Alkylpolysiloxane Glass Capillary Columns Combining High Temperature Stability of the Stationary Liquid and Deactivation of the Surface*

Thermal Treatment of Dealkalinized Glass Surfaces by the Stationary Liquid Itself

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Key Words

Glass capillary GC
Heat resistant surface deactivation
Testmixtures
Polycyclic aromatic hydrocarbons

Summary

A new method of making alkylpolysiloxane (OV 1, OV 101, OV 17, Dexsil 400, SE 52, SE 54) columns with high stability at temperatures above 300 °C of both the stationary liquid itself (low bleeding) and of the surface deactivation (no tailing of polar solutes with extended use at temperatures beyond 250 °C) is described. The best results were achieved on dealkalinized alkali glass but also on borosilicate surfaces which have been additionally HF treated before coating in both cases. The procedure can also be applied to leached alkali and borosilicate surfaces successfully. The best deactivations of the glass surface are attained in a two step procedure: firstly by treatment with gaseous HF/N_2 mixture and secondly by simple heating of the coated and closed column at temperatures between 350° and 450 °C for several hours. The tailing behaviour of such columns for polar solutes is considerably improved by this procedure as shown by test chromatograms. The procedure can also be applied to leached alkali and borosilicate surfaces successfully.

Introduction

From the work of Schomburg et al. [1], Blomberg et al. [2] and Venema et al. [3] it is known that methyl- and methylalkyl(phenyl)-polysiloxanes can be used as stationary liquids in glass capillary columns at temperatures above 300 °C only if glass of low alkali and/or alkali earth content like the borosilicate glasses Pyrex or Duran is used. The same temperature stability can be achieved, however, by selective removal of the alkali from the surface of alkali (soft) glasses and probably by leaching with water or dilute aqueous HCl.

As described previously by the authors [4] the dealkalinisation of glass surfaces can also be achieved by dynamic treatment with gaseous HCl for 2 to 3 hours at 450 °C to 500 °C and subsequent rinsing with water. During the treatment with gaseous HCl crystalline layers of NaCl and other alkali and alkali earth chlorides are formed on the surface (Tesaric et al. [5], Alexander et al. [6], Schomburg [7]). A thin-layer of the glass surface is dealkalinized by migration of the alkali ions to the surface which is accelerated at the elevated temperatures if the alkali chlorides are subsequently removed from the surface by rinsing with water at room temperature. After having flushed the column with acetone and dried at elevated temperatures, the surfaces obtained can be easily coated either dynamically or statically with polysiloxanes (OV 1, OV 101, OV 17, SE 30, SE 52, SE 54 or Dexsil 400) [4].

Especially after intermediate "dynamic" treatment of these dealkalinized glass surfaces by gaseous HF (highly diluted in N_2) at about 450 °C capillary, columns are already obtained which combine fairly good deactivation with high temperature stability of the alkylpolysiloxane films. Such columns exhibit the same temperature stability as borosilicate columns. In the diagram of Fig. 1 the results of earlier and recent quantitative bleeding measurements [1] on methylpolysiloxanes as coatings on various types of untreated and specially treated glass surfaces are plotted. The rapid bleeding of alkali glasses even after $BaCO_3$ deposition may be recognized from the plot.

Columns with alkali free surfaces have been successfully used for the separation of compounds of low volatility like polyaromatic hydrocarbons containing up to seven and more rings such as coronene. By using low film thicknesses (< 200 nm) and hydrogen as the carrier gas retention temperatures as low as 200 °C for the isothermal elution of the benzpyrenes can be achieved, Borwitzky and Schomburg [4]. The columns do not lose an appreciable proportion of their stationary liquid under such conditions even after extended use for several weeks and no appreciable decrease of separation efficiency is observed during such periods of usage.

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* Extract also presented at the 8th National Meeting on Analytical Chemistry of the Swedish Chemical Society, Lund, June 1979 and at the 10th International Symposium on Chromatography and Electrophoresis, Venice, Italy, June 1979.

0009-5893/79/10 0651-10 $ 02.00/0

A further important requirement in high temperature work and for the performance of glass capillary columns coated with the weakly polar alkylpolysiloxanes is the stability of the surface deactivation for the unperturbed separation of strongly polar solutes like alcohols, amines, ketones and heterocyclics; i.e. without tailing and irreversible adsorption. This requirement is especially important in trace analyses where very low column loads of the compounds of interest are encountered.

Non or weakly polar stationary liquids are generally to be preferred for the separation of solutes of low volatility which also may have high polarity because of their lower molecular interaction with the stationary liquid. Shorter retentions are then achieved and/or lower column temperatures can be applied with still reasonable analysis times. The decomposition of both the stationary liquid and the solutes is decreased or completely avoided at such low column temperatures.

The tailing of polar solutes in non polar capillary columns can be kept low only if the glass surfaces are specially deactivated before coating without impairment of the film adhesion, which becomes more difficult on such surfaces, however, especially in the case of more polar stationary liquids.

Deactivation procedures like the decomposition of various kinds of polyethylenglycols at elevated temperatures as described for example by Cronin [8], Aue [9], Schomburg [7], Grob [10], and Franken [11] are generally used. Excess of deactivation reagent can be removed by solvent extraction without impairment of deactivation before coating with the actual stationary liquid. Nevertheless the polarity of the stationary phase is increased probably by an intermediate layer of chemically bonded polar polyethyleneglycol fragments. These kinds of deactivation are furthermore not sufficiently stable at temperatures beyond 250°C i.e. at temperatures at which thermal decomposition of the stationary liquid itself does not yet occur. As mentioned before Schomburg et al. [7, 12] described in previous papers the successful application of an additional high temperature (450 °C) treatment with a stream of gaseous HF for deactivation. This procedure can be applied either to HCl treated and dealkalinized alkali glass or to leached or untreated borosilicate glasses. Deactivations are achieved thereby which nearly reach the standard of the less temperature stable Carbowax deactivations. Moreover, the temperature stability of alkylpolysiloxanes on alkali glass surfaces is also slightly increased by the HF treatment (see Fig. 1).

Recently Grob [13] described a procedure for the manufacture of methylpolysiloxane columns with temperature stable deactivation involving silanisation of leached alkali or borosilicate glass surfaces. Grob made use of a silanisation procedure previously described by Welsch and Engewald [13] which is performed at elevated temperatures of about 300 °C and proposed to increase the silanisation temperature to about 400 °C.

Earlier experiments on the silanisation of pretreated glass surfaces by Novotny [15, 16] and also Schomburg [7] have not been very successful probably because much too low temperatures had been used to accomplish the silanisation of the silanol groups on the surfaces which reaction is probably the cause of the deactivation effect. In recent experiments the authors used the thermal decomposition products of alkylpolysiloxanes for silanisation e.g. deactivation of dealkalinized glass surfaces following earlier observations on improvement of deactivation by simple overheating of

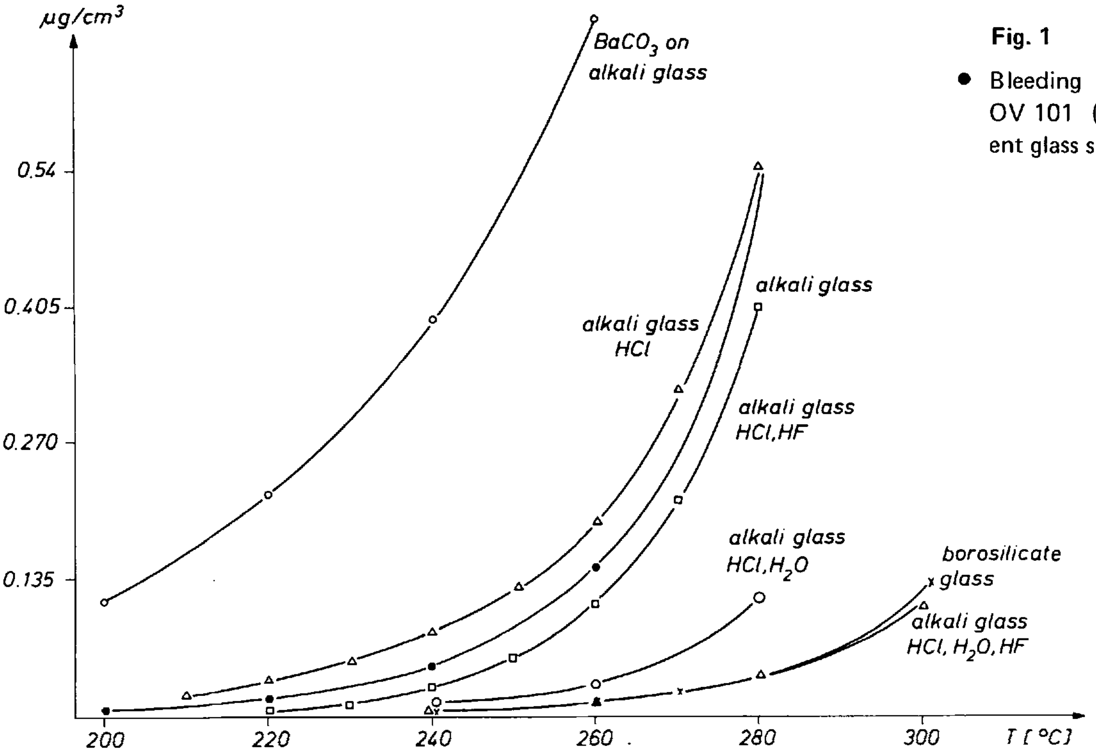


Fig. 1

- Bleeding of methylpolysiloxanes OV 101 (MG ≈ 30000) on different glass surfaces with temperature.

stationary liquids of the polysiloxane type analogous to deactivation by thermal polyethyleneglycol treatment.

The deactivation of porous support material for packed columns by the thermal decomposition of methylpolysiloxanes has already been mentioned by Aue [17] whereas the authors [12] mentioned the effect in a previous paper as being useful also for the deactivation of glass capillary surfaces.

They stated:
"This observation supports the assumption that at high temperatures methylpolysiloxanes undergo simultaneous decomposition and chemical bonding of decomposition products to the surface similar to the Carbowax deactivation procedure of Aue."

At present the authors are engaged in investigations on the deactivation of various kinds of untreated and pretreated glass surfaces the important parameters being the temperature stability of the stationary liquid (bleeding), the tailing behaviour i.e. the adsorptivity against strongly polar solutes, the temperature stability of the deactivation and the separation efficiency of the columns obtained.

Experimental

In Table I a resumé of the experiments executed on glass capillary surfaces and of the chromatographic test measurements is given.

The dealkalinisation of the alkali glass surface was achieved by dynamic HCl gas treatment for 2–4 h at 450 °C as described previously [7]. The alkali and alkali earth chlorides formed on the surface can be easily removed by flushing the capillaries with water. The surfaces obtained are smooth as can be seen from electron micrographs, but can be easily coated by most of the alkylpolysiloxanes. The amount of alkali (preferably Na) and alkali earth (Ca) are higher if higher temperatures are applied during treatment, because the migration rates of the metal ions to the surface are increased (compare Britton [18]). In Table II quantitative data of the amounts of chlorides removed from alkali glass capillaries by water after HCl treatment in both the static and dynamic mode and at different temperatures are given.

After twofold static treatment further amounts of chlorides can be flushed from the surface by water if our high temperature dynamic treatment is applied.

The subsequent HF treatment of the dealkalinized surfaces is performed under a continuous flow of highly diluted HF gas (< 0.1 vol %) in nitrogen also at 450 °C.

The dilution of the HF is achieved in a double stage process by pressing nitrogen (ca. 20 bars) onto a commercial HF-cylinder. A part of the HF/N_2 mixture thus obtained is transferred to another cylinder where further dilution by nitrogen is done.

The surfaces obtained and for comparison also leached alkali and borosilicate surfaces, were coated with alkyl-

Table I. Surface treatment procedures applied to columns used for Figs. 1–8

Columns	Treatment steps	Chromatograms
I. a	A → OV 101	Fig. 2
b	A → OV 101 → 300 min, at 350 °C → solvent extr. → OV 101 (recoat.)	
II. a	A → HCl (gas) 3 h 450 °C → H_2O rins. → $(CH_3)_2CO$ → OV 101	
b	A → HCl (gas) 3 h 450 °C → H_2O rins. → $(CH_3)_2CO$ → OV 101 → 100 min, 380 °C → solvent extr. → OV 101 (recoat.)	Fig. 3
III. a	A → HCl (gas) 3 h 450 °C → H_2O rins. → $(CH_3)_2CO$ → HF (gas) 2 h 450 °C → OV 101	
b	A → HCl (gas) 3 h 450 °C → H_2O rins. → $(CH_3)_2CO$ → HF (gas) 2 h 450 °C → OV 101 → 30 min, 450 °C → solvent extr. → OV 101 (recoat.)	Fig. 4
	(see also separate amine and phenol test chromatograms)	Fig, 5, 6
IV.	A → HCl (aq.) 20%; 16 h 150 °C → H_2O rins. → $(CH_3)_2CO$ → OV 101 → 16 h 360 °C → cond. (carrier gas flow) *	Fig. 7
V.	A → HCl (aq.) 20%; 36 h 80 °C → H_2O rins. → $(CH_3)_2CO$ → OV 1 (static coat. 0.4%) → 16 h 350 °C → cond. 290 °C (carrier gas flow) *	Fig. 8
VI.	A → HCl (gas) 3 h 450 °C → H_2O rins. → $(CH_3)_2CO$ → HF (gas) 2 h 450 °C → OV 17 → 20 h 350°C → cond. (carrier gas flow) *	Fig. 9
VII.	A → HCl (gas) 3 h 450 °C → H_2O rins. → $(CH_3)_2CO$ → HF (gas) 2 h 450 °C → Dexsil 400 → 6 h 350 °C → cond. 300 °C (carrier gas flow)	Fig. 10

A = Alkali glass D = Duran (borosilicate) glass

* = Instead of solvent extraction thermal conditioning after opening columns ends under carrier gas flow was executed but not recoating with stationary liquid. All other operations where heating is involved have been performed with column ends closed.

polysiloxanes such as: OV 1, OV 101, OV 17, Dexil 400 without and with previous HF pretreatment. For coating the dynamic mercury plug method was preferred for time saving reasons.

The deactivation by "baking" with the stationary liquid itself was by heating the coated, nitrogen filled, capillaries up to 450 °C for periods between 2 and 20 h, the column ends being sealed by melting. Depending on the catalytic activity of the glass surface partial decomposition of the polysiloxanes takes place. On dealkalinized surfaces between 10% and 20% of the polysiloxanes are decomposed during the baking as concluded from capacity ratio k, measurements of a standard compound (hydrocarbon).

The decomposition products probably undergo chemical bonding to the glass surface, i.e. to the silanol groups. After this baking procedure the column ends are opened and the volatile unbonded decomposition products are removed by thermal conditioning at temperatures up to 300 °C and beyond. In other experiments the non bonded fragments and the undecomposed stationary liquid were removed by solvent extraction. The capillary is then recoated with the same stationary liquid in order to attain a film of defined thickness and polarity using either the static or the dynamic coating method.

The columns obtained by both procedures exhibit the normal excellent temperature stability of the alkylpolysiloxanes on alkali-free glass surfaces which allows working temperatures beyond 300 °C if no catalytic effects are to be encountered, but depending also on the stability of the stationary liquid itself, however. The adsorptivity of the surfaces or the quality of the deactivation by chemical bonding (silanisation by decomposition products) is tested by the usual chromatographic measurements with polarity mixtures. The composition of the polarity mixture used by us is given in Table III. Moreover, special amine phenol mixtures were used for testing, the composition of which is given in the legends of Figs. 5 and 6. The test chromatograms obtained are given in Figs. 2–11.

Table III. Assignment of components of polarity mixture for Figs. 2–10

Composition of polarity mixture	
$C_{10,11,12}$-n-paraffines	1, 3, 6
$C_{10,11,12}$esters	7, 8, 9
n-octanol	2
2,6-dimethylphenol	4
2,6-dimethylaniline	5
dicyclohexylamine	10

At present the authors are engaged in further investigations on the parameters of the different steps of column making for further optimisation of column performance.

Discussion

By baking a methylpolysiloxane on an untreated alkali glass surface (columns I in Table I) fairly good deactivation is achieved as can be seen from the two chromatograms of Fig. 2, the comparison of which also illustrates the deactivation effect of the baking – like the two chromatograms of Fig. 3 which have been obtained with a similar surface treatment, but after previous dealkalinisation of the same alkali glass capillaries (columns II, a and b, in Table I).

Table II. Determination of amounts of Na^+ and Ca^{2+} formed on inner surface of alkali glass capillaries by etching with HCl gas; column lengths 150 m, in each case i.d. 0.27 mm

No of etched column	etching	temperature	time [h]	Na^+ [mg]	Ca^{2+} [mg]	remarks
9 columns, mean value	dynamic	450	4	14.8 ± 2.7	0.45 ± 0.04	
B 1292	dynamic	450	4	14.2	0.45	1st etching
B 1292	dynamic	450	4	0.4	< 0.01	2rd etching
B 1332	static	450	4	6.8	–	1st etching
B 1332	static	450	4	3.8	0.6	2rd etching
B 1332	dynamic	450	4	6.2	0.2	3rd etching
B 1183	static	350	2	2.0	< 0.1	

Chloride was determined in ca. equivalent quantities to the amounts of Na^+ and Ca^{2+}. Later on traces of Mg, Al, and Co were found. The oxides of these cations are also trace components of alkali glass. According to Venema [3] they degrade polysiloxanes at elevated temperatures.

Columns B 1292 and B 1332 were etched twice and thrice, respectively. The second and third etchings of these columns were performed after having flushed the columns with water to remove chlorides formed by the previous etching.

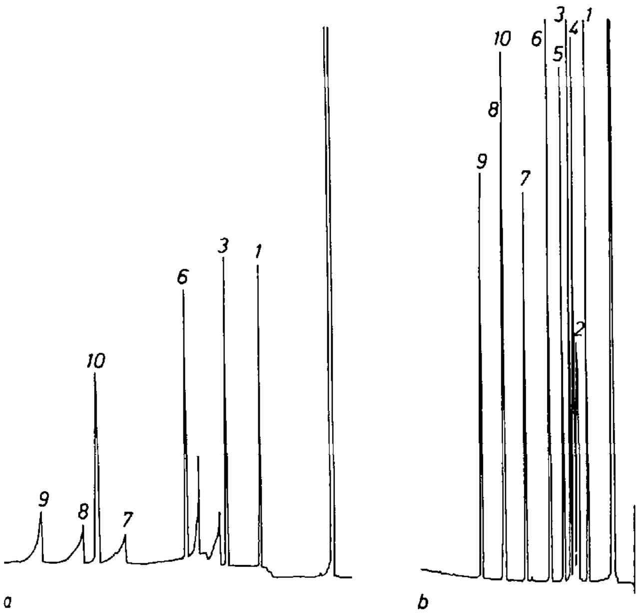


Fig. 2

- Alkylpolysiloxane glass capillary columns with temperature stable surface deactivation.

I. a) Alkali glass capillary, OV 101 coated (dyn) 20 m, i.d. 0.27 mm,
   b) same column, but heated 300 min at 350 °C with closed ends, solvent rinsed and recoated with OV 101.

Result: good deactivation, limited temperature stability of stationary liquid.

Temperature: 90 °C–220 °C, 15 °C/min
Carrier gas: N_2, 0.7 bar
Sample: see Table III

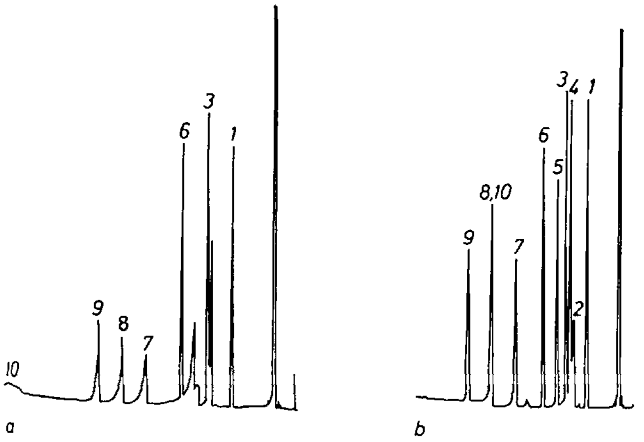


Fig. 3

- Alkylpolysiloxane glass capillary columns with temperature stable surface deactivation.

II. a) Alkali glass capillary, dealkalinized (HCl gas, H_2O rinsed) OV 101 coated (dyn) 20 m, i.d. 0.27 mm,
   b) same column, but heated 100 min at 380 °C with closed ends, solvent rinsed and recoated with OV 101.

Result: insufficient deactivation, good temperature stability.

Temperature: 90 °C–220 °C, 15 °C/min
Carrier gas: N_2, 0.7 bar
Sample: see Table III

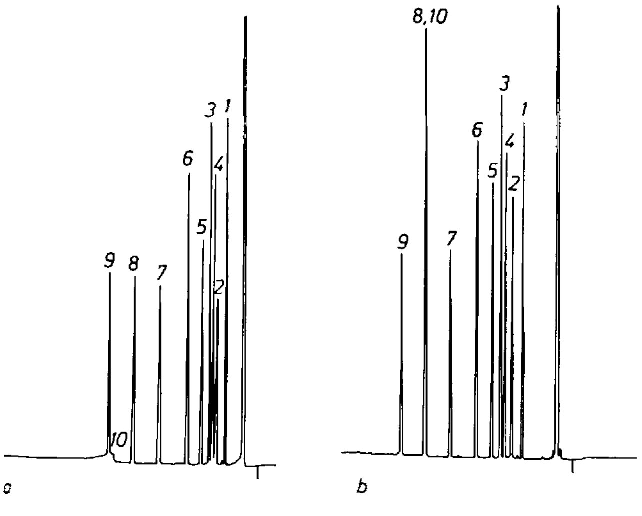


Fig. 4

- Alkylpolysiloxane glass capillary columns with temperature stable surface deactivation.

III. a) Alkali glass capillary, dealkalinized (HCl gas, H_2O rinsed, HF/N_2 gas treatment OV 101 coated (dyn) 10 m, i.d. 0.27 mm,
   b) same column, but heated 30 min at 450 °C with closed ends, solvent rinsed and recoated with OV 101.

Result: deactivation perfect and good temperature stability.

Temperature: 90 °C–220 °C, 15 °C/min
Carrier gas: N_2, 0.7 bar
Sample: see Table III

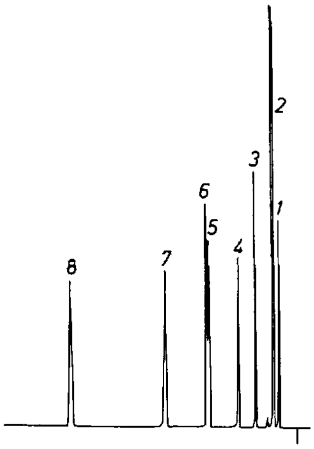


Fig. 5

- Alkylpolysiloxane glass capillary columns with temperature stable surface deactivation.

Column III: 10 m alkali glass capillary, dealkalinized (HCl gas, H_2O, rinsed) HF gas treatment, OV 101 coated (dyn), 30 min at 450 °C with closed ends, recoated with OV 101 after solvent rinsing.
Sample: amines
1 ethylenediamine, 2 toluene, 3 aniline, 4 n-octylamine, 5 n-nonylamine, 6 2,6-dimethylaniline, 7 n-decylamine, 8 dicyclohexylamine.
Temperature: 100 °C -150 °C, 5 °C/min
Carrier gas: N_2, 0.6 bar

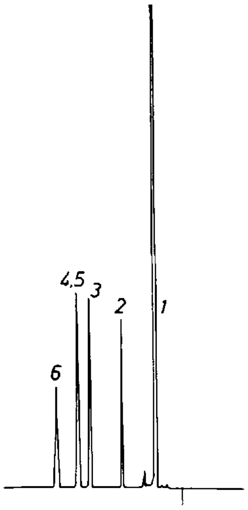


Fig. 6

- Alkylpolysiloxane glass capillary columns with temperature stable surface deactivation.

Column III: 10 m alkali glass capillary, dealkalinized (HCl gas, H_2O rinsed) HF gas treatment, OV 101 coated (dyn), 30 min at 450 °C with closed ends, recoated with OV 101 after solvent rinsing.
Sample: phenols
1 Toluene, 2 phenol, 3 o-cresol, 4 + 5 m + p-cresol, 6 2,6-dimethylphenol
Temperature: 90 °C
Carrier gas: N_2, 0.6 bar

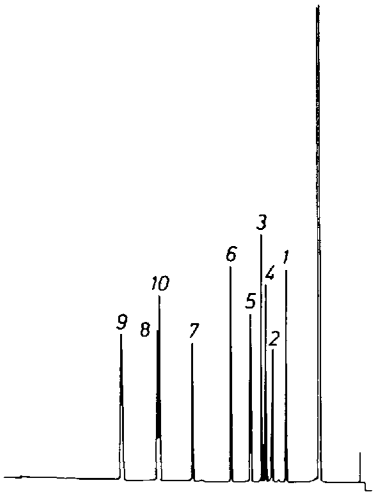


Fig. 7

- Alkylpolysiloxane glass capillary columns with temperature stable surface deactivation.

Column VI: Alkali glass, *leached* 16 h 150 °C with 20% aq HCl, H_2O, acetone rinsed, coated dyn with OV 101, heated with closed ends 16 h 360 °C, and conditioned with carrier gas flow; 20 m, i.d. 0.27 mm.
Sample: see Table III
Temperature: 80 °C–200 °C, 15 °C/min
Carrier gas: N_2, 0.6 bar

The temperature stability of the stationary liquid itself in the dealkalinized columns (II) is of course much higher than that of the undealkalinized types (I). HF treatment before coating as used for the columns III (a and b) improves both the temperature stability of the stationary liquid but even more the deactivation of the surface – as can be seen from the chromatograms of Figs. 4, 5 and 6.

Column IV has been made for comparison purposes by leaching an alkali glass capillary with dilute aqueous HCl (20%) for 16 h at 150 °C whereas column V was obtained by leaching a Duran glass capillary with the same aqueous solution of HCl for 36 h at 80 °C. The chromatograms obtained with these two columns are given in Figs. 7 and 8. They show that the baking procedure can also be applied to leached surfaces successfully. The temperature stability of the stationary liquid and deactivation of these columns has not yet been tested, however. Additional HF deactivation also has not been used for leached surfaces up to now.

In column VI the stationary liquid was the methylphenylpolysiloxane OV17. The deactivation of the column obtained was of the same standard as that of a Grob type

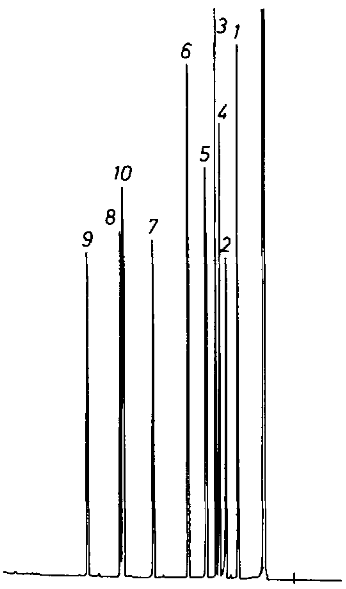


Fig. 8

- Alkylpolysiloxane glass capillary columns with temperature stable surface deactivation.

Column V:	Duran (borosilicate) glass capillary, *leached* 30 h 80 °C with 20% aq HCl, H_2O, acetone rinsed, coated stat. with OV 1 (0.4% in n-pentane), heated with closed ends 16 h 350 °C, conditioned with carrier gas flow 290 °C 15 m, i.d. 0.27 mm.
Sample:	see Table III
Temperature:	80 °C–200 °C, 10 °C/min
Carrier gas:	He, 0.6 bar

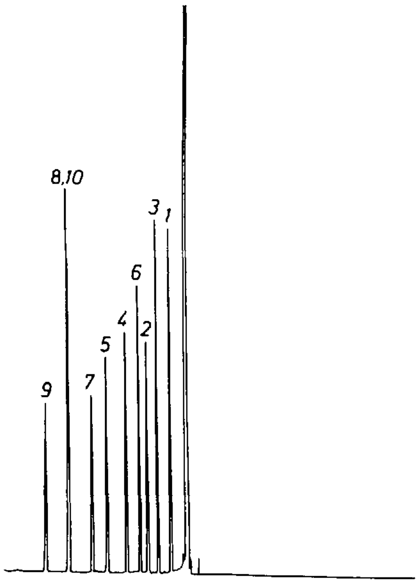


Fig. 9

- Alkylpolysiloxane glass capillary columns with temperature stable surface deactivation.

Column VI:	Alkali glass capillary, dealkalinized (HCl gas, H_2O, acetone rinsed), HF/N_2 gas treatment, coated (dyn) with OV 17, heated with closed ends. 20 h 350 °C, conditioned 16 h with N_2, 0.5 bar; 20 m, i.d. 0.27 mm.
Sample:	see Table III
Temperature:	80 °C–180 °C, 10 °C/min
Carrier gas:	He, 0.6 bar

Fig. 10

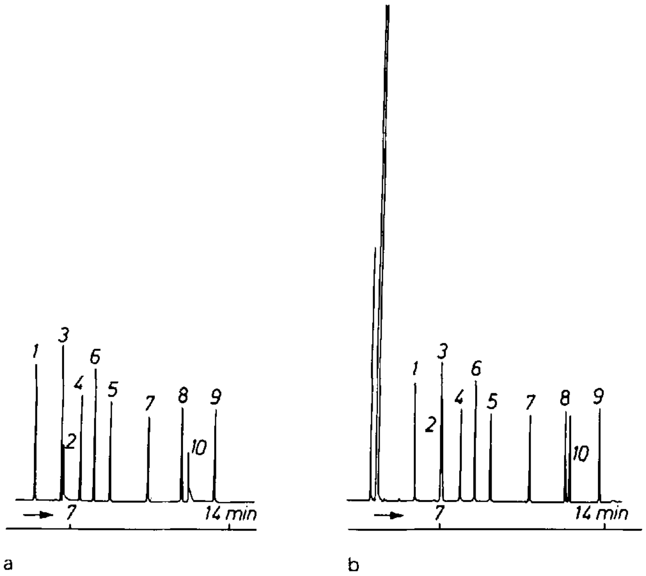
- Methyl-phenylpolycarboranesiloxane glass capillary column with temperature stable surface deactivation.

a) Alkali glass capillary, dealkalinized (HCl gas, H_2O rinsed, HF) Dexsil 400 coated (stat),

b) same column, but heated 300 min at 350 °C with closed ends.

Result: good deactivation, good temperature stability.

Column:	50 m, i.d. 0.27 mm
Film thickness:	86 nm
Temperature:	80 °C–220 °C, 10 °C/min
Carrier gas:	N_2, 1.0 bar
Sample:	see Table III



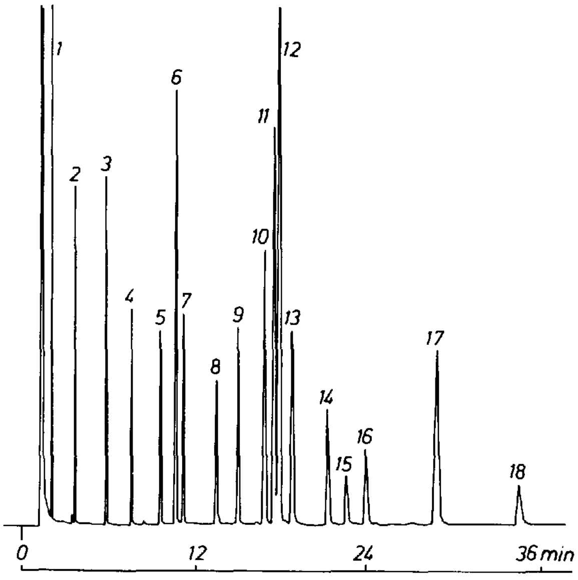
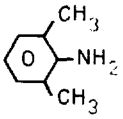
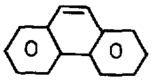
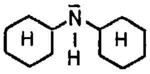
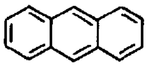
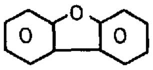
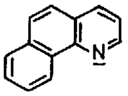
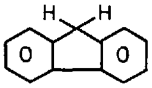
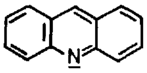
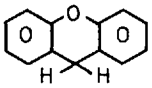
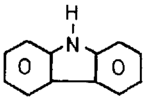
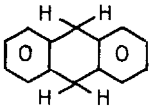
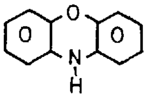
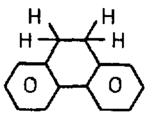
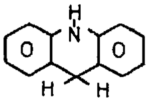
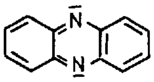
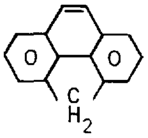
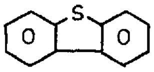
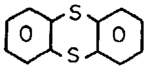


Fig. 11

- Sample: polynuclear and heterocyclic aromatic hydrocarbons

Column: 26 m, i.d. 0.27 mm
Stationary phase: Dexsil 400 (methyl-phenyl-carboransiloxane)
Film thickness: 170 nm
Column temperature: 160 °C
Carrier gas: Hydrogen, 0.35 m/s

Assignment of peaks

Peak no:	compound:	structure:	Peak no:	compound:	structure:
1	2,6-dimethylaniline		10	phenanthrene	
2	dicyclohexylamine		11	anthracene	
3	dibenzofurane		12	7,8-benzoquinoline	
4	fluorene		13	acridine	
5	xanthene		14	carbazole	
6	9,10-dihydroanthracene		15	phenoxazine	
7	9,10-dihydrophenanthrene		16	9,10-dihydroacridine	
8	phenazine		17	4 H cyclopenta[d,e,f] phenanthrene	
9	dibenzothiophene		18	thianthrene	

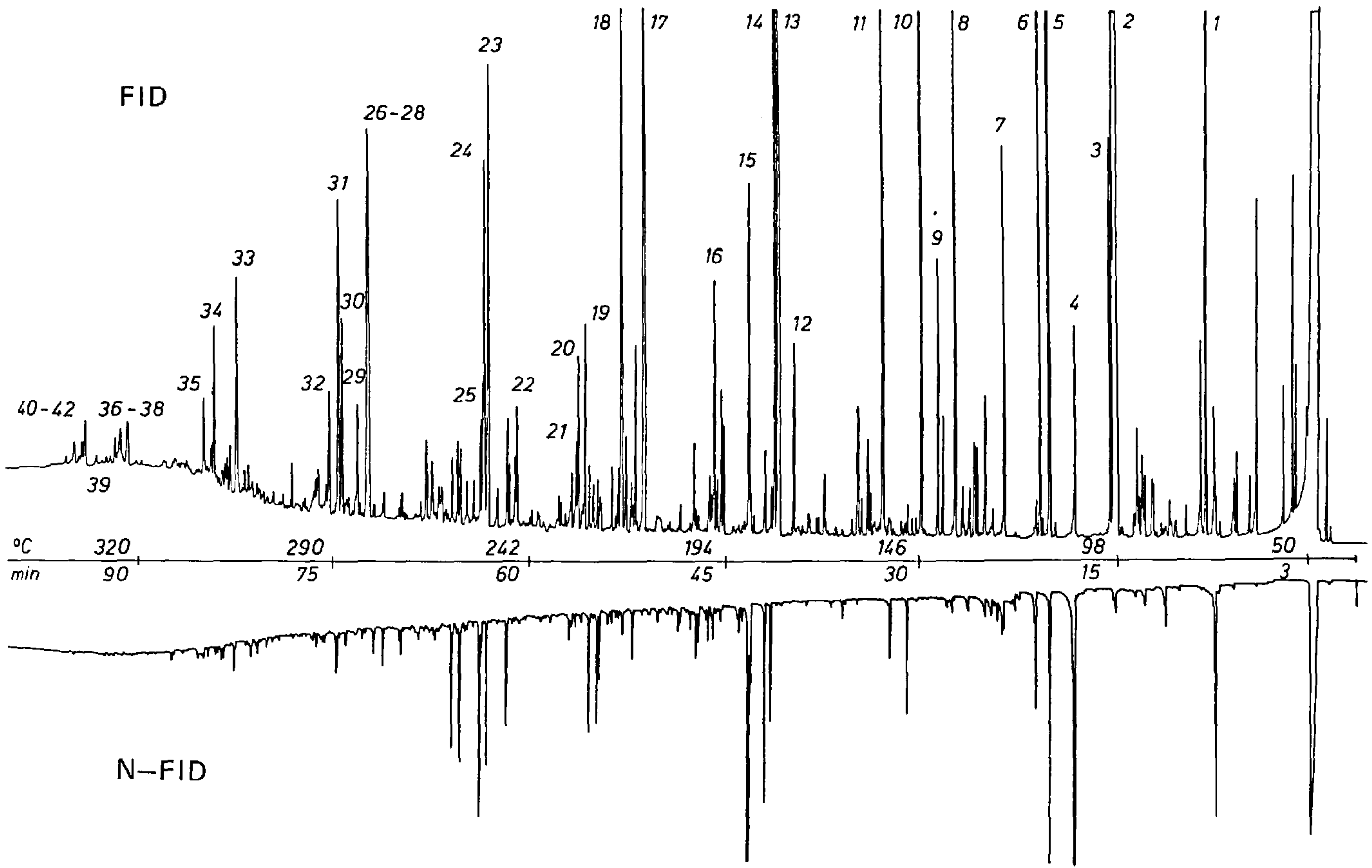


Fig. 12

Sample: coal tar
Column: 50 m, i.d. 0.27 mm
Stat. liquid: Dexsil 400, methyl-phenylpolycarboransiloxane
Film thickness: 86 nm (static coating)
Column temperature: 50 °C–320 °C, 4 °C/min
Carrier gas: He, 33 cm/s at 320 °C
Detection: Capillary FID N-FID

Assignment of peaks

1	Indene
2	Naphthaline
3	Benzo[b]thiophene
4	Quinoline
5	2-Methylnaphthaline
6	1-Methylnaphthaline
7	Biphenyl
8	Acenaphthylene
9	Acenaphthene
10	Dibenzofurane
11	Fluorene
12	Dibenzothiophene
13	Phenanthrene
14	Anthracene
15	Carbazole
16	4 H-Cyclopenta[d,e,f]phenanthrene
17	Fluoranthene
18	Pyrene
19	Benzo[a]fluorene
20	Benzo[b]fluorene
21	Benzo[c]fluorene
22	Benzo[c]phenanthrene
23	Benzo[a]anthracene
24	Chrysene
25	Triphenylene
26-28	Benzo[b]-,[i]-, and -[k]fluoranthen
29	$C_{20}H_{22}$-Isomer
30	Benzo[e]pyrene
31	Benzo[a]pyrene
32	Perylene
33	Indeno[1,2,3-c,d]pyrene
34	Benzo[g.h,i]perylene
35	Anthanthrene
36-38	Dibenzpyrene, -fluoranthene
39	Coronene
40-42	Dibenzpyrene, -fluoranthene

column obtained by silanisation of a leached and dehydrated surface by DPTMDS (diphenyltetramethyldisilazane, see Fig. 9). No problem with the vapour pressure of the silanisation reagents as mentioned by Grob in his paper arises in our procedure.

The deactivation by baking can also be applied to alkylpolysiloxanes of the Dexsil type which contain carborane groups. The columns group VI, a and b, have been obtained with Dexsil 400, the corresponding chromatograms are given in Fig. 10 which show again the deactivation effect of the baking procedure. The columns also exhibit excellent temperature stability at temperatures up to 330 °C.

The adsorptivity of the Dexsil baked surfaces may also be assessed from the chromatogram in Fig. 11 which has been obtained with a testmixture of O, S and N heterocyclic polyaromatic hydrocarbons. Excellent peak symmetry was achieved even for solutes containing NH-groups or more than one heteroatom.

A similar column was used for a coal tar separation executed under parallel double detection with FID and N-FID. Good peak symmetry for the N-containing polyaromatics was attained which could be assessed much better from the N-specific chromatogram because no overlapping by the natural hydrocarbon matrix is encountered (see Fig. 12).

Finally we would like to comment on the method of *in situ* oligomerisation of methyl- and methylphenylpolysiloxane oligomerisation first described by Madani and Chambaz [19]. A similar procedure has also been used by Blomberg et al. [19]. Both groups claim that the high temperature stability of the columns achieved is due to the formation of the stationary polysiloxane liquid by *in situ* oligomerisation on the glass surface.

We believe that in this procedure *in situ* silanisation of the silanol groups of the glass surface occurs in parallel with the formation of the polysiloxanes. The temperature stability of the stationary liquid is probably only dependent on the catalytic activity of the glass surface (alkali content for example) whereas the chemical bonding to the silanol groups preferably influences the tailing behaviour but not so much the temperature stability of the stationary liquid.

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