone during this time is shorter than the height equivalent to a theoretical plate. For ordinary analytical columns (4–6 mm I.D.), a similar calculation shows that the time of radial diffusion is sufficiently great and the distance passed by a zone during this time corresponds approximately to the height of one theoretical plate.

In order to check the hypothesis of the smoothing effect of radial diffusion, we studied the dependence of the efficiency in columns previously packed with an irregular (mixed) packing [a mixture of a gas–liquid chromatographic packing (*i.e.*, stationary phase on solid support) and an inert support]. The efficiency was measured on two

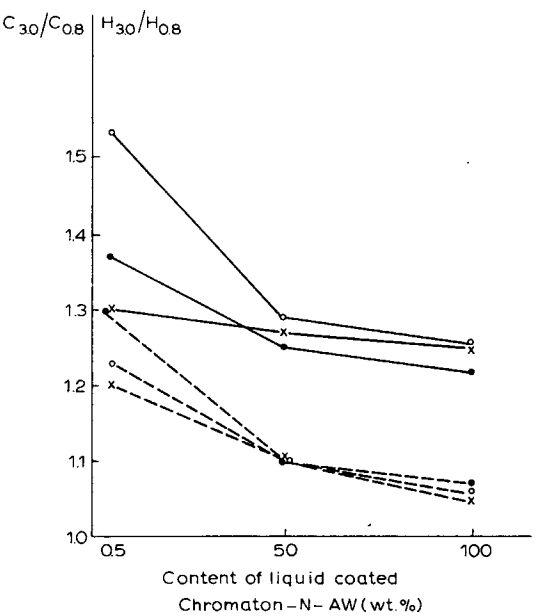

Fig. 2. Ratios of the resistance to mass transfer term (C) and of $H_{min.}$ in columns of 0.8 and 3.0 mm I.D. *vs.* packing composition. ●, *n*-heptane; ×, toluene; ○, *n*-octane. $C_{3.0}/C_{0.8}$, $H_{3.0}/H_{0.8}$.

spiral columns: glass (3 m × 0.8 mm) and metallic (2.9 m × 3 mm). Both columns were packed with the same packing, *viz.*, a mixture of Chromaton N-AW (diatomite support, Lachema, Czechoslovakia) without stationary phase and Chromaton N-AW with 5% of squalane (the ratios are shown in Table VII).

Fig. 2 shows the ratios of the resistance to mass transfer term and the ratios of the minimum HETP values *versus* sorbent composition in the columns investigated. It can be seen from these results that for all of the substances studied, the values of $H_{min.}$ and C are smaller in capillary columns. These properties decrease with decreasing irregularity of the packing, *i.e.*, on going from a column packed with 5% of packing with liquid phase to a column packed with 50% of the same sorbent and then to a column containing only the sorbent with liquid phase. These results are in agreement with an assumed greater effect of radial diffusion and hence a higher efficiency of packed capillary columns. The results also show the significant diffusion effect in the gaseous phase on $H_{min.}$ and C values. Otherwise, the effect of sorbent irregularity should not be so sharp.

These investigations have therefore demonstrated that the efficiency of packed capillary columns is appreciably higher than that of ordinary analytical columns. It should also be noted that for a gas–liquid version in the region of low linear velocities of the carrier gas [near the minimum of $H = f(u)$], the diameter of the columns employed (0.5–1.2 mm) does not have a significant effect on the column efficiency. At high velocities of the carrier gas, 0.5-mm diameter columns are preferable. However, the investigation of long columns with such a diameter is more complicated and it is reasonable to use columns of somewhat larger diameter (0.7–0.8 mm).

Applications of packed capillary columns

Long packed capillary columns, owing to their high resolution power and the possibility of using sorbents of different polarities, permit the investigation of multicomponent mixtures to be extended. Thus, efficient packed capillary columns were employed successfully for the analysis of complex hydrocarbon mixtures, the liquid fractions obtained from high-temperature pyrolysis. In the fraction of pyrocondensates investigated, 70 components were identified (96.3% of the total fraction). Figs. 3 and 4 show the separation chromatograms obtained on packed capillary columns.

An important application of packed capillary columns is the determination of physico-chemical characteristics by a micro-method, *i.e.*, with small amounts of the substance and sorbent (reagent). The method can be used in determining reaction rate constants and heats of adsorption.

The advantages of rate-constant measurements using packed capillary columns were demonstrated in the reaction of isoprene with maleic anhydride in the liquid phase by impulse chromatography. Stainless-steel columns (50 × 0.098 cm and 200 × 0.098 cm) were used, the amount of packing loaded was 0.25 or 1 g, the packing was prepared by coating with 45% of stationary phase (30% of maleic anhydride and 15% of tricresyl phosphate) the solid diatomite support TND-TS-M* and nitrogen was used as carrier gas, the ratio of flow division being 1:25. The degree of conversion was determined from the change in the peak areas of isoprene and unreacted *n*-pentane (internal standard) on the chromatogram. The activation energy calculated from the

* Spherokhrom-1, obtained by thermochemical processing of diatomite.

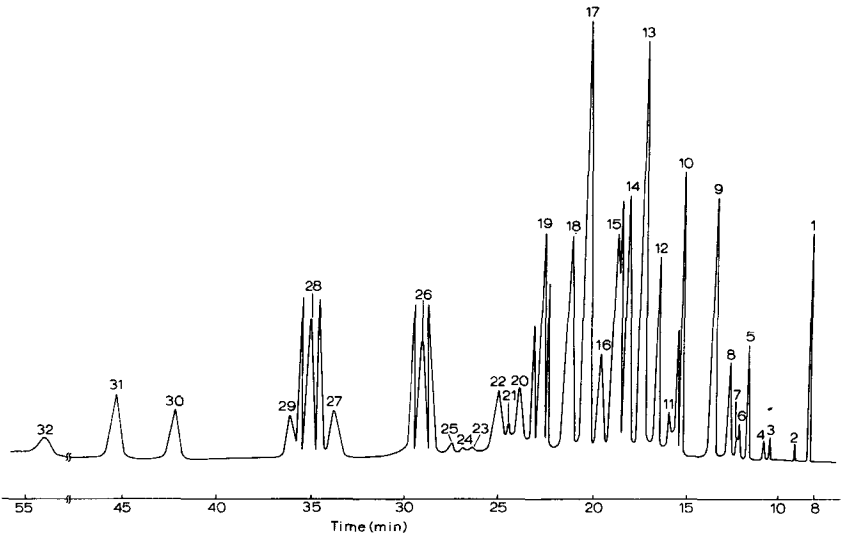

Fig. 3. Separation of a mixture of oxygen-containing compounds. Analysis conditions: 13.8 m × 0.8 mm column; sorbent, 15% Carbowax 4000 on Chromosorb P; 120°. Peaks: 1 = unidentified; 2 = *n*-pentane; 3 = diethyl ether; 4 = *n*-propyl methyl ether; 5 = diisopropyl ether; 6 = di-*tert*.-butyl ether; 7 = acetaldehyde; 8 = *tert*.-butyl isopropyl ether; 9 = unidentified; 10 = di-*n*-propyl ether; 11 = diisobutyl ether; 12 = formaldehyde methyl ethyl acetal; 13 = isobutyraldehyde; 14 = formaldehyde methyl isopropyl acetal; 15 = isopropyl formate; 16 = formaldehyde diethyl acetal; 17 = butyraldehyde; 18 = ethyl acetate; 19 = methyl propionate; 20 = dimethyl isobutyrate; 21 = *n*-propyl formate; 22 = 2-methylbutyraldehyde; 23 = 3-methyl-2-butanone; 24 = formaldehyde ethyl *n*-propyl acetal; 25 = *sec*.-butyl formate; 26 = *sec*.-butanol; 27 = *n*-propanol; 28 = formaldehyde 2,3-butylene glycol acetal; 29 = *n*-butyl formate; 30 = isobutanol; 31 = *n*-butyl acetate; 32 = *n*-butanol.

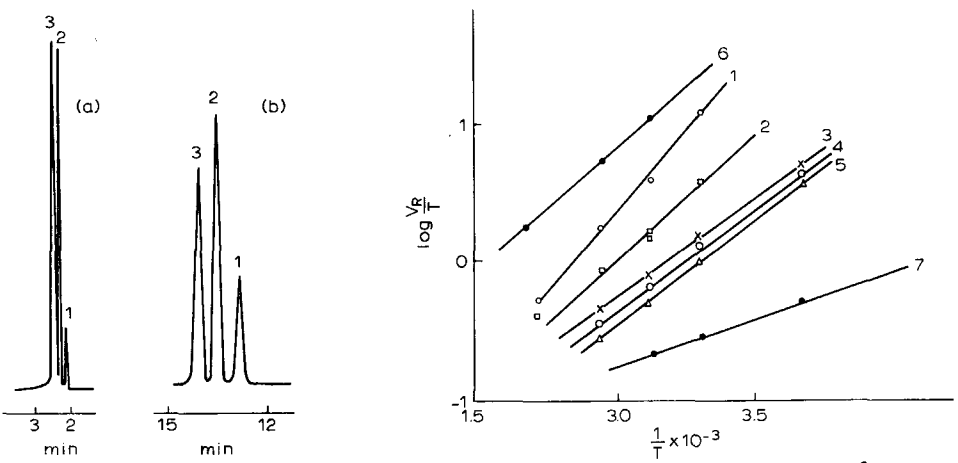

Fig. 4. Comparative separation chromatograms of three 3-methyl-2-pentene isomers on capillary columns: (a) wall-coated with stationary phase; (b) packed. 1 = 3-Methyl-2-pentene; 2 = 3-methyl-*trans*-2-pentene; 3 = 3-methyl-*cis*-2-pentene.

Fig. 5. Log V_R/T *vs.* $1/T$ for 1-butene on alumina, on modified alumina and also on squalane (on inert support). 1 = Initial alumina; 2 = treated with 3% NaOH; 3,4,5 = treated with 3% NaOH and modified with 3, 5 and 7.5% of squalane, respectively; 6 = treated with 3% NaOH, ordinary packed column; 7 = inert support TNKh-1 with 10% of squalane.

results obtained was 12.1 kcal/mole, which coincides with the literature data (12.1 kcal/mole)[42].

Thus packed capillary columns can be employed successfully in the study of kinetics of chemical reactions, which enables the amounts of reagent and substance used to be decreased. An advantage of such columns is the possibility of determining the rate constants of fast reactions (due to their high activity). Calculations show that the kinetic sorption–desorption coefficient (intradiffusion mass exchange) at maximum conversion is 2000 times greater than the rate constant (and by an order of magnitude lower for analytical columns).

Packed capillary columns can also be used for measuring heats of adsorption.

The heats of adsorption of 1-butene on various alumina samples were determined on a 50 × 0.058 cm packed capillary column at temperatures from −20° to 100° with an average linear carrier gas velocity of 1.7 cm/sec and, for comparison, one sample was measured on an ordinary column (100 × 0.4 cm). Fig. 5 shows the plot of $\log V_R/T$ against $1/T$ (V_R = corrected retention volume) for alumina and for alumina modified by different amounts of stationary liquid, and for a gas–liquid version on a column packed with inert TNKh-1* support with 10% of squalane. The heat of adsorption of 1-butene on pure alumina is the maximum value, the heats of adsorption being lower on the modified aluminas. However, on modified alumogels, the heats of adsorption are higher than the heat of dissolution of squalane, which shows a considerable adsorption effect on the squalane–aluminium interface.

According to the literature data[42], the heat of adsorption of *n*-butane is 8.2 kcal/mole, while the experimental heat of adsorption determined on packed capillary columns is 8.5–8.1 kcal/mole. The micro-method described above for the determination of heats of adsorption is reliable and accurate, which is of particular importance when only small amounts of sorbent and the substance being studied are available.

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