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Activity testing and surface characterization of pretreated fused-silica capillaries for gas chromatography

A new modification of existing intermediate column tests☆

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ABSTRACT

A new modification of existing intermediate capillary column tests for uncoated columns is presented. A short (1 m), thick film (2 μm) precolumn is coupled to the column to be tested. The use of a short precolumn results in a rapid test. This makes it attractive in terms of time to inject the test compounds separately, thus excluding mutual influences, in diluted solutions spiked with *n*-alkanes as references. Moreover, the short precolumn gives sharp Gaussian injection profiles on the second column. A simple versatile coupling device has been developed, which permits easy control and adjustment of pressures and carrier flows, monitoring of the effluents of the precolumn and introduction of sharp input bands on the second column. The monitor detector accurately shows the shape and time of introduction of the compounds on the second column. This permits the evaluation of peak distortion, peak shift and yield on the second column. Test compounds were selected on the basis of their physico-chemical properties (vapour pressure, acid–base properties, dipole moments, hydrogen bonding, complexation with metals, etc.). A number of differently pretreated capillaries were tested with these compounds under various external conditions. Accurate quantification and qualification of the activity of the capillary present difficulties. The test is a case of nearly ideal non-linear chromatography. When peaks of different sizes are superimposed, the tails lie on a common envelope. The k' of the end of the tail is fixed, irrespective of the amount injected, and forms an important parameter in the evaluation. Reconstruction of the chromatogram with a k' scale instead of a time scale eliminates the influence of carrier velocity and column length. The method is a sensitive tool for intermediate column testing and shows promises for surface characterization.

INTRODUCTION

For a number of years this laboratory has been studying the mechanisms of deactivation reactions for fused-silica capillary columns using fume silica as a model material and ^{29}Si magic angle spinning NMR [1–5]. The use of a model material is inevitable as hardly any spectroscopic or surface analysis method is available to study the interior of a capillary column. However carefully the situation inside a capillary column was imitated, the results were obtained under artificial conditions and the application of the NMR results to fused-silica columns remains conjectural. It is therefore important that this relationship is established more clearly.

Gas chromatography (GC) is an excellent method for studying the adsorptive properties of small surface areas [6], such as the internal surface of a capillary column. Present test methods for capillary columns, however, focus on the general analytical performance rather than on the surface activity and do not provide specific information. It is attractive to develop existing column tests further in this respect.

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Column tests

Ideally, any compound that can be volatilized without decomposition should be amenable to GC analysis. In practice, however, the shape, area and position of a peak are often affected by adsorption (reversible physisorption or irreversible chemisorption) and by decomposition or transformation of the analyte. A column test should be able to reveal the exact nature and extent of this activity. For general use tests should be standardized and universal, and the results should be expressed in numerical form.

In tests for adsorption a number of polar compounds are injected, either separately or as a mixture. The Grob "comprehensive quality test" [7,8] is well documented and standardized and generally applicable to a wide range of columns. A severer test was introduced by Lee and co-workers [9,10]: two mixtures of test probes were used, one containing basic compounds and the other acidic compounds.

Tests for catalytic activity [11–15] are based on the decomposition of labile compounds. The choice of the probes seems fairly accidental: the various workers used compounds which happened to cause problems in their regular analytical work. Chromatographic determination of the decomposition rate constant of a labile compound [12–14] gives an very valuable, absolute measure of catalytic activity.

Testing an uncoated column is another attractive option: (i) the pretreatment can be studied without the interfering effects of the stationary phase, (ii) the test can be performed at lower temperatures and (iii) much time can be saved because the lengthy coating procedure can be omitted. It is therefore very suitable as an intermediate test between pretreatment and coating. The introduction of the test probes presents difficulties: because of the lack of a stationary phase one cannot inject a mixture of test probes or diluted solutions. Undiluted test probes can be injected at high splitting ratio [16] or headspace vapour of the test probe [17,18] at normal splitting ratios. Schomburg *et al.* [19] placed a coated column before the uncoated column. Thus, injection of diluted solutions or of full test mixtures [20–24] is possible.

Silica surface and choice of the test probes

In order to be informative, the behaviour of the test probes must reflect the state of the fused-silica surface. The surface of silica is characterized by two types of surface groups: siloxanes (≡Si–O–Si≡) a silanols [≡SiOH or $=Si(OH)_2$]. The silanols relatively acidic and constitute the strongest adso tion sites. Their acidity, concentration and closen may change their adsorptive properties considerat On a fully hydroxylated silica the OH concentrat is about 8.2 μmol/m^2 [25], a quarter of which fc part of a $=Si(OH)_2$ [26]. About half of all hydro are close enough (<3.1 Å) to form a mut hydrogen bond. These "bonded" hydroxyl gro are less adsorptive [27,28] and on heating they ea split off water, forming strained, active siloxar Fused-silica columns, which are drawn at ab 1900°C, are largely dehydroxylated and cont only 0.31 μmol OH/m^2 [29]. Rehydroxylation c dehydroxylated silica surface is possible, but it slow process. Standard procedures have been p lished [30]. Rehydroxylation, *e.g.*, by hydrothen treatment, is common in capillary column prepa tion [31].

The probes should therefore be sensitive to hydroxylation, the acidity, the catalytic activity a the metal impurities of the surface. Monofunctio sterically unhindered probes preclude ambigu results. However, on a chemically modified surfa steric hindrance of the functional group may useful to study the accessibility of remaining adsc tive sites.

To test the polarity of the surface, probes wit large permanent dipole moment can be used, sucl amides, nitro compounds, nitriles and sulphoxi Few or none of these have been used in capill column tests. Polar interactions between molec are now often formulated as donor–acceptor Lewis acid–base interactions rather than dip interactions [32], and this concept has been app to glass and silica [33].

Aldehydes and ketones are useful probes hydrogen bonding [22–24]. The hydrogen b capacities of silanol groups can also be studied v alcohols. Alcohols are good probes for "fr silanols, but they adsorb less at "bonded" or hydrated silanols. Alcohols also interact with sil ane bridges, especially strained ones. It was dem strated [34] that this type of interaction, which r lead to chemisorption, is even the preferred on low coverages. As the surface of a fused-si capillary column is largely dehydroxylated, s (chemi)sorption of alcohols is probably import

To probe the surface acidity, organic bases are commonly used: strong bases (using the pK_a value in water as an indication of basicity) such as primary alkylamines (10.5–10.8)[a], aromatic nitrogen compounds such as pyridine, picolines and lutidines (5.25–7.0) and aromatic amines such as aniline, toluidines and xylidines (3.9–5.2). Alkaloids (pK_a 8–9) can be used to fill the gap between pK_a 7 and 10, *e.g.*, nicotine (8.0), but alkaloids are usually not monofunctional and may not give unequivocal results. In a (Lewis) acid–base scheme of test probes ketones, esters, (cyclic) ethers, (cyclic) sulphides, amides, nitriles, aromatic hydrocarbons, etc., must also be considered as bases.

Basic sites on the surface (which are not likely to occur on fused silica) can be probed with organic acids. Carboxylic acids (pK_a 4.7–4.9) are often used. Lower pK_a values are met with α-chlorocarboxylic acids. Unfortunately, carboxylic acids readily cause overloading problems on the precolumn. Phenol, cresols and xylenols are only weak acids (pK_a 9.9–10.6). Chloro- and nitro-substituted phenols have lower pK_a values (7.1–9.2), but also high boiling points. In an acid–base scheme of test probes, aliphatic and aromatic nitro compounds, alcohols and chloroform must also be considered as acids.

In high-purity fused silica, the total metal oxide content is less than 1 ppm, but in less pure qualities it may mount to 100 ppm. Liquid chromatographic packings have been tested for transition metals using metal-complexing probes such as diketones, sulphides, 2,2′-bipyridine and thiols [36]. Such probes have not been used in capillary GC.

Choice of test conditions

Judicious choice of the GC conditions contributes to standardization. The most important variables are carrier velocity and temperature.

Carrier velocity cannot be varied as easily as temperature. As a rule, most GC analyses are executed at velocities near or above the optimum velocity and so are column tests. The use of the optimum velocity minimizes dispersion effects, so that peak broadening due to adsorption processes is clearly visible.

Temperature markedly influences column activity: at high temperatures reversible adsorption decreases whereas catalytic decomposition increases [37]. Most tests for adsorption use moderate temperatures of 60–100°C. Following the practice of static adsorption measurements, the saturated vapour pressure of a test probe could be used as an indicator of the temperature of the test or, conversely, having fixed a temperature, for the selection of the test probes. In the Grob comprehensive test the programming rate is carefully adjusted to the column length in order to maintain constant elution temperatures. The figures we found in a particular case (see Table I) suggest a standardization to a vapour pressure of 1–5 mmHg. In our experience, vapour pressures up to 10 mmHg can still be used in isothermal tests. Many familiar test probes such as decylamine, phenol, octanol, nonanal and 2,3-butanediol have vapour pressures of 5–10 mmHg at 60–100°C. Injection of the probes with a splitter presents no problems at this range of temperatures and vapour pressures.

We prefer isothermal test conditions to programmed temperature conditions. In isothermal operation parameters such as carrier flow, temperature and column dimensions are independent of each other, whereas in a programmed run they are intertwined with each other in a complicated manner. An isothermal test allows (i) easier adaptation of the conditions to a wide range of column dimensions, (ii) severer conditions matching the activity of

TABLE I

ELUTION TEMPERATURES OF A GROB TEST

Column: 7 m × 0.32 mm I.D., deactivated PS-122, 0.14 μm SE-54.

Test probe	Elution temperature (°C)	Corresponding vapour pressure (mmHg)
2,3-Butanediol	43.6	1.0
n-Decane	53.6	9.2
n-Octanol	60.5	1.8
n-Undecane	63.3	6.3
Nonanal	63.6[a]	5.1
2,6-Dimethylphenol	63.6[a]	2.1
2-Ethylhexanoic acid	68.7	0.6
2,6-Dimethylanaline	69.9	4.3
Methyl caprate	92.1	4.7
Dicyclohexylamine	101.0	4.9
Methyl laurate	117.6	4.9

[a] Co-elution.

[a] pK_a values taken from ref. 35.

the column, (iii) fundamental interpretation of surface–probe interactions and (iv) studies of chemisorption or catalytic activity.

Precolumn and coupling device

Isothermal conditions limit the choice of probes to those having about the same vapour pressure at the selected temperature of the test. This hampers the formulation of comprehensive mixtures, because probes with about the same vapour pressure will probably co-elute on apolar columns.

If one uses a short, thick-film precolumn, just long enough to separate the test probe from the solvent and a pair of *n*-alkane standards, a test run takes little time. A selected number of test probes can be injected separately in the same time otherwise required to chromatograph a comprehensive mixture. One may fix the vapour pressure and adjust the temperature for each, separately injected, probe. Moreover, a thick-film column usually shows good elution profiles and permits large amounts to be injected.

A straight connection of the precolumn and test column is not attractive: to obtain reference chromatogram of the precolumn it must be disconnected and fed directly into the detector. It is much more convenient to divert part of the effluent from the precolumn permanently to a monitor detector. This permits detailed study of the effect that the second column has on the peak shape, peak area and retention. Moreover, if the columns are connected directly to each other, the carrier flows in the columns cannot be adjusted independently. A coupling device should permit (i) independent control of carrier flows, (ii) monitoring of the precolumn and (iii) easy exchange of the columns to be tested.

A commercial two-dimensional double-oven chromatograph has been used to good purpose in the intermediate test [23,24]. The use of two ovens is especially advantageous. However, its coupling device has been designed for two-dimensional chromatography with quantitative transfer and "live" switching without monitoring. Consequently, it requires careful adjustment of carrier and purge flows. Therefore, we developed a simple, versatile coupling device, which allows easy adjustment of flows and easy and frequent exchange of a wide range of the test columns.

Evaluation

Standard column tests rarely offer procedures for accurate quantification of column activity. Chromatograms obtained from an "intermediate" test of an uncoated column usually show very pronounced effects of peak shift and skew, which have a strong visual impact. On closer examination, however, accurate quantitative and qualitative evaluation of the results presents difficulties: peak position, width and tailing vary considerably with the amount injected. A test of an uncoated capillary column is a case of nearly ideal, non-linear gas–solid chromatography: the dispersion by the capillary being negligible, peak shape and peak position are determined solely by the form of the adsorption isotherm. Methods are available, although not common practice in capillary GC, to determine the adsorption isotherm from the shape of the peak [6,38].

Extreme tailing of a peak is an indication of heterogeneity of the sites. Heterogeneity of the surface hampers the application of peak-shape parameters derived from simple adsorption models [39,40]. Surface heterogeneity can also be studied by GC, resulting in adsorption energy distribution functions of the sites [41,42]. This has been used in the definition of a surface selectivity triangle representing acidic, basic and dipolar interactions [43,44]. Another approach to determining heterogeneity of the sites is "gas-phase titration" in which the most active sites are blocked with a known amount of an amine [45].

Inverse gas chromatography (IGC) has also been used in the study of modified silicas [24,46]. IGC requiring symmetrical elution profiles uses probes at infinite dilution and studies mainly dispersion (London) or weak polar interactions at near-zero coverage.

In this paper, however, only simple parameters based on the shift, tailing and area of the peak will be considered in relation to chromatographic conditions such as temperature, carrier flow and column dimensions.

EXPERIMENTAL

Materials and equipment

The coupling device (Fig. 1a) consists of a quartz glass tube (5 cm × 2 mm I.D. × 4 mm O.D.) deactivated with PS 122 [a poly(methylhydrosilox-

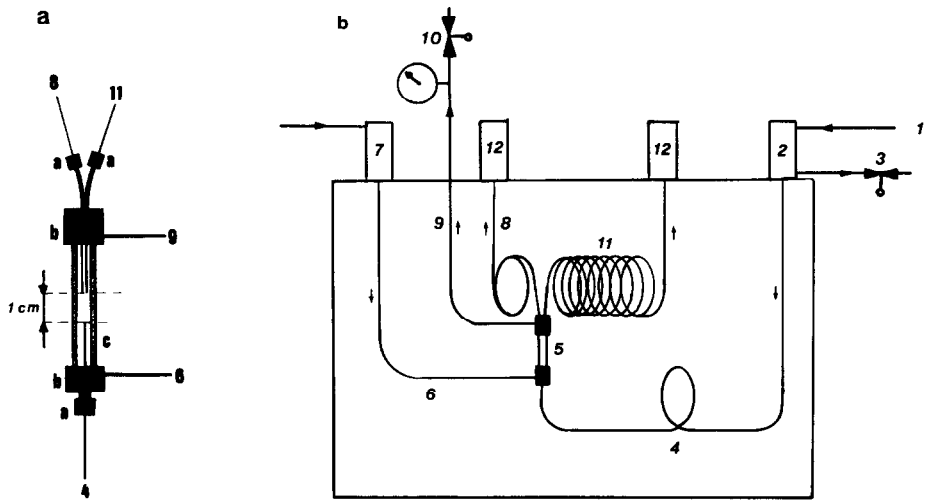

Fig. 1. (a) Coupling device and (b) arrangement for testing. Identification (for dimensions see text): 1 = carrier in (He); 2 = injector (splitter); 3 = split vent valve; 4 = precolumn; 5 = coupling device; 6 = purge gas line; 7 = second injector supplying purge gas; 8 = monitor line; 9 = vent line; 10 = needle valve and manometer; 11 = test column; 12 = flame ionization detector. a, 1/16-in. Swagelok connector; b, 4-mm coupling; c, quartz tube.

ane); Petrarch Systems, Bristol, PA, USA]. Couplings are fixed to the quartz tube with nuts and polyimide ferrules. One carries a soldered purge gas line and a 1/16-in. Swagelok connector for the precolumn, and the other one a soldered vent line and two soldered metal capillaries (2 cm × 1 mm O.D. × 0.5 mm I.D.) provided with 1/16-in. Swagelok connectors for monitor line and test column. These capillaries greatly facilitate alignment and exchange of the test column. Precolumn, monitor line and test column are positioned to a mutual distance of 1 cm. Control of carrier flow in the second column can be obtained by addition of purge gas and/or venting. This also allows the introduction of very small amounts on the second column (as a result of splitting in the device) and sharp input bands (by using high carrier velocities in the first column).

The coupling device was mounted in a Mega 5300 gas chromatograph (Carlo Erba, Milan, Italy) equipped with two flame ionization detectors and a conventional splitter injector (Fig. 1b). A second injector supplied the purge gas. The precolumn was 1.1 m × 0.31 mm I.D. with 2-μm chemically bonded 100% methylsilicone (CP-Sil 5 CB; Chrompack, Middelburg, Netherlands). The monitor line was 0.25 m × 84 μm I.D. fused-silica tubing (Siemens, Karlsruhe, Germany) deactivated with PS 122, following the same procedure as for column E (see *Columns*).

Chromatograms were evaluated and stored on disk with a PE-Nelson 2100 integration system in the dual-channel mode (PE-Nelson Systems, Cupertino, CA, USA).

Test probes

The probe substances were dissolved in carefully redistilled analytical-reagent grade cyclohexane (E. Merck, Darmstadt, Germany) at concentrations of about 20 and 2 mg/ml. For some polar substances dichloromethane or tetrahydrofuran had to be used as solvents. Each probe is accompanied by four *n*-alkanes, which surround the peak in the chromatogram. Table II gives an overview of the compounds and some physico-chemical properties pertaining to the test.

Columns

To explore the possibilities of the system, five fused-silica capillary columns were pretreated in different ways (see Table III).

Column A was used as received and not pretreated.

Column B was hydrothermally treated: at 100°C deionized water from a Milli-Q system (Millipore, Bedford, MA, USA) was forced through the column

TABLE II

TEST PROBES

Compound	Concentration, 2% solution (mg/ml)[a]	Alkanes added Carbon numbers				Temperature (°C)[b]				pK_a (25°C)[c]
						5 mmHg	10 mmHg	20 mmHg	760 mmHg	
Nonanal	20.40	9	10	12	13	58.4	71.6	85.0	185.0	
p-Tolualdehyde	(3.98)	9	10	12	13	67.6[d]	81.4	96.3	204–205	
Caprylonitrile	20.49	9	10	12	13	68.2[e]	81.8	96.5	206.9	
Pelargononitrile	20.77	10	11	13	14	83.2[e]	97.0	112.2	226.6	
p-Toluonitrile	19.84	9	10	12	13	71.3	85.8	101.7	217.6	
Phenol	20.44	8	9	11	12	62.5	73.8	86.0	181.9	9.89 (20°C)
Valeric acid	19.84	7	8	10	11	67.7	79.8	93.1	184.4	4.82
2-Chloropropionic acid	20.38	8	9	11	12	68.5[d]	80.3	93.3	184–187	2.83 (18°C)
p-Toluidine	20.13	8	9	11	12	68.2	81.8	95.8	200.4	5.08
Heptanol	20.32	8	9	11	12	64.3	74.7	85.8	175.8	
1,2-Propanediol	21.40[f]	6	7	9	10	70.8	83.2	96.4	188.2	
1,3-Propanediol	21.70[g]		7	9	10	87.1	100.6	115.5	214.2	
2,3-Butanediol	19.96[f]		7	9	10	68.4	80.3	93.4	182.8	
1,2-Pentanediol	19.36[f]	7	8	10	11	88.6[d]	101.0	114.4	206–210	
Octanethiol	20.21	9	10	12	13	63.3[d]	77.0	91.8	199.1	
p-Thiocresol	20.73	9	10	12	13	57.7[d]	71.5	86.5	194–195	8.03[h]
Nitrobenzene	19.86	9	10	12	13	71.6	84.9	99.3	210.6	3.98 (0°C)
3-Butylpyridine	20.54	10	11	13	14	72.4[d]	85.8	100.4	205–208	5.72–5.75[i]
Quinoline	19.76	11	12	14	15	89.6	103.8	119.8	237.7	4.90 (20°C)
Nonylamine	20.16	10	11	13	14	66.7[j]	97.0	112.1	220.5	10.64
Decylamine	20.21	11	12	14	15	83.0[j]	97.0	112.1	220.5	10.64
1,7-Diaminoheptane	20.61	10	11	13	14	85.0[d]	98.7	113.7	223–225	11.86, 10.76[k]

[a] 0.2% Solution made by tenfold dilution of a 2% solution.
[b] Data from ref. 47.
[c] pK_a values from ref. 35.
[d] Data from *Beilstein*, fitted according to Hass and Newton in ref. 35, p. D-186.
[e] Interpolated from ref. 48.
[f] Solvent dichloromethane.
[g] Solvent of 2% solution tetrahydrofuran is 0.2% solution dichloromethane.
[h] Data from ref. 49.
[i] Estimated from 3-methyl- and 3-ethylpyridine (*Beilstein*).
[j] Interpolated from ref. 50.
[k] $pK_{a,2}$ and $pK_{a,1}$ values, respectively, of 1,6-diaminohexane (*Beilstein*).

TABLE III

COLUMN TREATMENTS

Column	Supplier	Length (m)	I.D. (mm)	Treatment
A	Siemens	14	0.32	None
B	Siemens	14	0.32	Hydration: water (flow), 100°C, 5 h Drying: vacuum, 90°C, overnight
C	Polymicro	14	0.32	Acid leach: 10% HCl, 150°C, 1 h Drying: helium flow, 200°C, 2 h
D	Polymicro	14	0.32	Hydration: as for B Deactivation: D4, 390°C, 4 h + 405°C, 2 h
E	Polymicro	7	0.32	Half of column C (acid leached) Deactivation: PS 122, *ca.* 40 nm, 290°C, 2 h

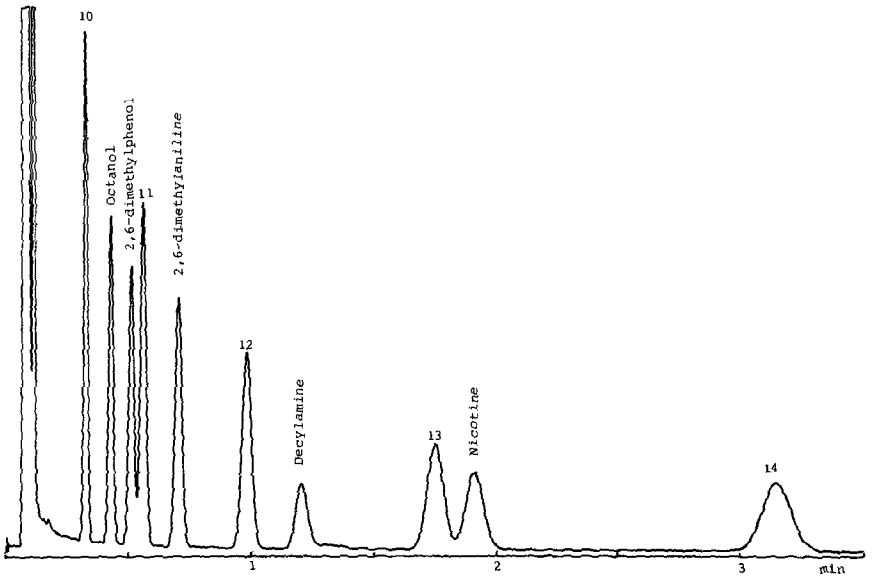

Fig. 2. Polarity mixture on the precolumn (recording of the monitor detector). Peak identification as in Fig. 3a.

at a rate of 0.2 ml/min for 5 h. Then the column was dried under vacuum at 90°C overnight.

Column C was treated with acid: 90% of the column was filled with 10% (w/w) hydrochloric acid (Merck Suprapur), flame sealed at both ends and heated at 150°C for 2 h. Then the column was opened, rinsed with deionized water and dried at 200°C for 2 h under a helium flow.

Column D was hydrothermally treated as described for B, and then deactivated with octamethylcyclotetrasiloxane (D4) (ABCR, Karlsruhe, Germany). The column was coated dynamically with pure D4 at a rate of 1 cm/s using nitrogen pressure. After coating, the column was purged for a few minutes with nitrogen, flame sealed and heated in a nitrogen atmosphere at 390°C for 4 h followed by 405°C for 2 h. Then, the column was rinsed with *n*-pentane and dried.

Column E was half of column C and was deactivated with polymethylhydrosiloxane (PMHS): the column was coated dynamically with a 2% (w/w) solution of PS 122 (Petrarch) in *n*-pentane at a rate of 1 cm/s. According to Bartle [51], this results in a film thickness of *ca.* 40 nm[a]. After coating, the column was flushed with nitrogen for 30 min, flame sealed and heated at 290°C for 2 h. Then the column was opened, rinsed copiously with *n*-pentane and dichloromethane and dried.

Performance of the system

Operation of the system and testing procedure. The inertness and performance of the system were checked by injection of a polarity mixture (Fig. 2). All critical compounds (octanol, decylamine, nicotine) show symmetrical peak shapes and correct peak areas.

As a rule, the following procedure was adopted: for each test probe two chromatograms were recorded, injecting 1 μl of the 2% and 0.2% solutions. Depending on the activity of the column, the oven was set to a temperature at which the saturated vapour pressure of the test probe was 5, 10 or 20 mmHg (in rare cases 1 or 40 mmHg). The temperature of the injector was set to the boiling point of the test probe. The mean carrier velocity of the test column was adjusted to about 40 cm/s and the carrier velocity of the precolumn was regulated in such a way that the last *n*-alkane eluted within 5–10 min. The splitting ratios of the precolumn injector and the coupling piece were both adjusted to about 1:40, resulting in an overall splitting ratio of about 1:1600. Injection of 1 μl of the 0.2% and 2% solutions then results in column loads of 2 and 20 ng,

[a] Assumed viscosity $1.8 \cdot 10^{-3}$ kg/ms, surface tension $2.5 \cdot 10^{-2}$ N/m.

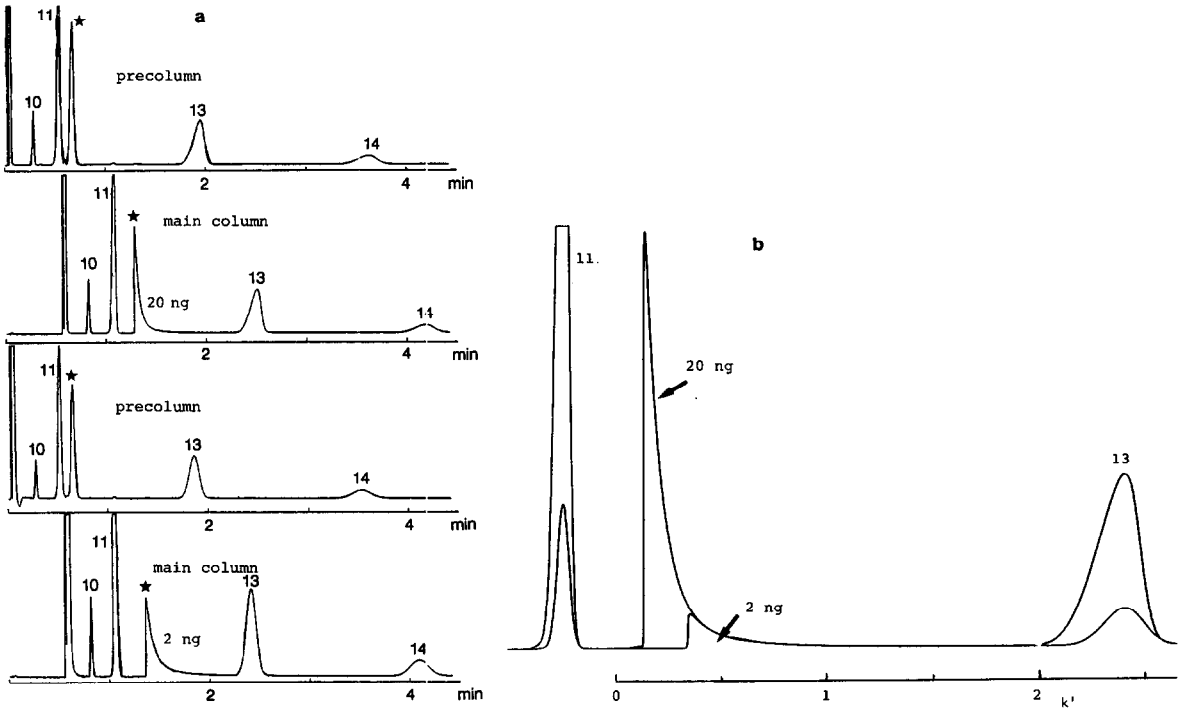

Fig. 3. (a) Operation of the system (nonylamine on column D, 94°C, 20 mmHg). Column load: upper pair of chromatograms, 720 (precolumn) and 20 ng (test column); lower pair of chromatograms, 72 ng (precolumn) and 2.0 ng (test column). Peak identification: t test probe is marked with an asterisk and *n*-alkanes are indicated with their number of carbon atoms. (b) Superimposed nonylamine pea in (a) (capacity factor scale relates to nonylamine); peak identification as in (a).

respectively (accounting for evaporation of an additional 0.4 μl from the needle). Fig. 3a and Table IV give a typical example of the operation of the system,

TABLE IV

EXAMPLE OF FLOWS AND VENTS (SEE FIG. 3a)

Column D, 94°C, normalized flows (20°C, 1 atm). Numbers in parentheses refer to items in Fig. 1.

Parameter	Value
Precolumn inlet pressure (2)	54 kPa (gauge)
Split vent, injector (3)	133 ml/min
Precolumn flow (4)	3.4 ml/min
Splitting ratio, injector	1:39
Coupling piece pressure (5)	39 kPa (gauge)
Purge gas flow (6)	65 ml/min
Monitor line flow (8)	0.5 ml/min
Vent, coupling piece (9)	66 ml/min
Test column flow (11)	1.85 ml/min
Splitting ratio, coupling piece	1:36
Overall splitting ratio	1:1400

using column D and nonylamine as a test probe

Selection of the amount to be injected. On compa ison of the injections of the 0.2% and 2% solutior notable differences in peak shift and peak shape a observed. Fig. 4a gives an example with toluonitri on column B. However, if the chromatograms a superimposed, it turns out that the tails of the pea coincide (Figs. 3b and 4b). It appears that this is case of almost ideal non-linear gas–solid chrom tography with a concave adsorption isotherm (t wards the c_g axis) without inflection points. T capacity factor k'_f of the front edge depends on t loading factor L_f[a] [40]. Consequently, the retenti time of the peak top or the front edge cannot be us as a parameter. However, it is advisable to inje several concentration levels of the test probe in ord to obtain an idea of the loadability and the numb of active sites of the test column. The end of t

[a] L_f is defined as the ratio of the sample amount to the amoun sample required to saturate the column.

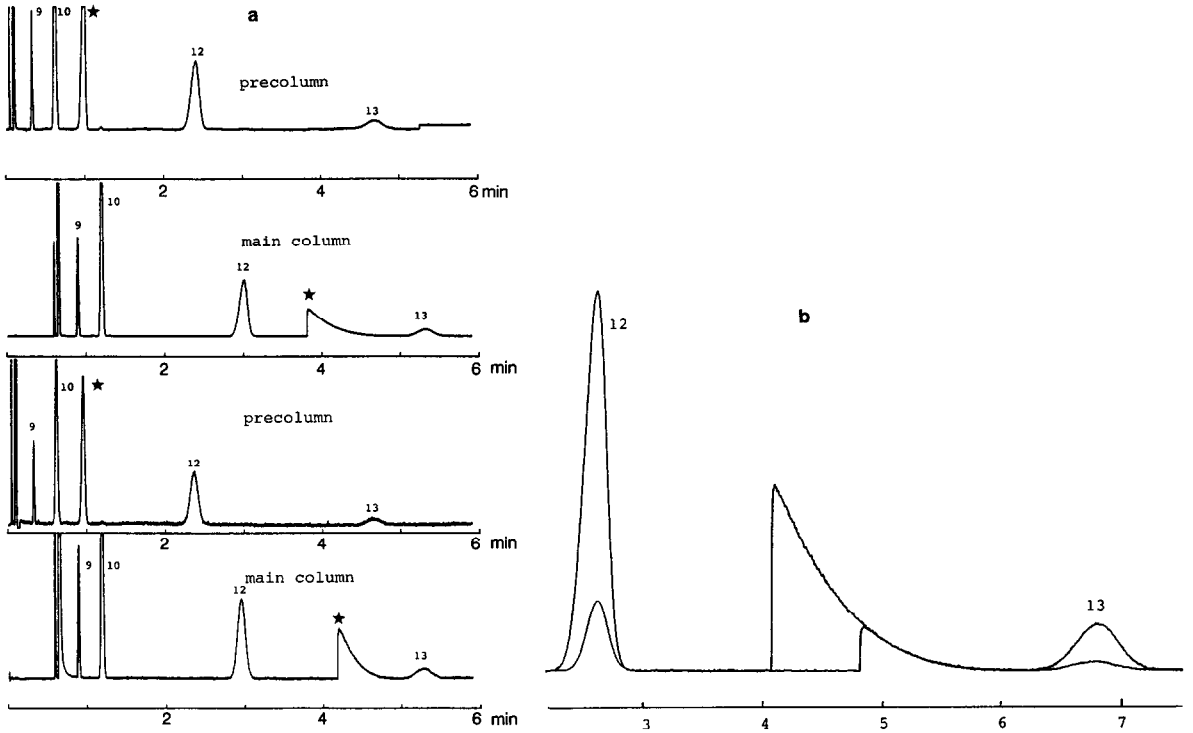

Fig. 4. (a) Influence of amount on peak shape and peak position (toluonitrile on column B, 86°C, 10 mmHg). Column load: upper pair of chromatograms, 660 ng (precolumn) and 14 ng (test column); lower pair of chromatograms, 77 ng (precolumn) and 1.6 ng (test column). Peak identification as in Fig. 3a. (b) Superimposed toluonitrile peaks in (a) (capacity factor scale relates to toluonitrile).

peak, in contrast, is fixed: its capacity factor k'_0 depends on the initial slope of the adsorption isotherm. The toluonitrile peaks (Fig. 4b), for instance, end at $k'_0 = 6.1$, but the ends of the nonylamine peaks (Fig. 3b) are lost in the elongated tail and cannot be determined exactly.

Appearance of the chromatogram and selection of carrier flows. The appearance of the chromatogram may be misleading: shift and tailing of a peak should not be judged at a glance. Especially the carrier flow of the precolumn affects the chromatogram strongly. Fig. 5a (caprylonitrile on column C) gives a typical example: when the carrier velocity was increased from 12.5 to 42 cm/s, the caprylonitrile peak shifted from a position between C_{10} and C_{12} to a position between C_{12} and C_{13} and the width of the tail was doubled relative to the widths of the *n*-alkane peaks. However, if we reconstruct these chromatograms with a k' axis instead of a real-time axis, the peaks almost coincide (Fig. 5b).

Quantitative aspects. The yield (Y_i) of a test probe can be defined as the ratio of the amount that enters the test column and the amount that elutes from it. Assuming that the coupling device splits all compounds in the same proportions between vent, monitor line and test column, Y_i can be calculated from the peak areas (A):

$$Y_i = (A_{i,p}/A_{i,t})/(A_{s,p}/A_{s,t})$$

where the subscript p refers to the precolumn, t to the test column, i to the test probe and s to a non-adsorbed standard, *e.g.*, an *n*-alkane. We found that for the four *n*-alkanes in the test chromatograms the ratio $A_{s,p}/A_{s,t}$ generally followed a smooth trend. Interpolating between these values to obtain a "local" value for $A_{s,p}/A_{s,t}$, it turned out that in the great majority of cases Y_i was within 90–110%. Deviations usually resulted from incorrect integration because of excessive tailing by which the last part of the peak was lost in the noise, drift and wander of the baseline. This lost area is a crude but not particularly accurate parameter for tailing.

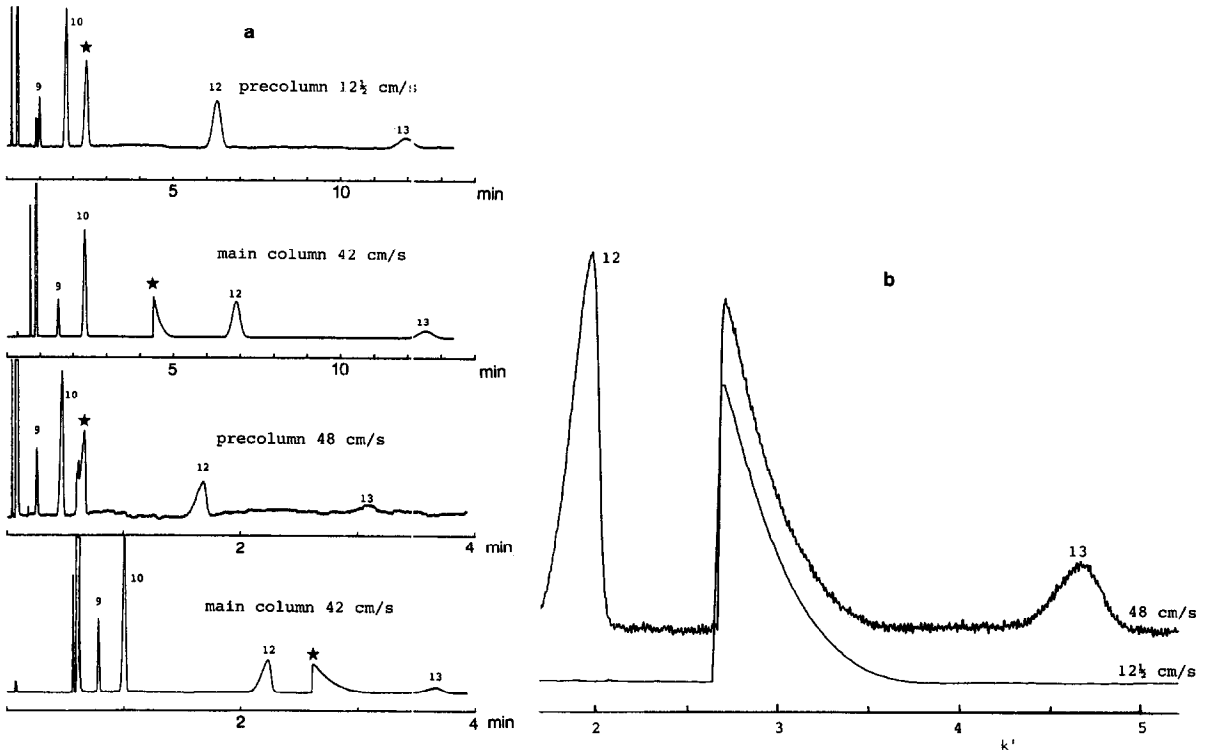

Fig. 5. (a) Influence of carrier velocity of the precolumn on general appearance of the chromatogram (caprylonitrile on column C, 94°C, 20 mmHg). Peak identification as in Fig. 3a. (b) Caprylonitrile peaks in (a) superimposed on a k' scale (scale relates to caprylonitrile).

Moreover, real losses by decomposition may remain unnoticed.

RESULTS AND DISCUSSION

The chromatograms produced by the system under various operating conditions vary greatly. Standardized chromatographic conditions are therefore necessary. However, this is not always feasible and therefore it is important to ascertain the consistency of the results obtained under various conditions of temperature, flow, length of the test column, etc.

Moreover, to achieve efficient use of time, only a limited number of test probes matching the (expected) activity of the column should be injected. To that end, the set of test probes should be ordered according to adsorptive properties, regarding vapour pressure, acidity–basicity, dipole moment, etc.

Influence of vapour pressure

The possible use of the saturated vapour pressure (p^0) as a selection criterion was considered. To investigate the influence of vapour pressure on peak shape, nonanal was injected on column A at temperatures of 57.4, 71.8, 85.4 and 100.2°C, corresponding to vapour pressures of 5, 10, 20 and 40 mmHg, respectively (Fig. 6). At vapour pressures of 5, 10 and 20 mmHg the nonanal peaks have sharp front edges and distinct ends. The k'_0 values are 10.68, 3.28 and 1.34, respectively. Linear regression of $\ln k'_0$ *vs.* $1/T$ shows a correlation coefficient of 0.999. The peak widths from front edge to end of tail, expressed in k' units (w_b/t_m) decrease: 3.50, 0.91 and 0.28, respectively. At 40 mmHg, the nonanal peak has no sharp front edge, although the peak is still tailing.

We also checked whether members of a homologous series gave similar peak shapes when injected at the same vapour pressure. Caprylonitrile ($C_7H_{15}CN$) and pelargononitrile ($C_8H_{17}CN$) were injected on column A at vapour pressures of 5, 10 and 20 mmHg (Fig. 7). Table V lists the end times, $t_{R,0}$, and the widths, w_b, of the peaks. Linear regression of $\ln (k'_0)$ *vs.* $1/T$ gave correlation coeffi-

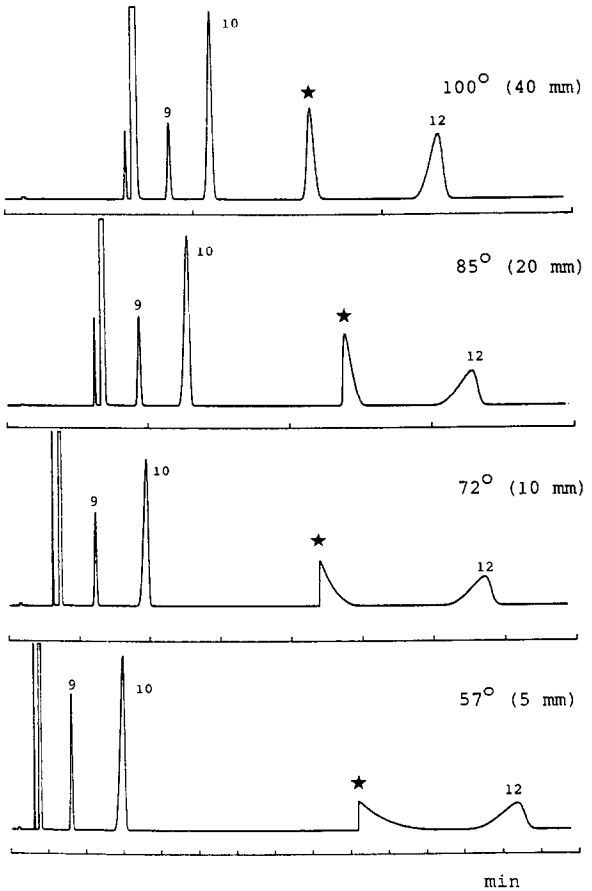

Fig. 6. Influence of vapour pressure on peak shape and peak position (nonanal on column A). Peak identification as in Fig. 3a.

cients of 0.99999. At corresponding vapour pressures, k'_0 and w_b/t_m of the peaks are of the same order of magnitude. It seems that within a limited range of temperatures and alkyl chain lengths, injection at corresponding vapour pressures gives roughly comparable results.

Influence of carrier velocity on peak shape

If the test is indeed a case of ideal non-linear chromatography, the velocity of the carrier gas should have no influence on peak shape and peak position, provided that the kinetics of adsorption and desorption are fast.

To check this, caprylonitrile was injected at 95°C (p^0 20 mmHg) on column C at mean linear velocities of 9.9, 20.7, 41.9, 81.3 and 119.0 cm/s (Fig. 8a). The chromatograms were stored on disk and reconstructed with a k' axis (Fig. 8b). At further enlargement the peaks showed distinct ends at nearly the same k' value (mean k'_0 3.71 $\pm$ 0.09). The tails have the same shape and almost coincide. The front edges, however, do not do so because the load on the test column was not strictly controlled.

The results obtained indicate that the linear velocity of the carrier gas has no influence on the position of the end and the shape of the tail of the peak over a wide range of values.

Influence of length of test column

Often, columns that have to be tested are of different length. To permit comparison of such columns with each other, the influence of column length on peak shape and peak position must be established. In a study on the necessary length of the test column [21], it was observed that reduction of the length resulted in gradually better and, ultimately, symmetrical peak shapes. However, such a gradual improvement is at variance with the theory of ideal non-linear GC. Therefore, we carried out a similar experiment under isothermal conditions and controlled carrier gas velocities.

Caprylonitrile was injected at 80°C (p^0 10 mmHg) on to pieces of 13.40, 6.85, 3.40 and 1.70 m lengths taken from column C. Inlet pressures were set so as to give for each piece (theoretically) the same linear outlet velocity (about 49 cm/s). The existing split vent settings resulted in column loads of about 0.6–1.1 ng. The chromatograms were recorded on disk and plotted with a k' axis (Fig. 9a). At further enlargement the peaks show distinct ends. At short lengths the determination of the retention time on the test column becomes inaccurate, because the travelling time through the monitor line can no longer be neglected. Calculations of k'_0 resulted in values varying from 12.3 to 13.9. To make visual comparison easier, the ends of the peaks in Fig. 9b were aligned by shifting the k' axes. The tails of the peaks have similar shapes, whereas the tops and fronts elute at different k' values. The elution profile of caprylonitrile on the 1.7-m column is different: its front edge is less sharp and it is rounded at the top. This column is of insufficient length to complete the transformation of the Gaussian input profile to the "adsorption GC profile". On the basis of these results, it can be concluded that column length

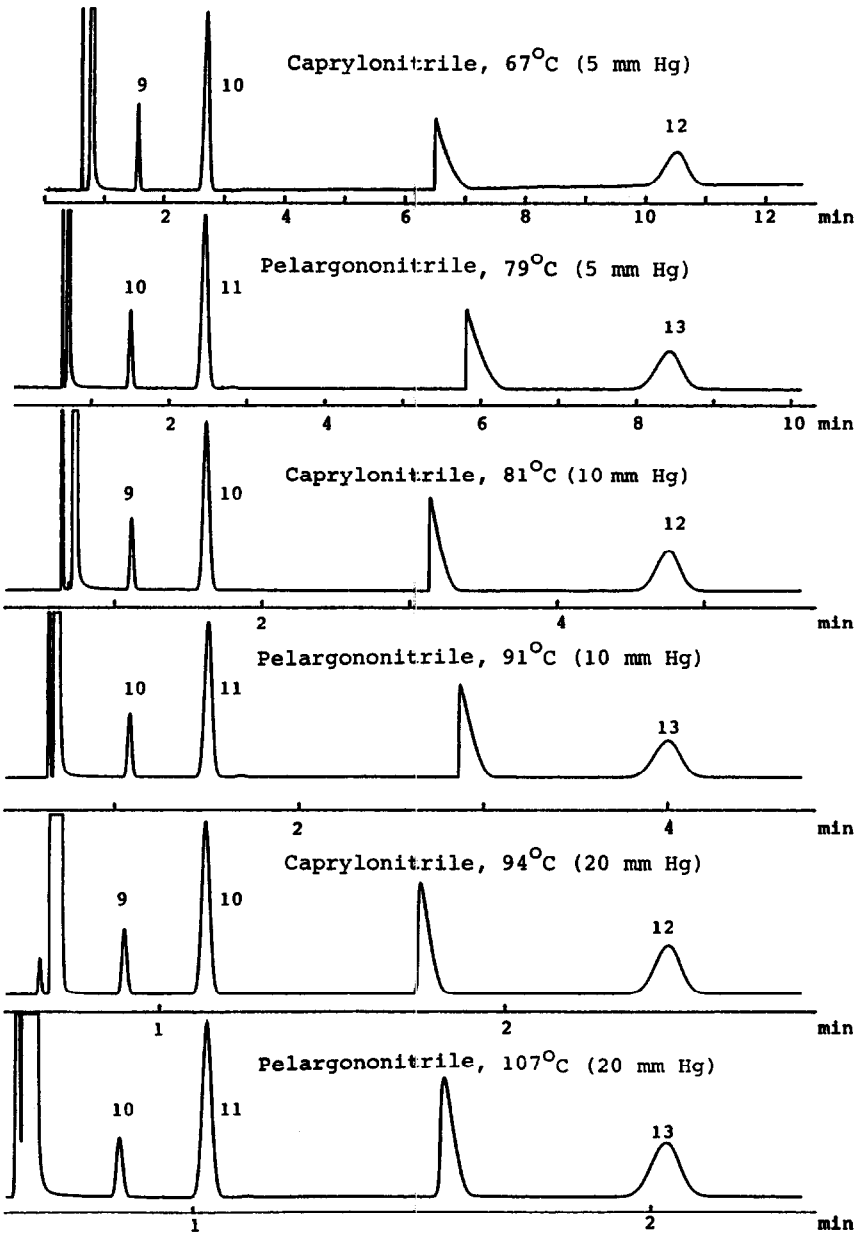

Fig. 7. Influence of vapour pressure and alkyl chain length on peak shape and peak position (column A). Peak identification as in Fig. 3a.

generally has no influence on peak shape and peak position. However, a certain length of column is required to produce the typical profile with its tail and front edge.

Some idea of the necessary length, L_{req}, can be obtained from the following approximation: at the front of the Gaussian input band, the low concentrations, travelling more slowly, are gradually overtaken by the high concentrations. Thus, a steep, self-sharpening front edge is formed. Finally, the top overtakes the front edge and the typical profile emerges. At the rear, the low concentrations lag

TABLE V

INFLUENCE OF SATURATED VAPOUR PRESSURE AND ALKYL CHAIN LENGTH ON PEAK END AND PEAK WIDTH

Caprylonitrile (7-CN) and pelargononitrile (8-CN), column A.

p^0 (mmHg)	Temperature (°C)	Test probe	$t_{R,0}$ (s)	k'_0	w_b (s)	w_b/t_M
5	67.3	7-CN	250	6.24	33.7	0.98
	79.2	8-CN	227	5.51	29.0	0.83
10	80.5	7-CN	118	2.32	11.7	0.33
	91.4	8-CN	113	2.08	10.5	0.29
20	94.3	7-CN	70.3	0.88	4.80	0.13
	106.9	8-CN	68.1	0.78	4.71	0.12

behind and the typical tail is formed. Let k'_0 now be the capacity factor for the zero concentration, k'_t that for the concentration at the top of the profile, $w_{in} = 4\sigma_{in}$ the width at the base of the input peak, $w_{out} = t_m(k'_0 - k'_t)$ the width at the base of the transformed peak and u_m the linear velocity of the carrier gas. Then, the base of the peak moves with a velocity $u_m/(1 + k'_0)$ and its top, lagging 0.5 w_{in} behind at the entrance of the test column, with $u_m/(1 + k'_t)$. The top would then overtake the base at time $0.5\, w_{in}(1 + k'_0)/(k'_0 - k'_t)$. The corresponding distance, which is the necessary length L_{req}, is

$$L_{req} = 0.5\, w_{in} u_m/(k'_0 - k'_t) = 0.5\, L(w_{in}/w_{out})$$

The necessary length therefore depends on the ratio of inlet and outlet band width. The outlet band width is determined by the carrier velocity and the difference in capacity factor between the top and end of the peak, which in turn is correlated to the curvature of the adsorption isotherm, the number and activity of the adsorption sites and the surface area of column.

Summarizing, high carrier velocities, weak adsorption, little curvature of the adsorption isotherm and small-diameter columns increase the necessary

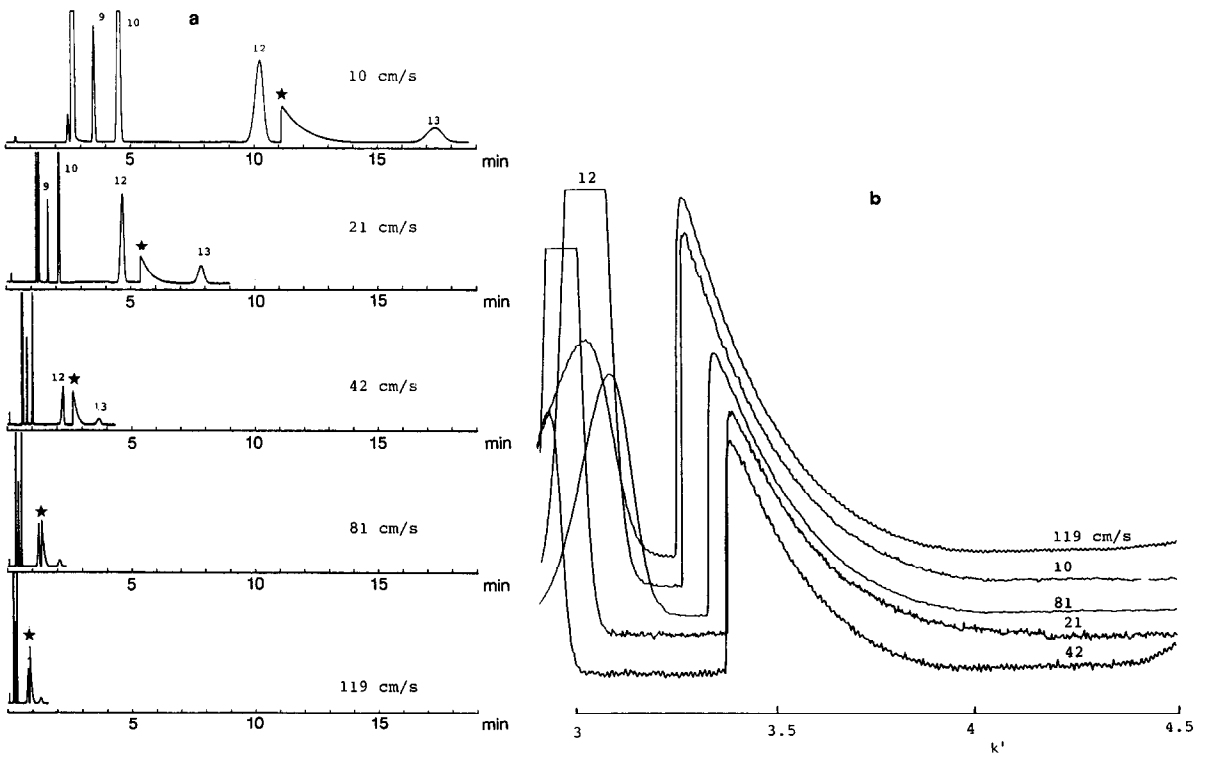

Fig. 8. (a) Influence of carrier velocity on peak shape and peak position (caprylonitrile on column C, 95°C, 20 mmHg). Peak identification as in Fig. 3a. (b) Caprylonitrile peaks in (a) superimposed on a k' scale (scale relates to caprylonitrile).

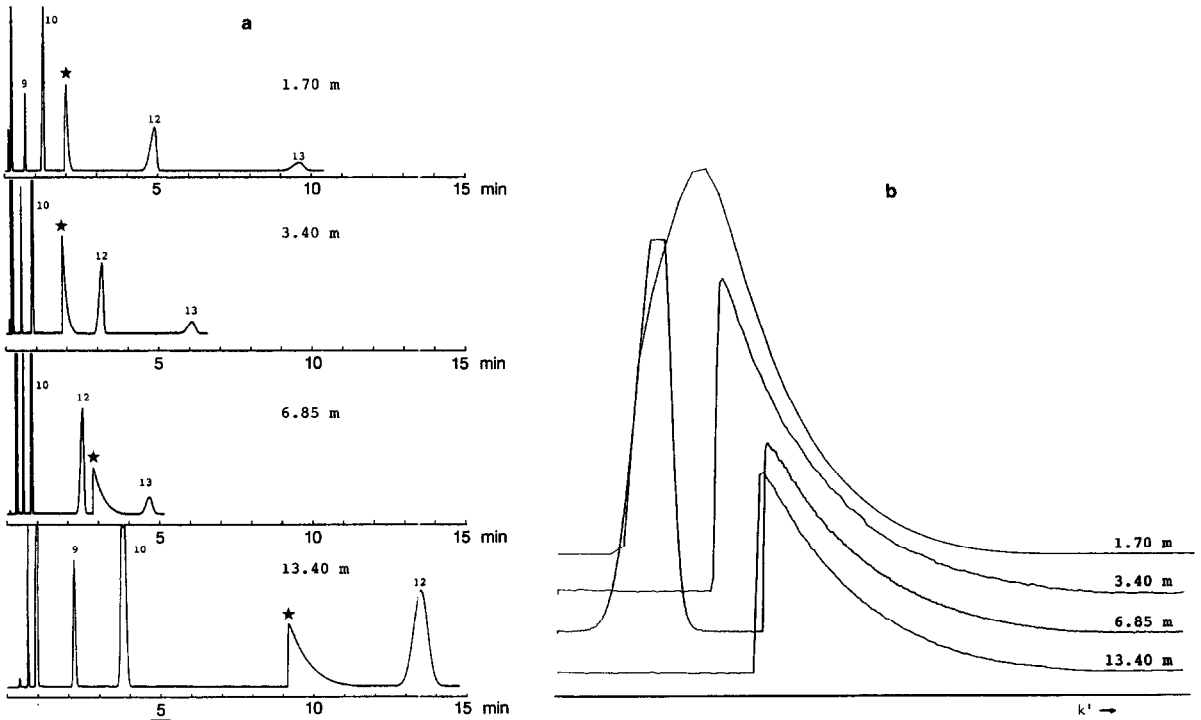

Fig. 9. (a) Influence of test column length on peak shape and peak position (caprylonitrile on column C, 79°C, 10 mmHg). Peak identification as in Fig. 3a. (b) Caprylonitrile peaks in (a) superimposed on a k' scale.

length of the test column. In an evaluation of column activity, these factors must be taken into consideration against the length of the column. Fortunately, the coupling device permits manipulation of the ratio w_{in}/w_{out} by varying the carrier flows in the precolumn and the test column.

Behaviour of test compounds

A broad variety of compounds were tried for use as test probes (Table II): aliphatic and aromatic nitriles, aldehydes, amines and thiols, aliphatic alcohols, diols, diamines and carboxylic acids, phenols and N-heterocyclics.

On the basis of their tailing behaviour, the probes were divisible into two main groups. One group consisted of alcohols, amines, phenols and carboxylic acids. These compounds are characterized by a hydrogen in their polar group. They showed a very curved tail which returned only asymptotically to the baseline. This is indicative of a very heterogeneous adsorption mechanism. Also, when small amounts were injected the peaks remained tailing and tended to be lost in the noise.

The other group consisted of nitriles, aldehydes and nitro compounds. These more weakly adsorbing compounds have no hydrogen atom in their polar group. They showed a more triangular peak shape with a distinct end of the tail. This is indicative of more homogeneous adsorption. When small amounts were injected the peaks became symmetrical and were not lost in the noise.

As a rule aromatic nitriles, aldehydes, amines and thiols adsorbed less than the corresponding aliphatic compounds. Probing the surface for metal ions with aliphatic or aromatic thiols was without result: a test with fused-silica can dispense with the use of thiols. Part of the test probes could be ordered according to strength of adsorption: nitrogen bases > aldehydes > nitriles > nitro compounds > thiols. Hydroxyl-containing probes could not be fitted in with this sequence. Within the group of nitrogen bases, ordering according to pK_a is possible (see next section).

The columns received treatments which are not likely to change the chemical nature of the surface considerably. It remains essentially acidic in nature,

only the concentration of silanol groups changes. Accordingly, the use of acidic test probes (carboxylic acids, phenols, alcohols, diols) was inconclusive. Moreover, carboxylic acids and diols were easily overloaded on the apolar precolumn. Alcohols are common probes for surface hydroxyl groups. In practice, their behaviour towards changes in the silanol concentration was not very pronounced. Possibly adsorbed water from the carrier plays a role here.

The use of bifunctional probes (diamines, diols) is questionable. The peak shifts and peak shapes of mono- and diamines were very similar when plotted with a k' axis (see next section). Lower diols (propanediol, butanediol) showed stronger adsorption than monofunctional alcohols. However, their vapour pressures, especially those of the α,ω-diols, are aberrant from those of monofunctional alcohols. Also, they showed very low retention on the apolar precolumn. For these compounds the saturated vapour pressure proved to be an incorrect selection criterion.

Organic N-bases as test probes

Basic test probes are appropriate indicators of the activity of the silica surface. As an example, the use of organic nitrogen compounds will be considered (Fig. 10). k'_0 cannot be given exactly here, as these test probes did not show a clearly marked end of the tail. Instead, the time where k' of the test probe is zero is marked with △, and a round figure of k' near the end of the tail is marked with ▽.

The behaviour of *p*-toluidine, quinoline and 3-butylpyridine on column A at temperatures corresponding to a vapour pressure of 10 mmHg is shown in Fig. 10a. Peak tailing and peak shift tend to increase with increasing pK_a value, but aromaticity also plays a role here.

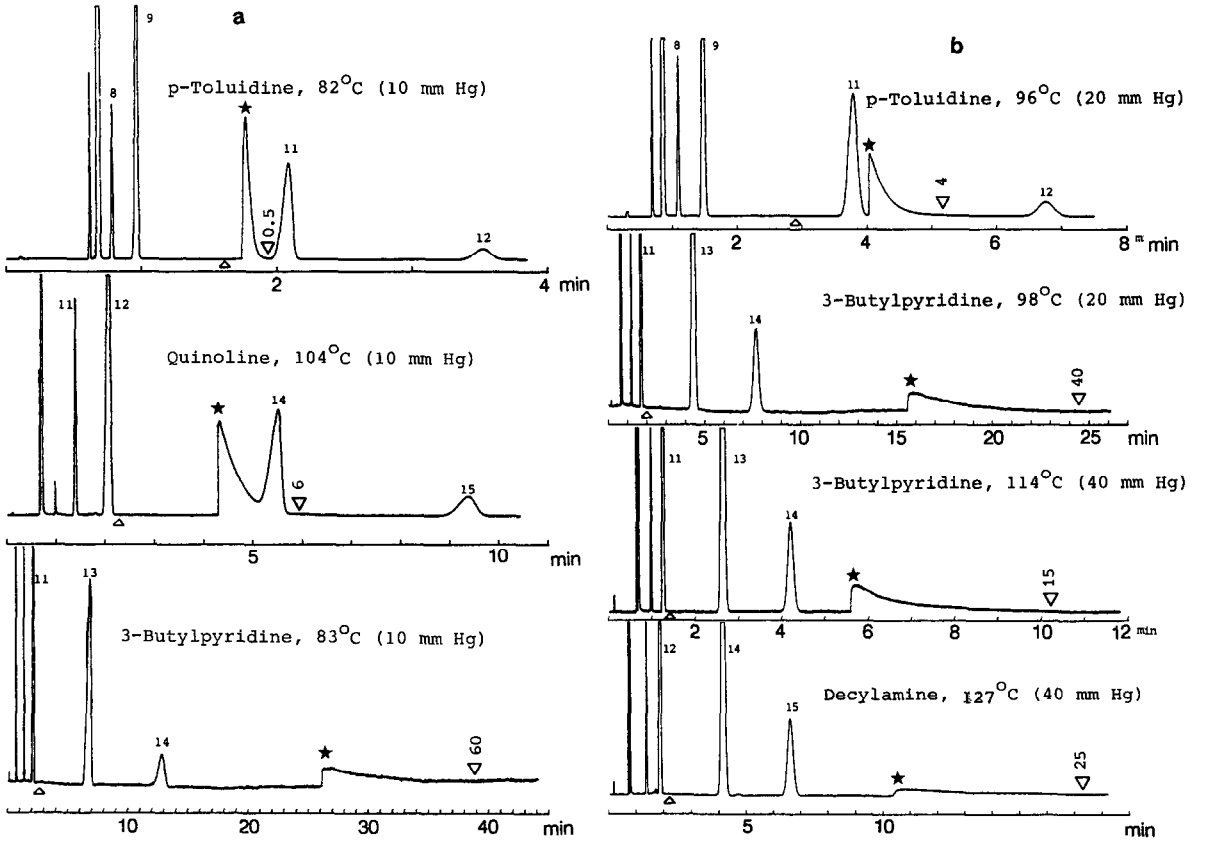

Fig. 10.

(Continued on p. 286)

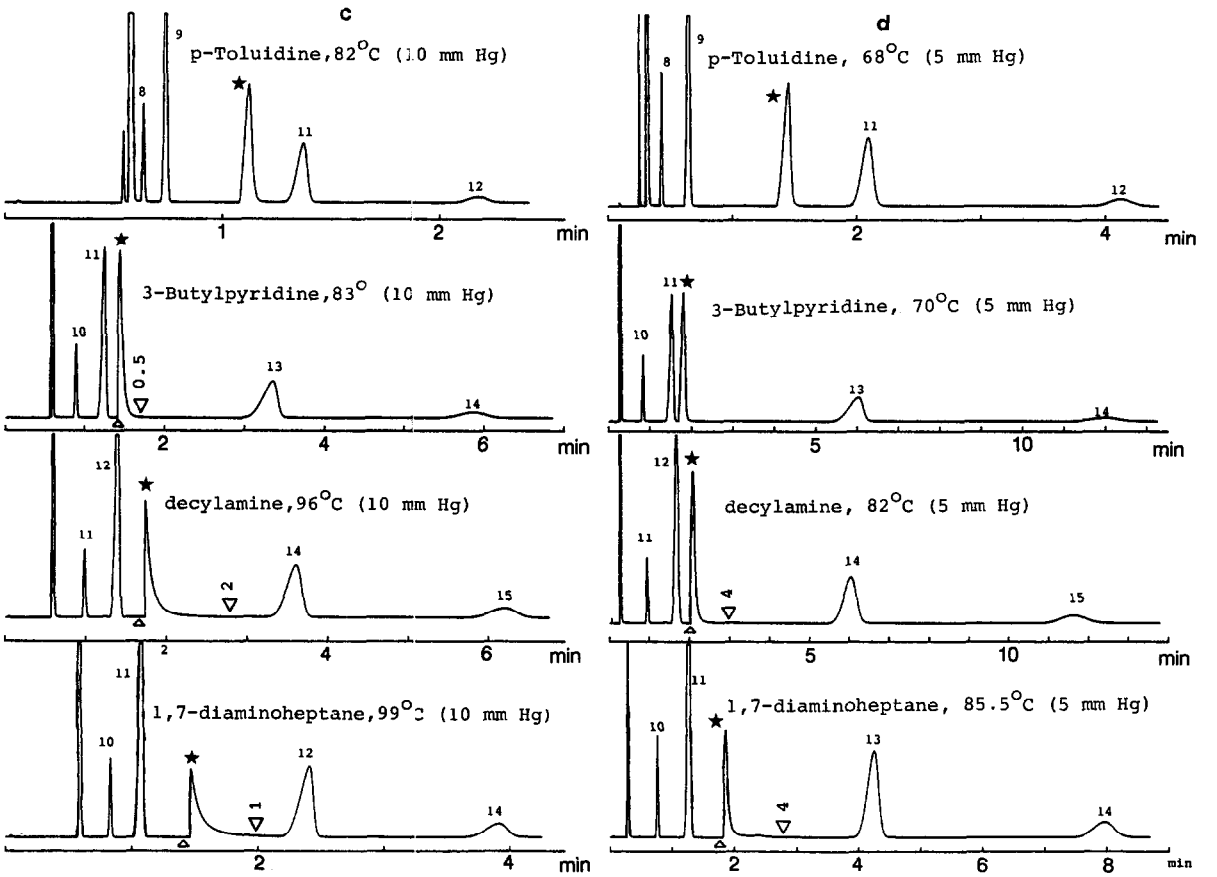

Fig. 10. Organic nitrogen bases as test probes. Peak identification as in Fig. 3a. △ indicates $k' = 0$; ▽ indicates an arbitrary k' value at the end of the tail. (a) Column A, load *p*-toluidine 8.5 ng, quinoline 9.4 ng and 3-butylpyridine 5.2 ng; (b) column C, load *p*-toluidine 7.6 ng, 3-butylpyridine 7.0 ng (20 mmHg) and 6.1 ng (40 mmHg) and decylamine 8.0 ng; (c) column D, load *p*-toluidine 7.0 ng, 3-butylpyridine 28 ng, decylamine 36 ng and 1,7-diaminoheptane 28 ng; (d) column E, load *p*-toluidine 7.2 ng, 3-butylpyridine 17 ng, decylamine 17 ng and 1,7-diaminoheptane 24 ng.

Column C received a more intense pretreatment with hydrochloric acid and was expected to have a higher activity. Therefore, *p*-toluidine was injected at 20 mmHg, 3-butylpyridine at 20 and 40 mmHg and decylamine at 40 mmHg (Fig. 10b). As compared with column A, the peak shift and peak tailing are much increased. Again, shift and tailing increase with increasing pK_a values.

On deactivated columns better peak shapes are expected. Therefore, we added 1,7-diaminoheptane to the test. At a vapour presure of 10 mmHg, *p*-toluidine, 3-butylpyridine, decylamine and 1,7-diaminoheptane were injected on column D (Fig. 10c). *p*-Toluidine is symmetrical and 3-butylpyridine is almost symmetrical. The amines still show tailing but, in comparison with column C, the shift and tailing are much less. The shift and tailing of 1,7-diaminoheptane are comparable to those of decylamine. This suggests that bifunctional compounds are not severer test probes than monofunctional compounds.

Fig. 10d shows the results on column E, which was deactivated with PMHS. As the best results were expected here, the probes were injected at 5 mmHg. *p*-Toluidine and 3-butylpyridine are symmetrical. Decylamine and 1,7-diaminoheptane are only slightly tailing. In spite of the higher symmetry, the k' values are higher than on column D. This is in

accordance with earlier conclusions [5,10] that deactivation with PS 122 creates a polymer layer on the surface of fused-silica.

The examples show that N-bases are good test probes for fused-silica columns. Their pK_a values in water are useful indicators of their adsorptive properties and can be used to select a probe matching the expected or observed activity of the column.

CONCLUSIONS

The coupling device is a simple yet valuable tool to study the activity of uncoated capillary columns. The device is versatile: it permits rapid and easy exchange of test columns, it allows wide variations of carrier flows and splitting ratios and flows and splitting ratios can easily be adjusted to columns of different dimensions. However, such variations also lead to very different appearances of the chromatograms. Either standardized chromatographic conditions have to be used or the chromatogram has to be reconstructed with a k' axis. The monitor line proved indispensable to numerical evaluation of the results. The short, thick-film precolumn gives fast, ample separations even at relatively high carrier flows and temperatures. This results in rapid tests and sharp Gaussian input profiles on the test column. The thick-film also permits the injection of fairly large amounts of the test probes (up to 0.5–1 μg), which largely precludes adsorption problems in the precolumn and monitor line.

The velocity of the carrier gas has no influence on peak shape and peak position expressed in k' units. Neither has column length, although a minimum length is necessary to produce the typical peak profile. This necessary length depends on the ratio of inlet and outlet peak widths.

Temperature strongly influences peak shape and peak position, especially of weakly adsorbing probes (aldehydes, nitriles, etc.). The vapour pressure of the test probe is a useful parameter in this respect. Vapour pressures of 5–10 mmHg give good results. The effect of alkyl chain length can in a limited range be counterbalanced by performing the test at a standardized vapour pressure.

The test is a case of nearly ideal non-linear GC. Peaks obtained with different amounts of the test probe can be superimposed and the tails then coincide. The typical peak shape with a sharp front edge and a tail was nearly always observed. The end of the tail is fixed and its capacity factor k'_0 forms an important quantity for evaluation, but the front edge and the peak top shift with the load. It is recommended to inject several concentration levels of a test probe, in order to obtain an impression of the column loadability. The yield of a probe on the test column is mostly 100% even for strongly adsorbing compounds, and seems not an effective parameter in this test based on reversible adsorption.

For active surfaces compounds with a large dipole moment such as nitriles, nitro compounds and aldehydes are good test probes. For deactivated surfaces more strongly adsorbing test probes are necessary, such as alcohols or amines. For fused-silica surfaces organic nitrogen bases have proved to be good test probes. They adsorb roughly according to their pK_a values in water and hence a selection can be made matching the observed or expected activities of the column. Acidic compounds, on the other hand, are not useful test probes for fused-silica.

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