CAPILLARY COLUMN GAS CHROMATOGRAPHY OF COMPOUNDS OF LOW VOLATILITY

TEMPERATURE STABILITY OF STATIONARY LIQUIDS ON VARIOUS GLASS SURFACES

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SUMMARY

Several problems relating to gas–liquid chromatography in glass capillaries at high temperatures are discussed. Studies on the temperature stability of stationary liquids and solutes in the temperature range 250–390° were concerned with the parameters that influence column bleeding, especially of silicone phases from glass capillaries. The following parameters proved to be important:

(1) Type of glass (alkali or borosilicate) with special regard to the alkali content: methylsilicones such as OV-101 and SE-30 are more stable on borosilicate and less stable on alkali glass.

(2) Surface properties after roughening and/or deactivation: most deactivations are not stable at temperatures above about 240°. Barium carbonate does not decrease the decomposition of methylsilicones; an increase in decomposition was observed instead. Treatment with hydrogen chloride decreases but does not completely prevent the decomposition of methylsilicones.

(3) Type and origin of methylsilicone: SE-30 and OV-1 proved to be much more stable than OV-101, even on alkali glass surfaces.

In the standardized bleeding measurements, the column length, carrier gas flow-rate and film thickness were kept constant. The separation efficiency, tailing behaviour and decomposition or adsorption of methyl stearate as a more polar standard compound were controlled in parallel during the bleeding measurements. POLY S 179 (sulphonated polyphenyl ether) proved to be the most stable polar stationary liquid in glass capillary column work and could be used even on alkali glass surfaces at temperatures up to 390°.

The most important application for which columns with improved temperature stability have been developed was the rapid separation of the polynuclear aromatic hydrocarbons in coal tar with high resolution.

INTRODUCTION

The major limitation to the use of gas–liquid chromatographic methods in separating compounds of low volatility is the thermal decomposition of either the

solute and/or the solvent (stationary liquid) on the column surfaces or on surfaces of óther sections of the chromatographic system with which the liquids come into contact.

On active surfaces, decomposition of compounds to be separated may occur at the temperatures that are necessary in order to ensure reasonable elution times, symmetrical peak shapes and avoidance of condensation and/or adsorption. Active surfaces may occur not only in poorly deactivated or coated columns but also in extra-column devices such as injector or detector connections.

In practical gas chromatographic (GC) analysis, the volatility of solutes is increased for two different reasons when using a special stationary liquid:

(1) The analysis time (elution time of the last-eluted component of a sample that is of analytical interest) needs to be shortened for economic reasons (handling of a larger number of samples by fewer operators) or because low cycle times in process chromatographic applications must be achieved.

(2) The peak-height or peak-area ratio needs to be increased in order to attain steep profiles and therefore high signal-to-noise ratios for the use of various types of detectors (mass flow and concentration-dependent, including mass spectrometers, for example).

An isothermal mode of column operation cannot be applied to the separation and quantitation of mixtures with a wide range of component volatilities in a single run. By temperature programming, components of low volatility can be eluted within moderate retention times at a resolution that is not appreciably lower than that achieved under isothermal column operation after proper optimization of the flow-rate. Sufficient resolution is also ensured for the more volatile components that are eluted at the beginning of the temperature programme.

In many practical routine examples the application of multi-stage and multi-dimensional GC is preferable and can be adopted successfully in order to improve the resolution of selected parts of a mixture and to reduce the analysis time by pre-separation using different column polarities and temperatures and by back-flushing the uninteresting, less volatile components from the pre-column.

The application of GC to the separation of high-molecular-weight compounds can be improved by various means other than elevation of the column temperature. The following are of importance:

(1) The total amount of stationary liquid in the column determines the elution times[1], depending on the phase ratio and column length. For high-temperature work in routine analysis columns should be used in which the total content of the stationary liquid is low, at just adequate or higher separation efficiencies. Capillary columns with thin films[2] of the stationary liquid meet this requirement. Short columns allow the use of lower column temperatures but, of course, have correspondingly lower separation efficiencies. Because of the high permeability of capillary columns, long columns can be used even at higher flow-rates, which is preferable for high-temperature work. Thin films are to be recommended, especially in long columns with respect to short retentions and low column temperatures (see Fig. 2).

(2) Hydrogen should be used as the carrier gas. Because of its low viscosity[3] maximal separation efficiencies are achieved at about three times the average carrier gas flow-rate with nitrogen or argon, as shown by Scott and Hazeldean[4] as early as 1960.

Shorter retentions without an increase in column temperature are obtained. At higher flow-rates (*i.e.*, higher than optimal) the HETPs are considerably lower when using hydrogen than with nitrogen or argon or even helium because of the higher diffusin constant of solute in the gas phase (D_G) and the lower temperature dependence of the viscosity of hydrogen. Moreover, hydrogen can be used at much lower pressure drops (see Fig. 2 and compare the chromatograms in Figs. 7 and 8).

(3) Stationary liquids of low polarity (showing not too strong intermolecular interaction with the solutes) should be used. In general, very few polar stationary liquids are available for high-temperature work, however, because of the limited temperature stability of most of the common polar stationary liquids, which do not permit column temperatures higher than 220–240° to be used.

(4) Derivatization of strongly polar constituents of the sample with the aim of decreasing intermolecular interactions with the stationary liquid. Often an increase in the thermal stability of the derivatized compounds is also observed, *e.g.*, with sugars.

For high-temperature work, the entire chromatographic system, including devices for sample introduction, column connection and detectors, has to be heated to a temperature that is at least equal to that in the column. Attention should be paid to the fact that in capillary column GC temperatures can generally be kept relatively low (see above). Usually the injectors and detectors are operated at a higher temperature than that of the column itself. Different arguments have been advanced to justify this provision, which often proves to be dangerous with regard to the decomposition of sensitive compounds. In the injector rapid vaporization of the sample, especially with respect to the components of lowest volatility, is claimed to be important. In practice, the arbitrary boiling points of the major components are simply considered for the selection of adequate column and injector temperatures. In capillary column GC the amount of stationary liquid involved in the separation can be kept low in columns with good separation efficiencies. The corresponding sample capacity is also very low and only very low solute concentrations in the carrier gas arise. Partial pressures are so low that the equilibrium pressures for partition and/or adsorption are not reached.

In conclusion, boiling point considerations lead to much too high sampling and column temperatures, but can give information on the relative volatilities of the various components of a mixture if no strong polarity influences are to be considered.

During sampling by split injection, carrier gas flows through the vaporizer at very high flow-rates. Formation of aerosols may occur, which leads to discrimination with respect to volatility (molecular weight) during splitting, and inaccurate quantitation is achieved. Aerosol formation can be avoided by using glass-wool packings in the vaporizer, etc.[5,6], and also by the selection of a suitable injector temperature and a suitable solvent for dilution of the sample components to be determined.

Many commercial instruments suffer from unbalanced temperature gradients in and between the system elements, caused by inhomogeneous heating, especially in the connection lines. In order to avoid cold sections of the chromatographic system, which may act as cold traps and where adsorption may take place, temperatures are increased substantially in the integral parts of the system where temperatures

are measured and controlled, such as in injectors (and also in column ovens and detectors). In the injector explosive vaporization and aerosol formation or decomposition of the solute and the stationary liquid (in the column) occur. Too high injector temperatures are also frequently used with splitless injection to achieve complete vaporization and to prevent adsorption on the injector and septum surfaces of large amounts of solvents or major components of the sample. With splitless injection, overheating of the injector is especially dangerous because of the long residence times of the sample at the low carrier gas flow-rates that are typically used for splitless injection. Adsorption of the sample at the septum and on the surfaces of the injector may occur and thermal decomposition may be accelerated by catalytic effects. In septum flushing one must prevent volatile silicon products evolving from the heated septum material from entering the carrier gas flow and also the column. Especially in temperature-programmed work the presence of these products generates ghost peaks. Glass is now generally used in all sampling systems; stainless steel should not be used because of its high catalytic activity. Investigations on the influence of various types of glasses in this regard have not yet been carried out. The surface properties of glass-lined metal tubing have not so far been tested in comparison with normal glass surfaces.

Sampling difficulties of the aforementioned kind are avoided by using the direct sampling technique that has been developed in our laboratories. In this system, a micropipette–lock system is used for introduction of liquid samples into glass capillaries without any pre-vaporization of the sample before entering the column or overheating of the column inlet. Results on the comparison of the various sampling techniques with regard to discrimination and decomposition effects have been published previously[5,6]. A similar technique of direct sampling by means of a special syringe was proposed by Grob and Grob[7] and was presented at the 1978 Pittsburgh Conference in Cleveland, Ohio, U.S.A.

In order to prevent surface (adsorption) catalysed thermal decomposition of sensitive components of the sample, the following fundamental requirements for the technique of connection in capillary chromatographs must be met. Short connection lines should be made from inactive or deactivated tubing material, preferably glass. Optimally, the column ends themselves, and no special connecting tubings, should act as part of the injector and the splitting system. The end of the column should be introduced either into the jet of the flame-ionization detector (FID) itself or into a connection piece from glass to which the tip of the jet is fixed and into which a scavenger gas is led. Thus high gas flow-rates at the column ends (split flow in the injector and hydrogen or scavenger gas flow in the detector) reduce the residence time in the extra-column sections of the chromatographic system with their active surfaces and compensate for peak broadening as a consequence of dead volumes, for example in electron-capture detectors (ECDs). Introduction of make-up gas, of course, decreases the ECD sensitivity because this detector is of the concentration-dependent type. Proper heating and thermally stable sealing of the connection lines are important, as pointed out before. Graphite is the best sealing material for column connections and, of course, all other connections in the heated part of the chromatographic system.

In the past, many chromatographers doubted that glass capillary columns could be made with temperature stabilities comparable to those of packed columns.

This critical attitude to capillary columns is slowly disappearing as a result of the good results that have been achieved recently. Considerable progress has been made during recent years in special treatments of glass capillary surfaces with regard to the following aims:

(1) improvement of film fixation and avoidance of droplet formation, especially at elevated temperatures;

(2) generation of deactivated and roughened surfaces that do not contribute to the partition of the solute between the mobile and stationary phases, and

(3) optimal film homogeneity, *i.e.*, perfect coverage of the more or less active glass surface by the stationary liquid even at very low film thicknesses.

Deactivation procedures and support activity in general should not change the selectivities of stationary liquids and increase the column bleeding, *i.e.*, catalyse the thermal decomposition of the stationary liquid. Up to now insufficient emphasis has been laid on the investigation of the factors that determine the temperature stability of the stationary liquid on the various surfaces generated during the different methods of column manufacture.

EXPERIMENTAL

Glass capillaries of I.D. about 0.28 mm and O.D. 0.8 mm were drawn with a slightly modified Hupe and Busch machine from tubing of O.D. 8.0 mm and I.D. 3.5 mm. The types of glass used were AR (alkali) and Duran 50 (borosilicate) obtained from Schott (Mainz, G.F.R.). Surface treatment with gaseous hydrogen chloride and/or hydrogen fluoride was performed according to procedures described in previous papers[8-10]. Deactivation was executed by means of Carbowax 20M or Emulphor-0 using the procedures described by Cronin[11], Grob and Grob[12], Sandra and Verzele[13] and ourselves[10]. Coating with the stationary liquid was effected either dynamically using our mercury plug method[8] or by the static method first described by Bouche and Verzele[14]. The latter procedure was preferred for short columns (25 m) and when defined film thicknesses were to be achieved or with stationary liquids of very high viscosities (for example, SE-30). For the tailing tests the usual "polarity mixtures" as proposed by ourselves[8-10] and Grob and Grob[15] were applied.

All necessary further information on the quantitation of bleeding and on the chromatographic parameters for the various separations are either given in the text or in the legends to the figures.

NEW RESULTS AND WORK AT HIGH TEMPERATURES WITH GLASS CAPILLARY COLUMN SYSTEMS

Improved connection technique for glass capillary columns based on graphite as the packing material

Previously conical graphite ferrules of the Swagelok type have been preferred. We present here a new and cheap connection technique that has been used successfully in our laboratories for about 3 years. The construction can be seen from Fig. 1. A brass or stainless-steel sleeve contains a flat graphite packing with a hole of about the size of the column outside diameter. It is of low weight and can be fitted to the column ends; it may remain there indefinitely, but can also be removed easily and
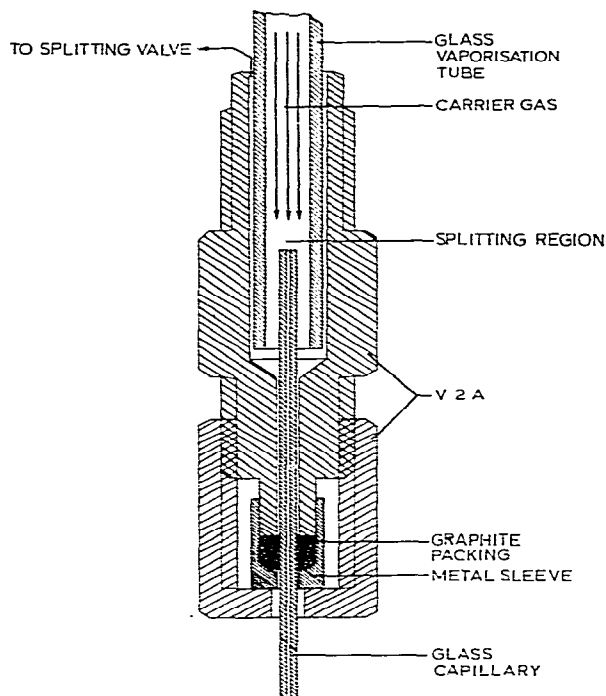
Fig. 1. High-temperature connection for glass capillary columns.

can be used again for the connection of another column. The straightened column end is introduced into a hole of a counterpart which is connected either with the injector or the detector. The column end penetrates the glass insert of the splitter or the detector jet. Thus glass-to-glass connections are guaranteed.

By means of a screw cap that has been slit for removal from the column if it is not used, the graphite packing is pressed against the flat surface of a nose of the counterpart which fits properly to the ferrule sleeve. By this construction fusion of the graphite in the wrong direction is prevented; the fusing graphite only tightens the glass tube against the packing itself. The connections of a glass capillary to the instrument by this technique proved to be very gas-tight and could also be used successfully for GC–MS work. (The most important piece of the new connection technique, the graphite-packed ferrule, is termed a "graphpack-ferrule".)

Improvement of the separation of a low-volatility mixture (coal tar) by optimization of various column parameters

The principles of optimized high-temperature work discussed in the Introduction have been applied to the separation of coal tar with the aim of maximal resolution in the benzopyrene range. In the isothermal mode of column operation hydrogen was used as the carrier gas with a 45-m SE-54 glass capillary column (see Fig. 2). By using a very thin film of the stationary liquid a column temperature as low as 200° could be applied in order to achieve a perfect separation of the benzopyrene isomers within only 30 min. Under the same conditions benzo[*ghi*]perylene (with a
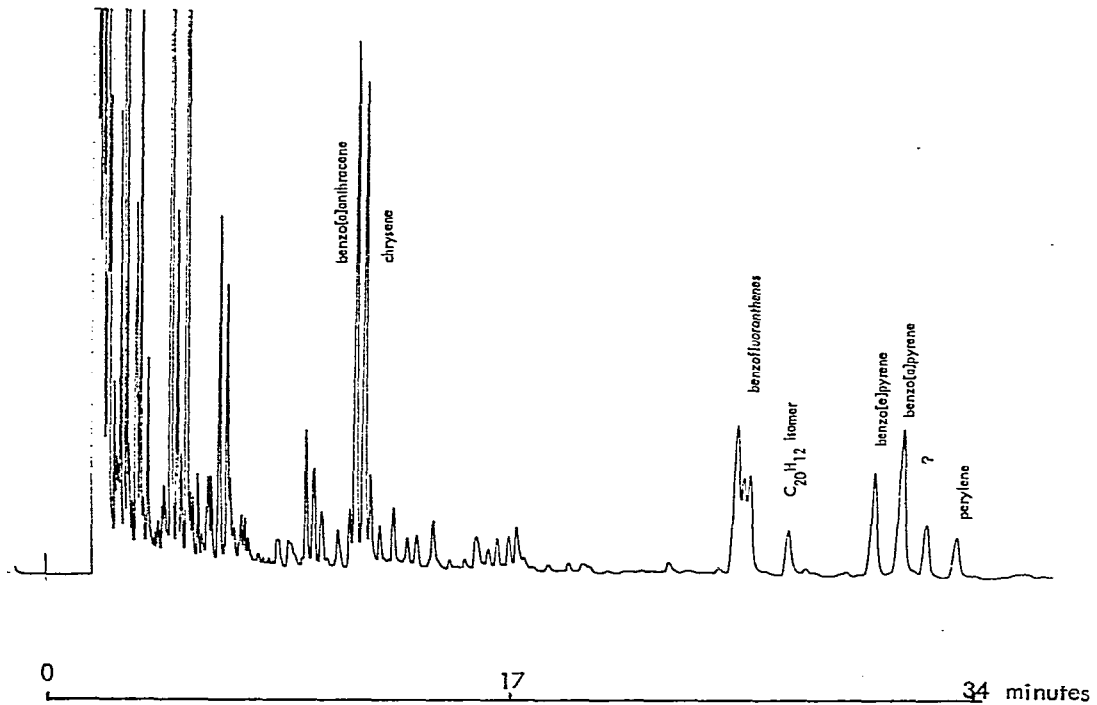
Fig. 2. Separation of coal tar (same sample as in Fig. 7). Influence of film thickness and type of carrier gas on column temperature and/or retentions. Column: SE-54, 45 m × 0.27 mm I.D. Temperature: 210°, isothermal. Carrier gas: hydrogen, 0.35 m/sec.

boiling point of about 500°) is eluted after 75 min. In practice it is a great advantage to be able to apply low column temperatures as the lifetime of the capillary column is extended. The sample capacity of such columns with very thin films of the stationary liquid is low, of course. This problem can be overcome, however, by applying an appropriate sampling technique.

Sample constituents with higher retentions have to be back-flushed from a pre-separation column by using valveless flow switching, as has been described previously[16], in order to save analysis time.

Application of the polar stationary liquid POLY S 179 in glass capillary columns up to 390°

There are very few polar stationary liquids that can be used at column temperatures above 240° for extended periods. The strongly polar Carbowax 20M seems to be stable up to 260° under special circumstances. The sulphonated polyphenyl ether POLY S 179, which was first described by Mathews *et al.*[17], is a polar stationary liquid with a much higher temperature stability. We have been able to coat glass capillary surfaces with this stationary liquid after etching with hydrogen chloride. Such columns can be used at temperatures up to 390° for a longer period. The

viscosity of this stationary liquid is very high and therefore column temperatures below 200° cannot be used without a considerable decrease in separation efficiency. Fig. 3 shows a temperature-programmed chromatogram of coal tar obtained with a POLY S 179 column.
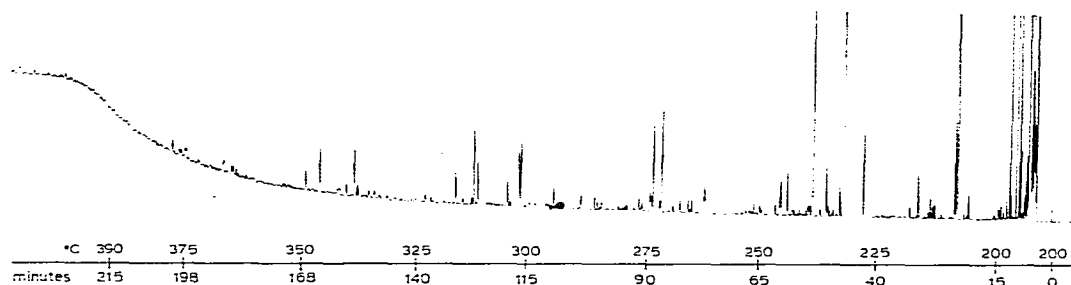

Fig. 3. Separation of coal tar. Column: POLY S 179, 90 m × 0.27 mm I.D.; alkali glass (Schott, AR), HCl etched. Temperature: 200–400° at 1°/min. Carrier gas: hydrogen, 2.3 bar, 50 cm/sec (210°) to 35 cm/sec (390°).

Influence of injector temperature and solvent volatility on the quantitative analysis of wide range mixtures containing components of very low volatility

At a given temperature of the sampling unit and of the column inlet, the volatility of the solvent plays an important role in both split and splitless sampling methods with highly diluted components. Grob[32] has found that optimal resolution can also be achieved with isothermal column operation, but only if the boiling point of the solvent is slightly higher than the column temperature. On temperature programming, these conditions can easily be achieved by selection of an appropriate initial temperature of the programme (if the required separations in the early parts of the chromatogram allow this), whereas in isothermal work the solvent that dilutes the sample has to be replaced by one with a higher boiling point. This solvent has an influence on the retention, especially of the early peaks, depending on the polarity of the solutes and solvents[6].

Moreover, the volatility of the solvent also influences the discrimination according to volatility when performing quantitative analyses of mixtures with a wide range of molecular weights and polarities of the components in both split and splitless sampling (see Fig. 4). The influence of the solvent on reliable sample introduction with respect to both resolution and accurate quantitation can be explained by trapping of the sample vapour in large amounts of condensed solvent (which mixes with the stationary liquid) in the inlet of the column itself; further, it can be assumed that, owing to explosive vaporization and aerosol formation directly after introduction of the sample into the heated injector chamber, parts of the sample may be repulsed into the carrier gas inlet lines, which may be either unheated or insufficiently heated. The less volatile constituents of the sample are then irreversibly adsorbed or their transfer into the column will be retarded. The conclusion to be drawn from the results in Fig. 4 is that overheating of injectors can be prevented if solvents of not too high a volatility are used.
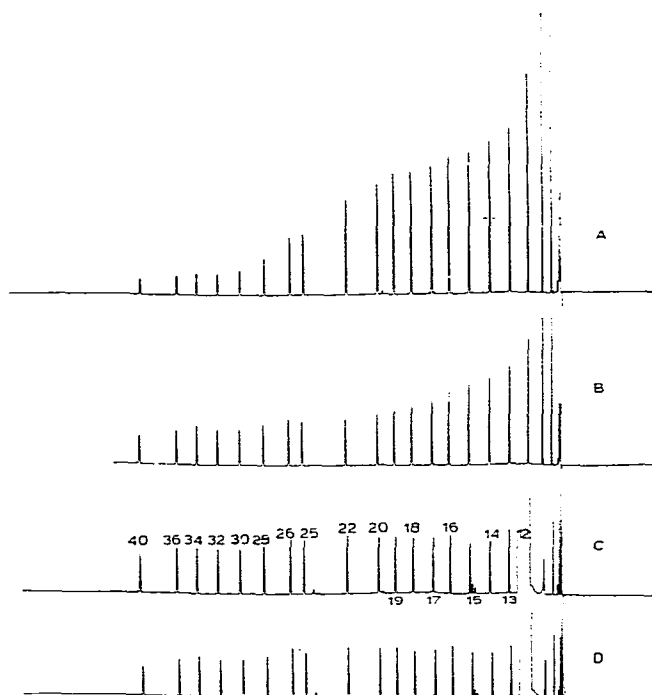
Fig. 4. Quantitative analysis of wide boiling range mixtures, instrument test for discrimination of high-molecular-weight compounds. Split sampling of C_{10}–C_{40} n-alkanes at different injector temperatures using solvents of different volatilities. Sample: 1 μl; column: OV-1, 10 $\times$ 0.27 mm I.D.; column temperature: 50–285° at 5°/min; carrier gas: hydrogen, 1 bar. Boiling points of solutes: C_{13}, 236°; C_{40}, 540°.

	Solvent	Injection temp. (°C)	Peak-area ratio (C_{13}:C_{40})	Boiling point (°C)
A	n-Octane	310	1:0.13	126
B	n-Octane	210	1:0.43	216
C	n-Dodecane	310	1:1.02	236
D	n-Dodecane	210	1:1.02	540

Investigation of temperature stability of various types of glass capillary columns coated with methylsilicones

The temperature stability of a capillary column cannot be assessed just by estimating the loss of stationary liquid by bleeding via measurement of the capacity ratios of selected standard compounds at defined temperatures of retention measurement. In addition to the quantitation of the mass flow of the bleeding products leaving the column, the following properties should not deteriorate or change substantially during extended high-temperature operation:

(a) separation efficiency in terms of number of theoretical plates per metre;

(b) status of surface deactivation for strongly polar solutes, especially when using non-polar stationary liquids (testing by tailing measurements) and irreversible adsorption of solutes at trace levels;

(c) polarity in terms of retention indices of standard compounds, as for example proposed by Rohrschneider[18] and others.

For the results reported here flame ionization was used exclusively for detection and a standardizable method for comparison of column bleeding was required. With increasing column bleeding an increase in the background signal is to be expected. With certain assumptions, a constant rate of formation of the degradation products from the stationary liquid can probably be observed at constant temperature. The amount of volatile decomposition products formed in the column per unit time depends on the stationary liquid, temperature (exponential), surface properties of the support, surface area covered by the stationary liquid and film thickness. The mass flow of bleeding products at the column outlet depends on the column length, carrier gas flow-rate and rate of formation of bleeding products (directly proportional), whereas the background signal from the FID depends on the mass flow-rate of bleeding products (directly proportional), the detector sensitivity (directly proportional) and the response of bleeding products (directly proportional).

With reference to the early studies of Novotny and Zlatkis[19], we have also qualitatively observed large differences in "bleeding" intensity, especially of methylsilicones, on comparing our glass capillary columns with those of commercial origin that had been manufactured using different methods. For the test procedure, OV-101 or SE-30 coated columns of similar length and internal diameter were preconditioned by operating for about 12 h at 280° at carrier gas flow-rates of about . 1 ml/min. We considered this temperature to be high enough for a good standard column according to the literature and our own practical experience. Beyond 260° the degradation of silicones accelerated more and more.

In some instances a substantial proportion of the total amount of stationary liquid may have been removed from the column during conditioning. Some of the columns tested by us exhibited very bad performance with regard to tailing behaviour and separation efficiency after the standardized conditioning procedure, owing to removal of a significant proportion of the stationary liquid as a result of decomposition, as could be concluded from a considerable decrease in the capacity factor of a standard compound. For columns with very small amount of stationary liquid and therefore low capacity ratios we observed decreased bleeding, which can be explained only by incompletely coated surfaces. No contribution to the bleeding can be expected from uncoated surfaces, of course. The amount of bleeding products formed per unit time is assumed to be proportional to the coated surface area. Columns containing too low amounts of stationary liquid after pre-conditioning could therefore not be considered for comparison.

In Fig. 5 the results of bleeding tests with ten different methylsilicone columns, preferably with OV-101 and SE-30 as the stationary liquid, are plotted for a temperature range between 200 and 280°. The columns had the same length of 25 m and were operated at the same carrier gas flow-rate of 1 ml/min (the bleeding does not increase proportionally with the column length and the carrier gas flow-rate). The measurement of the background signals was started at 280° and the column temperature was then decreased to 200°. A further decrease in temperature was not followed by a decrease in the background signal in most instances.

The influence of detector sensitivity on the results was eliminated by determining the peak area obtained by injection of a defined amount of a standard compound (C_{22} n-alkane (see Fig. 6). The peak areas were found to be independent of the column temperature, and therefore a constant sensitivity of the detector could
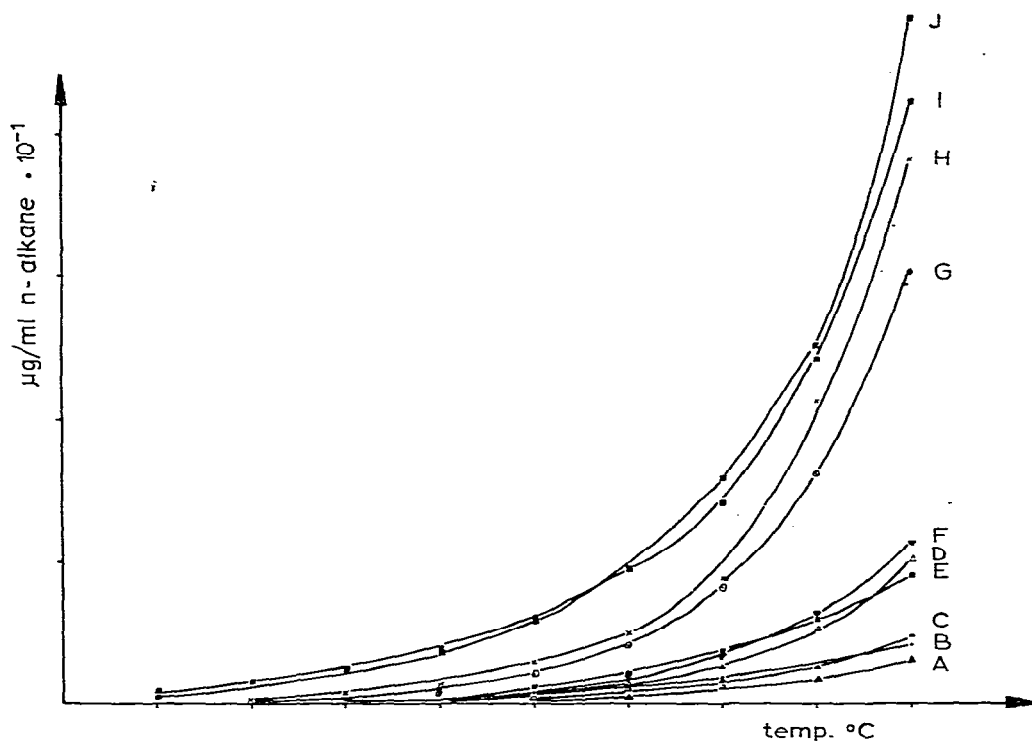
Fig. 5. Bleeding of methylsilicones OV-101 and SE-30 from alkali and borosilicate surfaces

Column	Type of glass	Pre-treatment	Stationary liquid	Origin of column
A	Borosilicate (Duran)	—	SE-30	Authors
B	Borosilicate (Pyrex)	?	OV-101	Manufacturer 1
C	Borosilicate (?)	SiO₂-depositing[20]	SE-30	Manufacturer 2
D	Alkali (Schott, AR)	HCl gas	SE-30	Manufacturer 3 — Authors
E	Borosilicate (Pyrex)	Benzenetriphenyl-phosphonium chloride	SE-30	Manufacturer 4
F	Borosilicate (Duran)	—	OV-101	Authors
G	Alkali	HCl gas + HF gas	OV-101	Authors
H	Alkali (Schott, AR)	BaCO₃ (ref. 33)	OV-101	Authors
I	Alkali (Schott, AR)	HCl gas	OV-101	Authors
J	Alkali	HCl gas + HF gas	*	Authors

* Methylphenylsiloxanes were oligomerized on the capillary surface according to the procedure described by Madani et al.[21].

All columns were pre-conditioned for 12 h at 280°. SE-30 seems to be more stable towards catalytic decomposition than OV-101, as can be seen from the bleeding curve for column D.

be assumed at least for the period of the experiment. The area of the rectangle constructed from the difference in the background signals at 200° and the adjusted test temperature and the section on the abscissa that corresponds to unit time (minutes) is proportional to the amount of decomposition products from the stationary liquid that have been eluted from the column if the response factors of these compound are known. By comparison of these areas with those of the n-alkane test
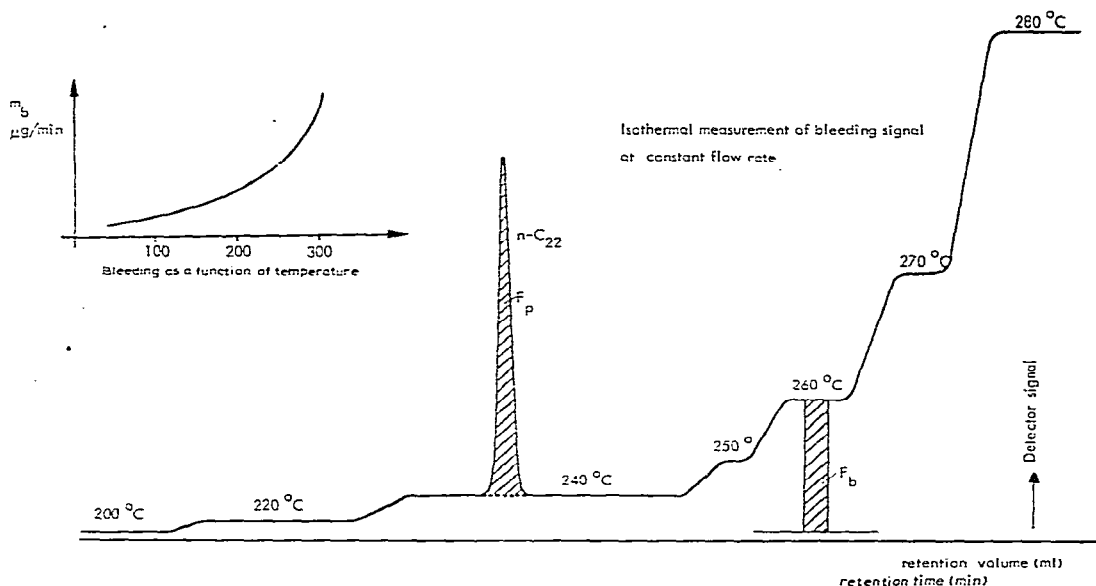
Fig. 6. Standardized bleeding test for gas chromatographic columns. Approximate determination of amount of bleeding products per millilitre of eluate by peak-area measurement with a known amount of standard n-alkane sample at defined column temperature, carrier gas flow-rate and column length. The mass of bleeding products eluted by 1 ml of carrier gas is approximately characterized by the mass of standard n-alkane, m_p, generating the same peak area as is obtained by the product of the bleeding signal and the corresponding distance on the abscissa:

$$m_b \approx \frac{F_b}{F_p} \cdot m_p$$

if the response of the bleeding products is assumed to be similar to that of the standard compound (n-alkane).

compound the loss of the stationary liquid from the column can be expressed as micrograms of n-alkane per minute if the response factors are considered to be similar, which is probably not true. Because silicon compounds have a lower FID response than hydrocarbons ($\approx 0.4 : 1$), the real loss of bleeding material is still about 2.5 times higher than the determined values standardized to the n-alkane. The standardization of the bleeding with regard to detector sensitivity for measurements in different gas chromatographs can be simplified by using a continuous feed of a volatile test hydrocarbon at a known concentration with the carrier gas. The most important conclusion from the results in Table I and the curves in Fig. 5 is that glass capillary columns made from alkali glass exhibit much greater bleeding than borosilicate (Duran) glasses. The results were roughly independent of the pre-treatment of the columns, including deactivation.

With some methods of column manufacture the alkali content of the glass surface is probably decreased. By treatment with gaseous hydrogen chloride and hydrogen fluoride, alkali metal and alkaline earth metal oxides (Na_2O, K_2O, BaO, CaO) are converted into the corresponding halides, whereas on pre-treatment with hydrochloric acid the metal oxides are removed from the columns. A decrease in the alkali

TABLE I

BLEEDING OF OV-101 (METHYLSILICONE) FROM ALKALI AND BOROSILICATE GLASS SURFACES: INFLUENCE OF BARIUM CARBONATE ON BLEEDING

Columns (25 m × 0.27 mm I.D.): A, alkali glass, untreated surface coated with 0.6% solution of stationary liquid using the static method; B, borosilicate glass, untreated, coated using dynamic mercury plug method; C, alkali glass, coated after $BaCO_3$ deposition and previous etching with hydrochloric acid, mercury plug method; D, borosilicate glass coated with a suspension of $BaCO_3$ in stationary liquid, mercury plug method. Carrier gas: nitrogen (1 ml/min) during all experiments. k = capacity ratios of n-C_{11} at 80°; n = number of theoretical plates; b = bleeding (micrograms of n-alkane per millilitre × 10^{-1}).

	A*			B*			C*			D*		
	k	n	b	k	n	b	k	n	b	k	n	b
Before conditioning	6.8	67,000	—	10.9	55,600	—	9.0	50,000	—	10.1	69,900	—
3 h, 280°	7.1	62,000	—	10.0	59,000	—	7.1	47,700	—	11.9	50,100	—
12 h, 280°	4.6	50,600	2.02	11.0	55,400	0.16	2.7	35,900	3,60	5.5	44,200	2.3

* A: Bleeding more than 10 times as high as with column B, although the content of stationary liquid in column A was lower. k decreased considerably because of strong bleeding during pre-conditioning. B: Lower bleeding than columns A, C and D; no decrease in k on pre-conditioning. C: Increased bleeding compared with column A, strong decrease in k because of bleeding. D: Very strong bleeding compared with column B, similar bleeding as column A, $BaCO_3$ seems to increase methylsilicone decomposition. With all four columns a certain decrease in separation efficiency was observed, probably owing to dehomogenization of films.

(Na_2O) content on the surface decreases the catalytic decomposition of methylsilicones. The catalytic activity of sodium chloride and also of barium carbonate[12] deposited from suspension or precipitated from solutions, respectively, is under investigation. Preliminary results on the influence of barium carbonate are given in Table I and are discussed below. Both alkali and borosilicate glasses contain alkali metal oxides, the latter glasses containing about 4% and alkali glasses up to three times as much. Duran columns show very low bleeding even if the methylsilicone film is deposited on the unpre-treated surface. Therefore, it has to be assumed that the low contents of alkali are chemically incorporated in the boroalumina silicate lattice in a different manner to the large amounts of alkali in soft glass which does not contain alumina. Deposition of silica[20] on the borosilicate glass surface does not increase the bleeding. Further, it has still to be investigated whether commercial methylsilicones exhibit a varying temperature stability. We found that some commercial methylsilicones (SE-30 and OV-1) exhibit a much lower degradability at elevated temperatures and/or on alkali catalysis than other silicone products.

The procedure of generating methylphenylsilicones *in situ*, i.e., on the inner walls of the glass capillary proposed by Madani et al.[21], does not lead to a higher temperature stability of the column if alkali glass is used (see curve J in Fig. 5). The temperature stability of the Madani-type columns may be caused by the choice of borosilicate glass only.

A higher temperature stability of these phases has also been observed by Novotny and Zlatkis[19]. By special treatment of the silicones, the Si–OH end-groups or siloxane rings could have been removed in order to increase the stability. It is known that the degradation of silicone chains catalysed by alkali begins from the Si–OH end-groups.

The much higher temperature stability of silicones on borosilicate glass surfaces (Table I, Figs. 5, 7 and 8) may also be explained by a certain deactivating effect of boric acid. Investigations on these questions and also more detailed work on the thermal decomposition of various methylsilicones by alkali catalysis and on the influence of surface deactivation on decomposition are currently being undertaken.

The catalytic activity of soda-lime glass on the decomposition of methyl-silicones can be explained by the high alkali content of this type of glass. In pre-liminary experiments alkali-coated Duran columns also showed a higher activity and therefore strong bleeding.

On using the common surface pre-treatment procedures, especially using gaseous and/or aqueous hydrogen chloride (hydrogen fluoride) the catalytic activity of the surfaces for the decomposition of silicones is slightly decreased but not completely removed. Barium carbonate layers[12] do not decrease the bleeding from alkali glass columns, whereas from borosilicate columns the bleeding is increased (see Table I). In none of our experiments did we observe an improvement in temperature stability on treatment with barium carbonate. The main effect of the deposition of barium carbonate on column performance is therefore an improvement in film fixation by surface roughening preferably for polar stationary liquids. Alkali and borosilicate glass surfaces can also be deactivated without previous treatments, such as etching with hydrogen chloride or deposition of barium carbonate by the usual methods such as heating to 280° with Carbowax, Emulphor-O, Pluronics[22], methyl-silicones[23], triethanolamine[13] and benzyltriphenylphosphonium chloride[24, 34]. On Carbowax- or triethanolamine-deactivated surfaces stable films can be generated (without etching with hydrogen chloride or deposition of barium carbonate) but the coating of the column by either the static or the dynamic method is less reliable. The deactivations are generally not stable at temperatures above about 250°.

Stable films of so-called "gum" phases (methyl- and phenylsilicones) can be generated on untreated glass surfaces of both types without difficulty. Such columns can be used successfully for the separation of polynuclear aromatic hydrocarbons but the nitrogen-containing compounds quinoline and isoquinoline, which have about the same basicity as aniline, show tailing.

In the chromatograms in Figs. 7, 8 and 9, coal tar was separated using two different columns containing SE-54 silicone on alkali glass (Fig. 9) and borosilicate glass (Figs. 7 and 8). From the chromatograms in Fig. 7 and 8 the advantage of the use of hydrogen as the carrier gas in comparison with nitrogen, with respect to lower retention temperatures, especially for the less volatile polyaromatic hydrocarbons such as coronene, can be seen.

In Fig. 10 the natural wax esters of the *Cistus* plant were separated using a very temperature stable OV-1 borosilicate column. The deactivation of the glass surface was effected simply by heating the coated column to above 300°. The high-molecular-weight esters (the structures of peaks 1 and 2 were determined by GC–MS) were not decomposed at temperatures above 300°, which commonly occurs with undeactivated glass surfaces, preferably when using thin films of stationary liquid.

Improved film stability on borosilicate glasses cannot be achieved by etching with hydrogen chloride as easily as with alkali glass (because of its low alkali content). The following methods have to be used: deposition of barium carbonate[12],
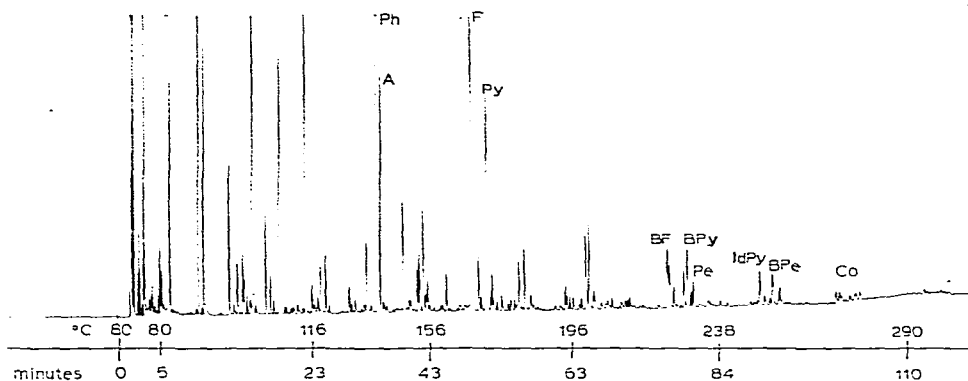
Fig. 7. Separation of coal tar. Bleeding of SE-54 on borosilicate glass (Schott, Duran). Influence of hydrogen carrier gas on retention temperatures. Column: 45 m × 0.27 mm I.D. Temperature: 80–290° at 2°/min. Carrier gas: hydrogen (0.35 m/sec) at 290° (optimum for separation efficiency). Peaks: Ph = phenanthrene; A = anthracene; F = fluoranthene; Py = pyrene; BA = benz[a]-anthracene; Ch = chrysene; BF = benzofluoranthenes; BPy = benzopyrenes; Pe = perylene; IdPy = indeno[1,2,3-cd]pyrene; BPe = benzo[ghi]perylene; Co = coronene.
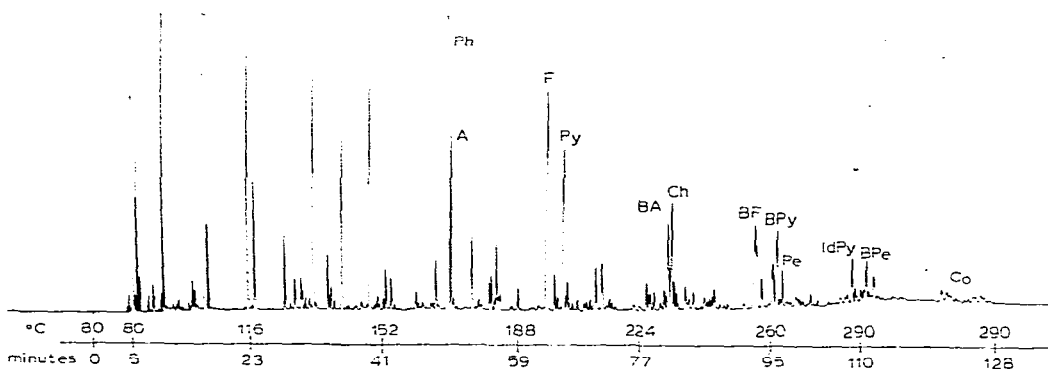

Fig. 8. Separation of coal tar (same sample as in Fig. 7). Bleeding of SE-54 on borosilicate glass (Schott, Duran). Influence of nitrogen carrier gas on retention temperatures. Column: 45 m × 0.27 mm I.D. Temperature: 80–290° at 2°/min. Carrier gas: nitrogen (0.12 m/sec) at 290° (optimum for separation efficiency). Peaks as in Fig. 7.

deposition of silica[20,25–27], deposition of sodium chloride[28,29] or the use of silica whiskers[13,30,31], but Sandra and Verzele[13] consider that whisker surfaces are not so suitable for non-polar silicone columns. The latter surfaces, of course, require repeated deactivation. These types of column have not yet been investigated in detail with regard to bleeding. It remains to be elucidated especially whether layers can be produced that are catalytically inactive and cover the active glass surfaces perfectly so that no contribution of the glass surface to bleeding is observed. In our degradation experiments we also tested the columns for separation efficiency, tailing behaviour and decomposition of methyl stearate. Hydrogen chloride-treated alkali glass showed an especially strong adsorption or tailing of methyl stearate, whereas after treatment with hydrogen fluoride this adsorption was no longer observed. On borosilicate surfaces no adsorption and only minor tailing of the methyl stearate occurred.
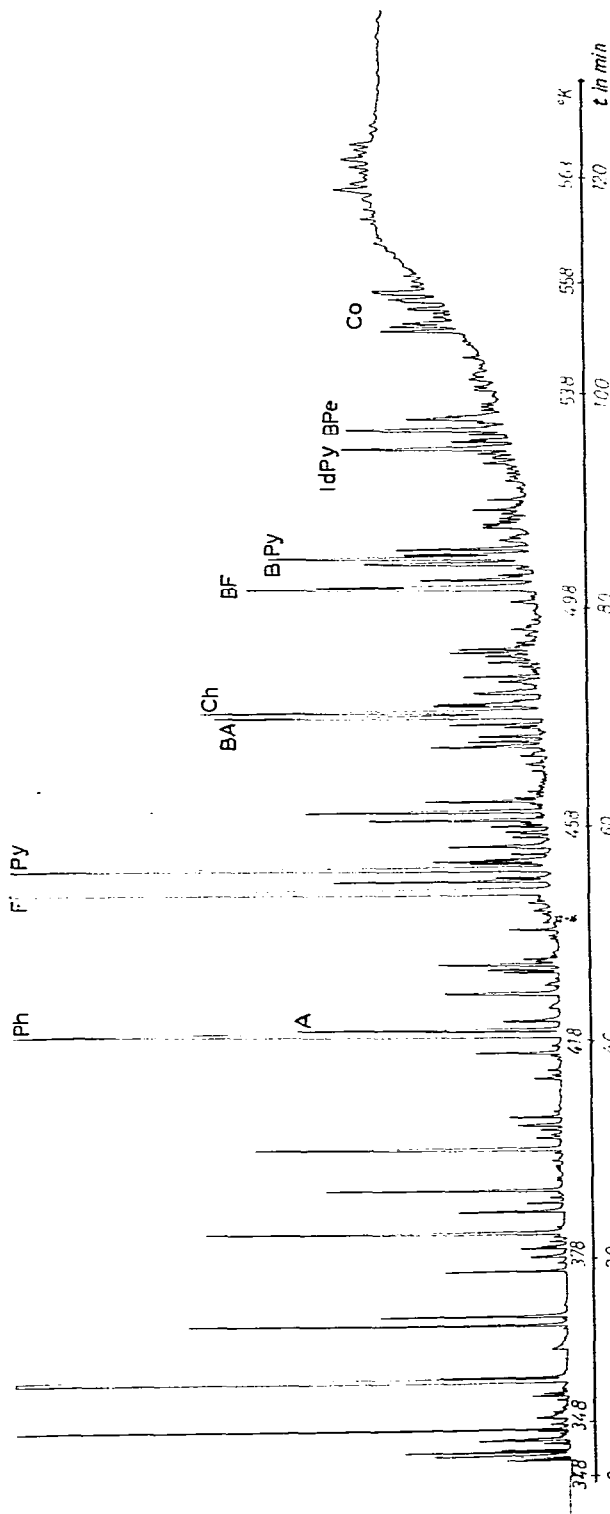
Fig. 9. Separation of coal tar (same sample as in Fig. 7). Bleeding of SE-54 on alkali glass (Schott AR). Column: 45 m × 0.27 mm I.D. Temperature: 80–290° at 2°/min. Carrier gas: hydrogen (0.35 m/sec) at 290° (optimum for separation efficiency). Peaks as in Fig. 7.
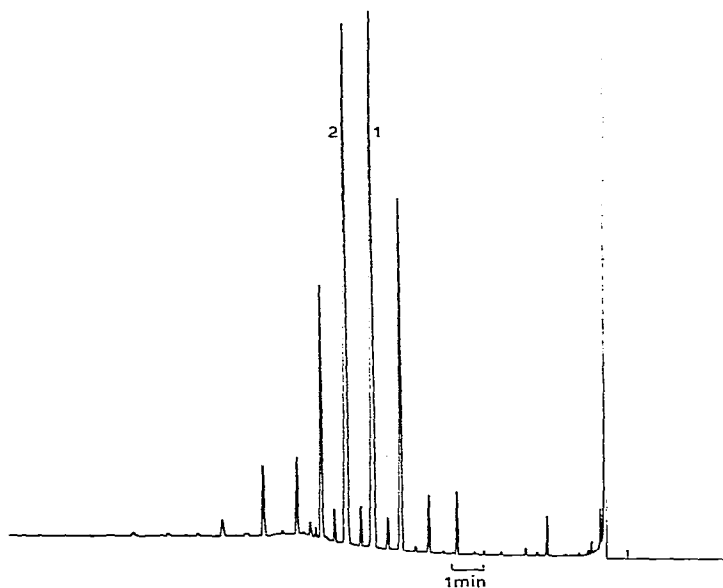
Fig. 10. Separation of wax esters of *Cistus* plant (Sample by courtesy of Dr. P. G. Gülz, Botanical Institute, University of Cologne). Column: OV-1 (20 m × 0.27 mm I.D.). Temperature: 250–350° at 10°/min. Carrier gas: hydrogen (1.5 bar). Main components: 1 = $C_{22}H_{45}$–O–C–$C_{21}H_{43}$; 2 = $C_{22}H_{45}$–O–C–$C_{23}H_{47}$.

For more detailed studies concerning the catalytic activity of glass surfaces for different kinds of solute molecules, more sophisticated polarity mixtures must be applied, such as that proposed recently by Grob[35], which also contains compounds such as aldehydes and free carboxylic acids that undergo adsorption and/or reactions with active sites on the various surfaces.

We shall report our results on the decomposition of polar stationary liquids on different types of glass and on differently treated or deactivated surfaces in the near future.

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