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HIGH-PURITY FUSED-SILICA CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY*

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SUMMARY

High-purity fused-silica capillaries (made of SiO_2 of 99.9999% or higher purity, containing less than 1 ppm of hydroxy groups and metal oxides) have been evaluated for gas chromatographic applications. Various types of conventional glass capillary column were compared for inertness, and untreated** high-purity fused-silica capillary columns were found to be the most inert.

Untreated fused-silica capillary columns were compared with those deactivated with PEG-20M, using the Grob test mixture and a test mixture containing primary amines. Untreated fused-silica capillary columns coated with methylpolysiloxane (OV-101) showed some activity after coating, but, after conditioning at 280–350°C, they showed almost the same degree of inertness as the deactivated columns.

In quantitative analysis of highly polar compounds containing a primary amine, the untreated fused-silica column showed no adsorption in the low concentration range of 0.1 ng for 2,6-dimethylphenol and dicyclohexylamine, 0.3 ng for octanol, and 2 ng for primary amine (laurylamine).

In order to examine the stability and service life in high-temperature operation, the heights equivalent to a theoretical plate (HETPs) before and after 550 h of continuous operation at 280°C column temperature were compared using an untreated fused-silica capillary column. The change in HETP was only 30%, and the chromatograms of polar compounds showed no significant difference.

An untreated high-purity fused-silica capillary column coated with methylpolysiloxane (OV-101) ensured better stability and almost the same degree of inertness, in high-temperature operation, compared with the same column deactivated with PEG-20M.

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** "Untreated" means that the column(s) were conditioned in an ordinary manner but not treated by silylation or PEG-20M precoating before coating of liquid phase.

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INTRODUCTION

Glass capillary columns have recently come to be used more and more in gas chromatography (GC) because they ensure excellent high resolution and good stability even in high-temperature operations.

Though glass is generally considered to be inert, it is not totally inert when used as column material for GC. The increased demand for trace analysis in GC has led to a greater demand for inert column tubings.

The activity of column tubings poses a problem when polar compounds are chromatographed on non-polar stationary phases —peaks may tail or even disappear[1–3]. It is known that such trouble is caused by the active sites on the inner surface of the column tubing[1–3]. It is also known that these active sites are attributable to the presence of metal oxides and silanol groups in the glass[4,5].

Several techniques have been developed to deactivate these active sites, such as silylation[6,7], PEG-20M treatment[2,4,8,9], utilization of surface-active agents[10,11], and alkylpolysiloxane degradation[12,13]. These deactivation methods, however, are time-consuming and require complicated operation. It is necessary to etch, leach and heat-treat the column tubing before coating with liquid phase.

Fused-silica capillary columns, introduced by Dandenau and co-workers[14,15] in 1979, have the advantages that they are very flexible and that they contain very small amounts of metal oxides compared with conventional glass capillary columns.

Dandenau and co-workers[14,15] deactivated the fused-silica capillary columns with PEG-20M prior to coating with non-polar methylpolysiloxane (SP-2100), in order to improve the inertness of the column. It was found, however, that deactivation with PEG-20M influences the retention indices of some components[16], and its effects cannot be expected to last long when the column temperature is above 250°C[16–18].

Though several reports on fused-silica capillary columns have been presented by Lipsky *et al.*[16], Schomburg *et al.*[13,19], and others, none of them referred to analyses of highly polar compounds such as dicyclohexylamine and primary amines or to quantitative analysis of polar mixtures.

Though fused silica of 99.9% or higher purity reportedly contains less than 1 ppm of metal oxides, it contains as much as 180–1200 ppm of OH groups, which are another cause of surface activity[16].

No reports have been presented about the GC application of high-purity fused-silica containing less than 1–5 ppm of OH groups.

We have tested high-purity fused-silica capillaries (of a purity better than 99.9999%) containing less than 1 ppm of OH groups and metal oxides, and evaluated them as the column tubing for GC.

High-purity fused-silica capillary columns were prepared without treatment prior to coating with the liquid phases. Non-polar high-purity fused-silica capillary (methylpolysiloxane: OV-101) columns were prepared to provide satisfactory separation of highly polar compounds without tailing or irreversible adsorption of the components.

This paper describes our investigation carried out to make:

(1) A comparison between untreated fused-silica capillary columns and ordinary glass capillary columns of various types;

(2) A study of the effect of the conditioning temperature and time on untreated fused-silica capillary columns;

(3) A comparison between untreated fused-silica capillary columns and fused-silica capillary column deactivated with PEG-20M;

(4) A study of the effect of the film thickness of the stationary phase;

(5) A quantitation of highly polar compounds by untreated high-purity fused-silica capillary column;

(6) A study of the thermal stability and service life of untreated high-purity fused-silica capillary columns.

EXPERIMENTAL

Preparation of fused-silica capillary columns

Fused-silica capillaries were produced by the technique used to produce optical fibres[14–16]. It is important to produce optical fibres with a low content of metals and OH groups[20]. It has recently become possible to produce optical fibres containing OH groups at the ppb (10^{12}) level[21]. The OH group content of the fused-silica capillaries used in our experiments was less than 0.3 ppm, measured from the optical absorption of the optical fibre produced in the same way. Such high-purity fused-silica capillaries have become available through the use of the chemical vapor deposition method[22].

The fused-silica capillaries were coated with a non-polar stationary phase, methylpolysiloxane OV-101 (Ohio Valley, Marrietta, OH, U.S.A.) by the dynamic coating method. All the fused-silica capillaries used in our experiments were 25 m × 0.2 mm I.D. The coating was made with a 10% (w/v) solution of OV-101. After the coating had been applied, the columns were conditioned at 280–350°C (for 10–40 h). Six capillaries of different film thickness were prepared by using different coating plug speeds, to be used for investigating the effect of film thickness on the adsorptivity of columns.

Deactivation of fused-silica capillary columns

Fused-silica capillary was deactivated by treating with a 0.2% solution of PEG-20M in methylene chloride. The method of deactivation was that proposed by Grob and Grob[9], the only difference being that the column was washed with methylene chloride after treatment at 280°C. The deactivation was repeated twice. Then the column was coated with the liquid phase as described in the Experimental section.

Preparation of conventional glass capillary columns of various types

A Pyrex® glass (borosilicate glass) tube, 1.5 m × 7 mm O.D., 2.5 mm I.D., was drawn by the Shimadzu GDM-1B glass-drawing machine (Shimadzu, Kyoto, Japan), into glass capillary tubes, 25–30 m long, 0.7 mm and 1.0 mm O.D., 0.25 mm and 0.3 mm I.D.

These glass capillaries were treated with a 10% (w/v) solution of OV-101 (methylpolysiloxane) in *n*-hexane by the dynamic coating method, by means of the Shimadzu MCT-1A micro-column treating stand.

The following six glass capillary columns were prepared for comparison with the fused-silica column:

(A) Untreated wall-coated open tubular (WCOT) column

(B) WCOT column deactivated with PEG-20M

(C) Support-coated open tubular (SCOT) column treated with Silanox® 101 (fine particles of silanized silica)

(D) WCOT column with a $BaCO_3$ layer deposited

(E) WCOT column deactivated with PEG-20M after deposition of a $BaCO_3$ layer

The SCOT column (C) was prepared by the two-step coating method proposed by German and co-workers[23,24]. The columns D and E were prepared by the method proposed by Grob and co-workers[9,25].

Equipment

The Shimadzu GDM-1B glass-drawing machine was used to produce the glass capillaries. The Shimadzu MCT-1A micro-column treating stand was used to prepare glass and fused-silica capillary columns. GC was carried out by the Shimadzu GC-7APrF and GC-mini2 gas chromatographs, equipped with a dual flame ionization detector. Helium was used as the carrier gas. The Shimadzu Chromatopac C-R1A recording data processor was used for data processing.

RESULTS AND DISCUSSION

Comparison of a fused-silica capillary column and glass capillary columns

Fig. 1 shows the chromatograms of a polar test mixture (Grob test mixture[26]) obtained with various glass capillary columns (Fig. 1A–E) and a fused-silica column (Fig. 1F). The chromatograms show the degree of inertness of the columns.

Fig. 1A shows that polar compounds such as butane-2,3-diol, octanol and dicyclohexylamine are not eluted from the untreated WCOT column A (*cf.* Fig. 1F).

Fig. 1B shows that when the WCOT column deactivated with PEG-20M is used, peaks have better shapes but butane-2,3-diol and octanol are still not eluted.

These data indicate the difficulty of obtaining good chromatographic peaks of polar compounds with non-polar capillary columns made of Pyrex glass, whether they are deactivated with PEG-20M or not, and that it is necessary to treat the inner surface further in order to improve the inertness.

Fig. 1C shows that the SCOT column treated with Silanox 101 has some activity and that butane-2,3-diol and octanol are not eluted from it. Though the active sites of the column are somewhat covered with the fine silanized silica particles, the column is still a little active: further deactivation is required.

Fig. 1D shows that when the WCOT column with a $BaCO_3$ layer is used, octanol is recorded as a small tailing peak but butane-2,3-diol is not eluted. The other compounds are recorded as peaks without tailing. This indicates that the active sites are covered by the $BaCO_3$ layer.

Fig. 1E shows that the WCOT column deactivated with PEG-20M after deposition of a $BaCO_3$ layer gives sharp peaks of all the compounds, except 2-ethylhexanoic acid and butane-2,3-diol.

The untreated fused-silica column, by contrast, gives sharp peaks without tailing for all the compounds, as shown in Fig. 1F. (The leading behaviour of the 2-ethylhexanoic acid peak is due to the overload of the column[19]; see Fig. 12).

The chromatogram shown in Fig. 1 indicate that the fused-silica capillary column has the most inert inner surface.

TABLE I

PEAK-AREA RATIO (%) ON VARIOUS TYPES OF GLASS CAPILLARY AND FUSED-SILICA CAPILLARY COLUMNS

Column type	*D**	C_{10}	*ol*	*P*	C_{11}	*ac*	*A*	E_{10}	*am*
(F) Fused silica	100	100	100	100	100	100	100	100	100
(A) WCOT (untreated)	–**	100	–**	46.2	98.7	–**	87.3	77.3	–**
(B) WCOT (PEG-20M)	–**	100	–**	56.5	96.1	–**	86.5	69.3	65.6
(C) SCOT (Silanox)	–**	100	–**	75.0	96.6	–**	84.0	69.8	28.7
(D) WCOT ($BaCO_3$)	–**	100	49.2	83.1	95.0	–**	85.3	69.0	67.1
(E) WCOT ($BaCO_3$ + PEG-20M)	64.9	100	71.5	***	***	–**	88.9	73.4	69.5

* For abbreviations, see legend to Fig. 1.

** No peak.

*** Unresolved peaks.

The ratios of the peak-area counts for the polar compounds, to *n*-hydrocarbon (*n*-decane), obtained with glass columns, were normalized using values obtained with the fused-silica column. The results are shown in Table I. Though the WCOT column deactivated with PEG-20M after deposition of a $BaCO_3$ layer and the fused-silica column give rather similar chromatograms, they give considerably different normalized peak-area values.

When a non-polar stationary phase is used in the analysis of highly polar compounds, ordinary glass capillary columns give tailed peaks or no peaks at all —the component vapor has been adsorbed on the inner surface of the column— as shown in Fig. 1. A high-purity fused-silica capillary column, by contrast, gives sharp peaks, without tailing, for all the compounds. This may be attributable to the extremely low concentrations of the metal oxides and OH groups as previously reported by Dandeneau and co-workers[14,15] and others[13,16,19].

Relationship of conditioning temperature and time to the inertness of a fused-silica capillary column

A fused-silica capillary column gives very sharp peaks without tailing in analysis of the Grob test mixture, as shown in Fig. 1F. The Grob test mixture does not contain primary amines, which are more polar than dicyclohexylamine. To test the inertness of high-purity fused-silica capillary columns we prepared a sample mixture containing primary amines.

We found that highly polar compounds give peaks of different shapes depending on the conditioning time of the column, and we studied the effect of the column conditioning time on the inertness of fused-silica columns.

GC columns are usually conditioned at a temperature around the maximum operating temperature of the liquid phase, after the coating procedure. This conditioning is essential if columns of high stability and performance are to be obtained.

After the coating had been applied the fused-silica capillary column was conditioned by raising the column temperature to 280°C at 2°C/min and keeping it at 280°C for 40 h. The peak areas of the highly polar compounds relative to *n*-hydrocarbon (analysed at 150°C) increased with the length of conditioning time. After 10 h of conditioning, nicotine and dicyclohexylamine were recorded at almost the same

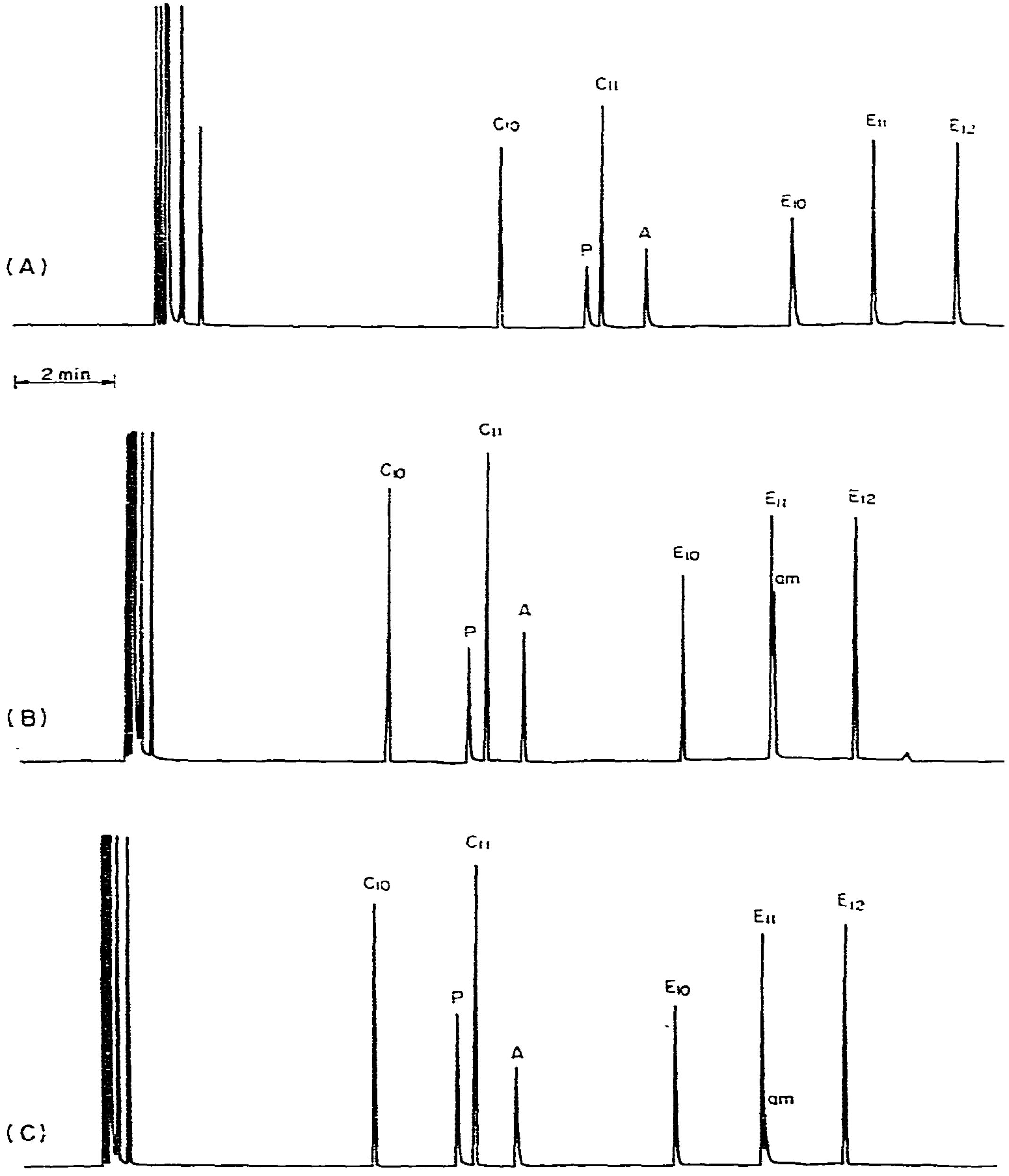


Fig. 1.

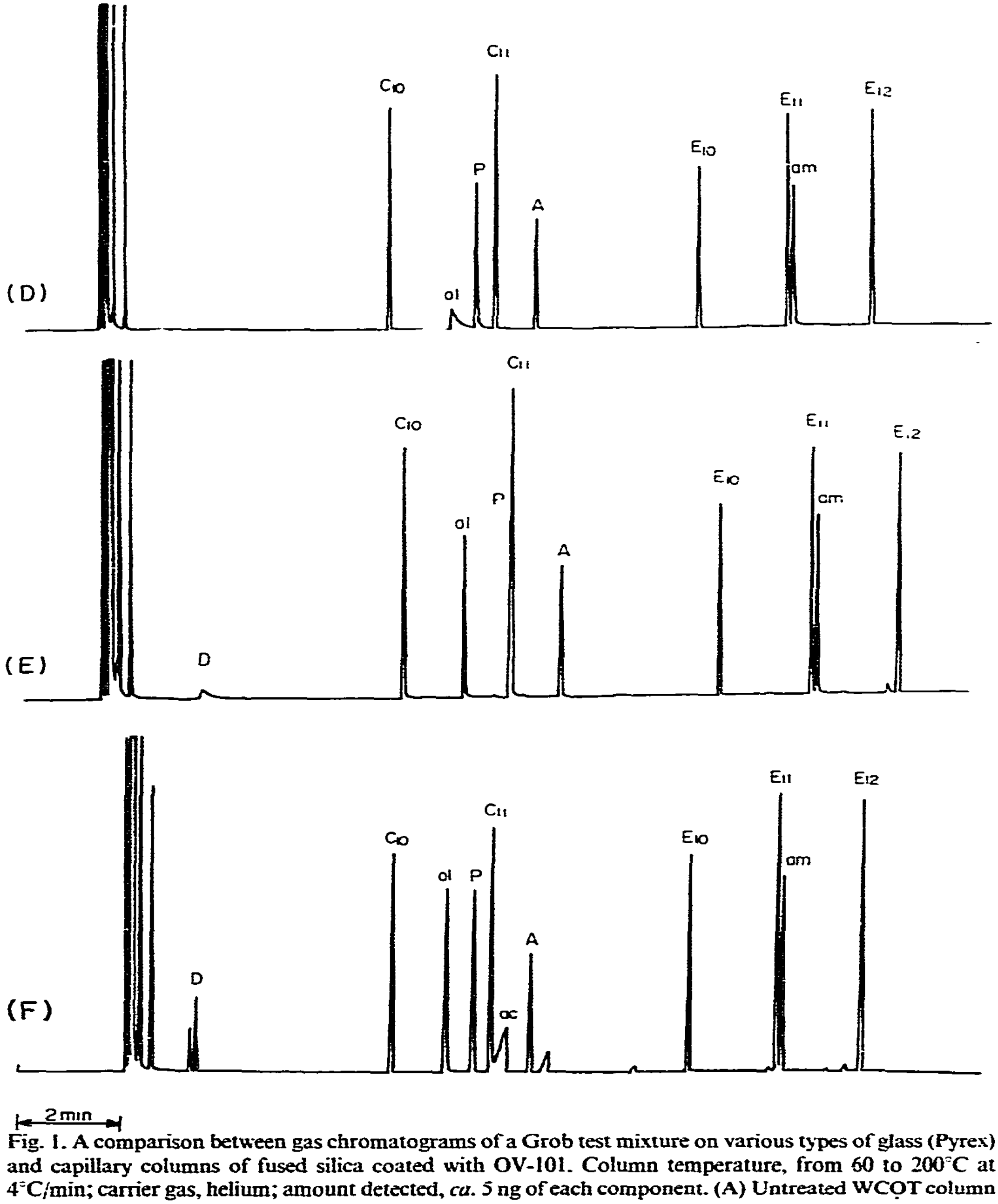


Fig. 1. A comparison between gas chromatograms of a Grob test mixture on various types of glass (Pyrex) and capillary columns of fused silica coated with OV-101. Column temperature, from 60 to 200°C at 4°C/min; carrier gas, helium; amount detected, *ca.* 5 ng of each component. (A) Untreated WCOT column (29 m × 0.25 mm I.D.); (B) WCOT column deactivated with PEG-20M (32 m × 0.25 mm I.D.); (C) SCOT column treated with Silanox 101 (28 m × 0.30 mm I.D.); (D) WCOT column with a $BaCO_3$ layer deposited (24 cm × 0.25 mm I.D.); (E) WCOT column deactivated with PEG-20M after deposition of a $BaCO_3$ layer (27 m × 0.25 mm I.D.); (F) untreated fused-silica WCOT column (25 m × 0.20 mm I.D.). Peaks: D = butane-2,3-diol; C_{10} = *n*-decane; ol = *n*-octanol; P = 2,6-dimethylphenol; C_{11} = *n*-undecane; A = 2,6-dimethylaniline; E_{10} = methyl caprate; am = dicyclohexylamine; E_{11} = methyl undecanoate; E_{12} = methyl laurate; ac = 2-ethylhexanoic acid.

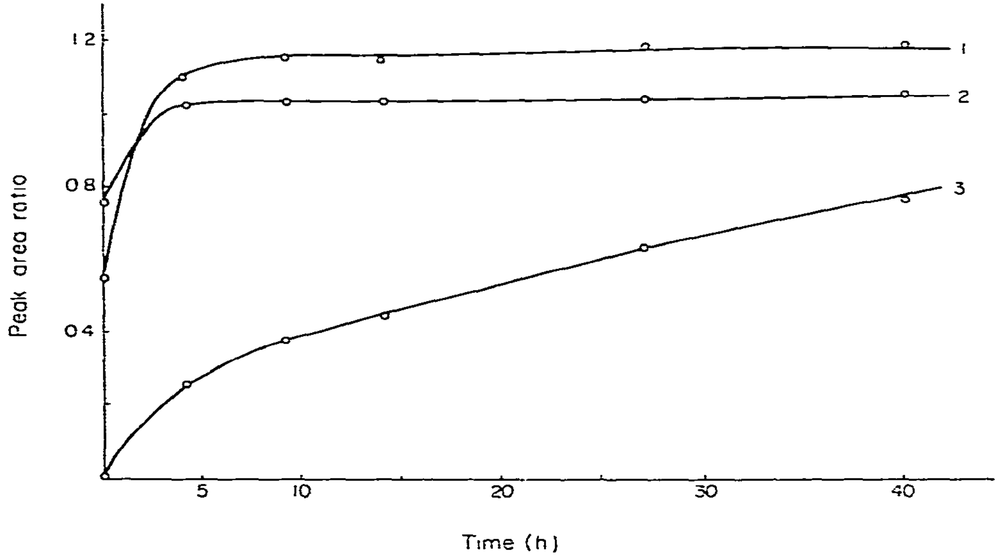


Fig. 2. Relationship of conditioning time (at 280°C) and peak-area ratio on OV-101 untreated fused-silica capillary column (25 m × 0.20 mm I.D.). Conditioning temperature, 280°C; column temperature during analysis; 150°C. Curves: 1 = dicyclohexylamine/n-C_{11}; 2 = nicotine/n-C_{11}; 3 = laurylamine/n-C_{11}.

response, but the response for laurylamine still increased with the length of conditioning time (Fig. 2).

When an unconditioned column was used (Fig. 3A), nicotine and dicyclohexylamine were recorded as tailing peaks, and laurylamine was not eluted at all, though n-alkanes were recorded as symmetric peaks.

When the column was conditioned for *ca.* 5 h, nicotine and dicyclohexylamine

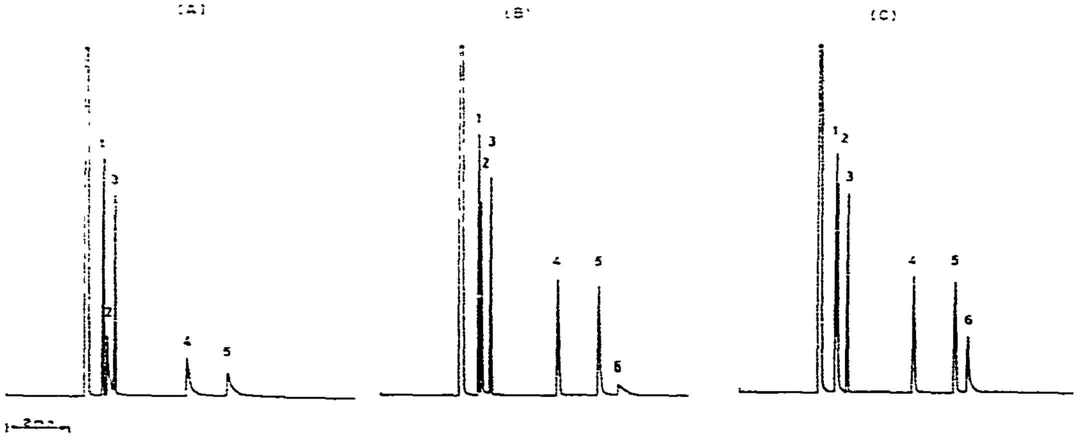


Fig. 3. Gas chromatograms after conditioning (at 280°C) for different periods. Column, fused-silica capillary coated with OV-101 (25 m × 0.2 mm I.D.); conditioning temperatures, 280°C; column temperature during analysis, 150°C. (A) Before conditioning; (B) after conditioning for *ca.* 5 h; (C) after conditioning for *ca.* 40 h. Peaks: 1 = n-decane; 2 = benzylamine; 3 = n-undecane; 4 = nicotine; 5 = dicyclohexylamine; 6 = laurylamine.

gave symmetric peaks but laurylamine, which is more polar, gave a peak with a rather large tailing (Fig. 3B).

When the column was conditioned for *ca.* 40 h, the laurylamine peak became more symmetric and increased in size (Fig. 3C).

These experiments show (a) that a high-purity fused-silica capillary column conditioned for *ca.* 10 h longer can give symmetric peaks of nicotine and dicyclohexylamine which are often used to test column inertness; (b) that a high-purity fused-silica capillary column, without any special treatment (deactivation), but conditioned in the ordinary way, can give sharp peaks without tailing for polar compounds, even for amines (except primary amines); and (c) that, in order to obtain sharp peaks for primary amines, it is necessary to condition the column at a temperature above 280°C.

Fig. 4 shows the relationship between the inertness of the column and the conditioning time. (The conditioning temperature was 350°C.) Nicotine and dicyclohexylamine are recorded at constant response after 5 h of conditioning, and laurylamine after 15 h. It may be concluded from Fig. 4 that merely raising the conditioning temperature renders the fused-silica capillary columns inert enough for analysis of primary amines, and that the tailing of the peaks for highly polar compounds can be reduced by conditioning the column for a longer time and/or at a higher temperature.

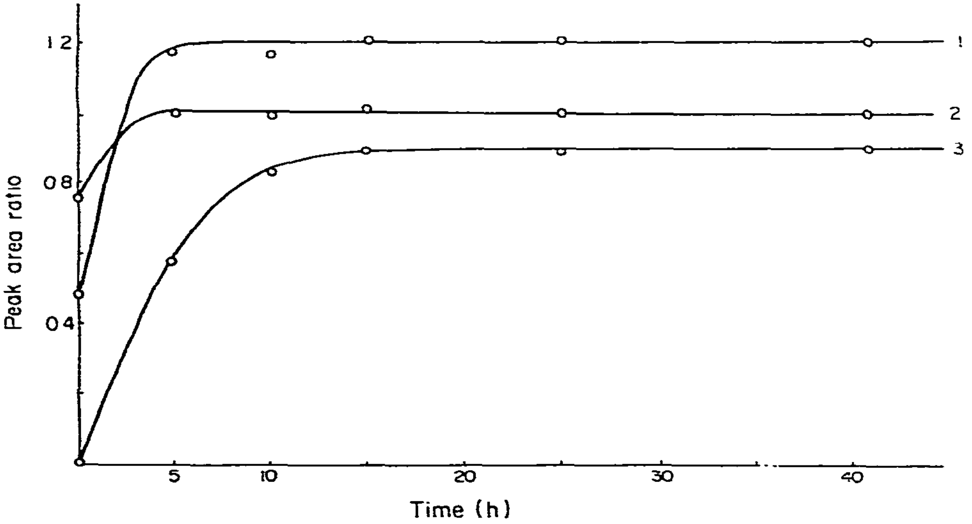


Fig. 4. Relationship of conditioning time (at 350°C) and peak-area ratio on OV-101 untreated fused-silica capillary column (25 m × 0.20 mm I.D.). Conditioning temperature, 350°C; column temperature during analysis, 150°C. Curves: 1 = dicyclohexylamine/n-C_{11}; 2 = nicotine/n-C_{11}; 3 = laurylamine/n-C_{11}.

Even the high-purity fused-silica capillary is not totally inert, but this residual activity can be reduced through conditioning. This deactivation effect may be explained by the fact that the polymethylsiloxane (stationary phase) decomposes partially, and the decomposition products become bonded to the active sites, as described by Schomburg *et al.*[12]. This deactivation process brings about no significant change in the capacity ratio (k). The decrease of the k value caused by 15 h of conditioning at 350°C was only 5%. It is not necessary to wash or re-coat the column after deactivation process, as reported by Schomburg and co-workers[12,13,19].

Comparison between an untreated fused-silica capillary column and that deactivated with PEG-20M

The fused-silica capillary column deactivated with PEG-20M was prepared by the method described in the Experimental section, except for the column conditioning. This column was not conditioned so that the deactivation effect would not be lost by conditioning at a rather high temperature. Then, after a coating of the liquid phase had been applied, this column was conditioned by raising the column temperature from room temperature to 280° at 2°C/min. The conditioning was stopped when the column temperature reached 280°C, and the column was cooled to 150°C. The highly polar test mixture was analysed, and a comparison was made with the untreated fused-silica capillary column. Fig. 5 shows the two chromatograms obtained; no differences can be seen.

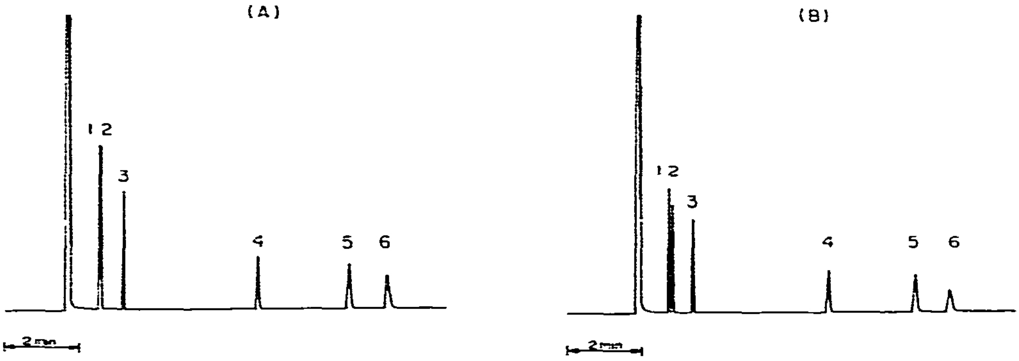


Fig. 5. Gas chromatograms of a polar test mixture on fused-silica capillary columns coated with OV-101. (A) Untreated fused-silica capillary column conditioned at 300°C (30 h) (25 m × 0.20 mm I.D.). (B) Fused-silica capillary column deactivated with PEG-20M (before conditioning) (25 m × 0.20 mm I.D.). Column temperature, 150°C. Peaks: 1 = *n*-decane; 2 = benzylamine; 3 = *n*-undecane; 4 = nicotine; 5 = dicyclohexylamine; 6 = laurylamine.

It has been reported that deactivation with PEG-20M loses its effect when the column is used at a temperature above 250°C[16–18]. In order to investigate this, a fused-silica capillary column deactivated with PEG-20M was conditioned at 280°C, and then compared with an untreated fused-silica capillary column.

Fig. 6 shows how the peak-area ratios of highly polar compounds to that of a *n*-hydrocarbon change with the length of the conditioning time at 280°C.

The relative responses for nicotine and dicyclohexylamine were almost constant, but that for laurylamine decreased greatly with the conditioning time, indicating that deactivation with PEG-20M loses its effect. The constant response for nicotine and dicyclohexylamine may be due to the high purity of the fused-silica capillary column.

It may be concluded from these data that a fused-silica capillary column deactivated with PEG-20M loses its inertness when used at a high temperature (280°C)

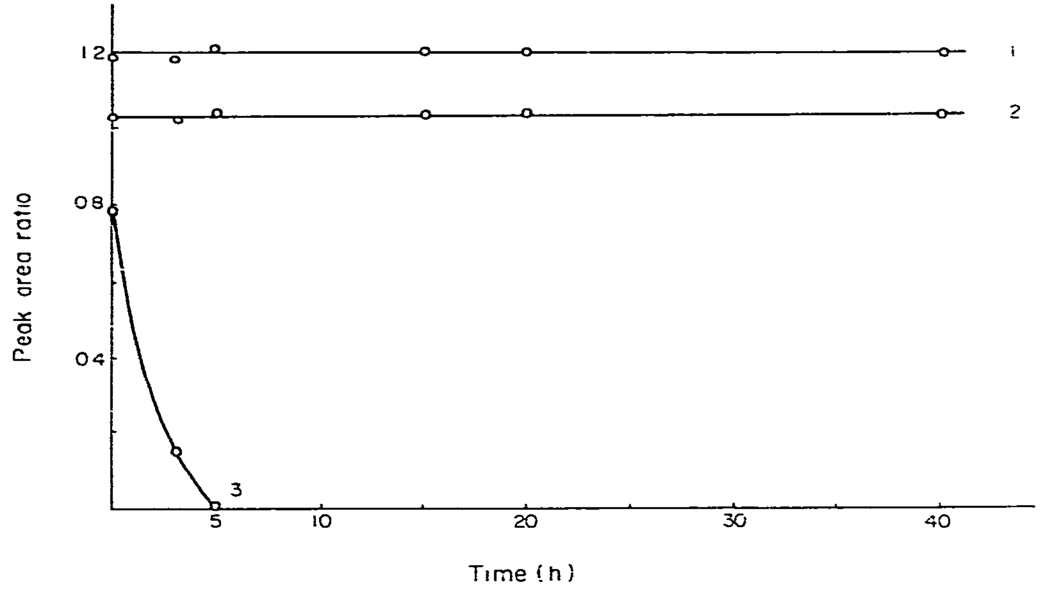


Fig. 6. Relationship of conditioning time (at 280°C) and peak-area ratio on OV-101 fused-silica capillary column (25 m × 0.20 mm I.D.) deactivated with PEG-20M. Conditioning temperature, 280°C; column temperature during analysis, 150°C. Curves: 1 = dicyclohexylamine/n-C_{11}; 2 = nicotine/n-C_{11}; 3 = laurylamine/n-C_{11}.

(Fig. 6), but that an untreated fused-silica capillary column retains its inertness even at temperatures above 280°C, as shown in Figs. 4 and 5.

Influence of stationary phase film thickness on column inertness

Six fused-silica capillary columns were prepared with different film thicknesses as described in the Experimental section and were conditioned at 300°C for 30 h. The test mixture sample containing primary amines was analysed using these columns, and the peak-area ratio of dicyclohexylamine and laurylamine to n-undecane were plotted against k which correspond to the film thicknesses (Fig. 7).

As shown in Fig. 7, the peak-area ratios are almost equal for the k values from 1.4 to 6.2. Calculated by Kaiser's equation[27], the k values 1.4 and 6.2 approximately correspond to film thicknesses of 0.17 μm and 0.52 μm, respectively.

Fig. 8 shows the chromatograms obtained by a thin-film (0.17 μm) column and a thick-film (0.52 μm) column. Both columns give sharp peaks, even for primary amines. It may be concluded that the inertness of column is not influenced at all by the thickness of the stationary-phase film in a range from 0.17 μm to 0.52 μm.

Quantitation of polar compounds with a high-purity fused-silica capillary column

It was necessary to perform a quantitative study in order to investigate the activity of the inner surface of a column. In analysis of polar compounds such as primary amines, the peaks have different shapes in the low column-load range. In order to investigate the inertness of the untreated fused-silica capillary column, sample mixtures of octanol, 2,6-dimethylphenol, dicyclohexylamine, laurylamine and

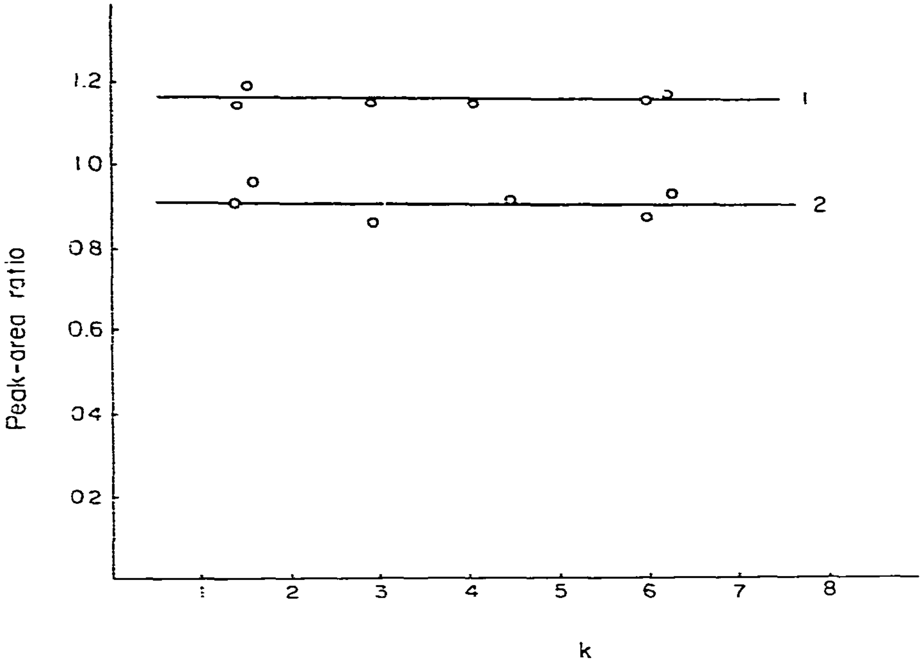


Fig. 7. Effects of capacity ratio (film thickness of stationary phase) on peak-area ratio. Column, untreated fused-silica capillary coated with OV-101 (25 m × 0.20 mm I.D.); column temperature, 150 C. Curves: 1 = dicyclohexylamine n-C_{11}; 2 = laurylamine n-C_{11}.

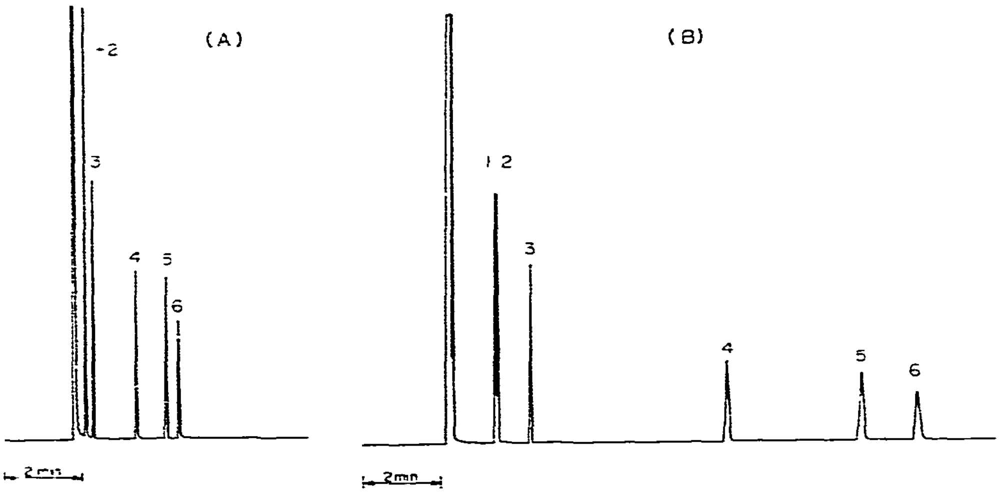


Fig. 8. Gas chromatograms of a polar test mixture on a fused-silica capillary column with different film thicknesses. Stationary phase, OV-101; column temperature, 150°C. Column A: film thickness, 0.17 μm (k = 1.4); 25 m × 0.20 mm I.D.; column B: film thickness, 0.52 μm (k = 6.2); 25 m × 0.20 mm I.D. Peaks: 1 = n-decane; 2 = benzylamine; 3 = n-undecane; 4 = nicotine; 5 = dicyclohexylamine; 6 = laurylamine.

n-alkanes were analysed. The ratios of peak areas of polar compounds to that of the *n*-hydrocarbon (*n*-undecane) were plotted against column loads. The data presented in Fig. 9 show (i) that 2,6-dimethylphenol and dicyclohexylamine are not adsorbed at all, even at the level of 0.1 ng, (ii) that octanol can be measured reliably down to the 0.3-ng level, and (iii) that laurylamine, which is more polar, can be measured down to the 2-ng level.

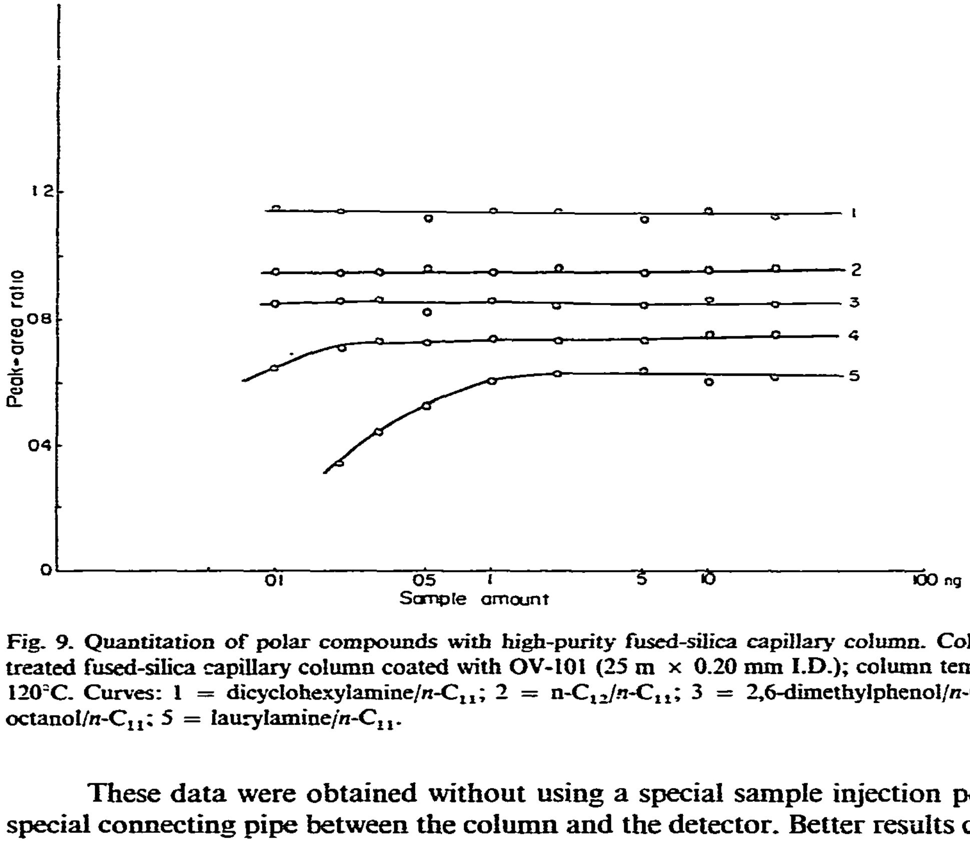


Fig. 9. Quantitation of polar compounds with high-purity fused-silica capillary column. Column, untreated fused-silica capillary column coated with OV-101 (25 m × 0.20 mm I.D.); column temperature, 120°C. Curves: 1 = dicyclohexylamine/n-C_{11}; 2 = n-C_{12}/n-C_{11}; 3 = 2,6-dimethylphenol/n-C_{11}; 4 = octanol/n-C_{11}; 5 = laurylamine/n-C_{11}.

These data were obtained without using a special sample injection port or a special connecting pipe between the column and the detector. Better results could be expected if a fused-silica liner were used in place of the glass liner in the sample injection port.

Schomburg[28] made quantitative analysis of polar compounds by means of a glass capillary column coated with polypropylene glycol, which has an intermediate polarity. (He did not try a non-polar liquid phase, which can cover the active sites of the column only incompletely.) The peaks of dicyclohexylamine (a secondary amine) and octylamine (a primary amine) show a strong adsorption below the 30-ng level[28]. Dandenau and Zerenner[14] analysed dicyclohexylamine and 3,5-dimethylphenol with a fused-silica capillary column deactivated with PEG-20M. They found that the column did not adsorb dicyclohexylamine, even at subnanogram levels, but that it did adsorb 3,5-dimethylphenol at the 10-ng level. (They used, as the index of adsorption, the ratio of peak areas to n-C_{15} for dicyclohexylamine, and to *p*-dimethylbenzene for 3,5-dimethylphenol.)

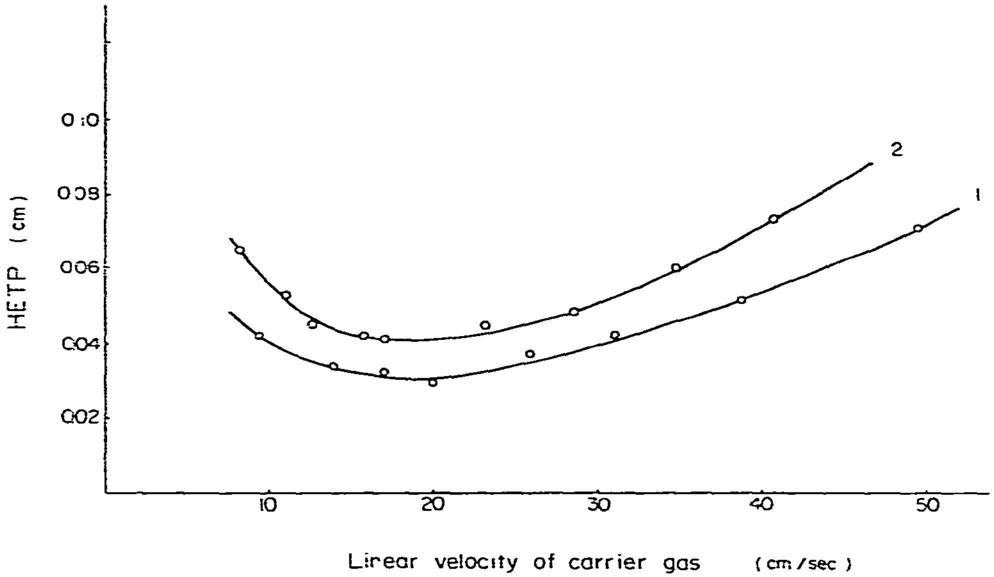


Fig. 10. HETP curves before and after 550 h continuous run at 280°C. Column, untreated fused-silica capillary coated with OV-101 (25 m × 0.20 mm I.D.); column temperature during continuous run, 280°C; column temperature during analysis, 120°C; samples, *n*-tridecane. Curves: 1 = before 550 h running; 2 = after 550 h running.

Compared with these data, our high-purity fused-silica capillary column ensures far better results, indicating the higher degree of inertness of the inner surface.

Thermal stability and service life of OV-101 high-purity fused-silica capillary column

In order to study the stability and service life at high temperatures, an OV-101 untreated fused-silica capillary column was operated at a column temperature of 280°C, a sample injection port temperature of 350°C, a carrier gas flow-rate of 0.5 ml/min, for 550 h continuously. This corresponds to *ca.* 70 working days (2.3 months), at 8 h per day. The column temperature of 280°C, which is almost the upper temperature limit of the liquid phase, is a severe condition for an OV-101 WCOT column.

Despite the severe conditions of this continuous run, the column efficiency did not decrease greatly during the test (see Fig. 10); the smallest height equivalent to a theoretical plate (HETP) increased by only 30%, from 0.029 cm (*ca.* 3400 plates/m) to 0.041 cm (*ca.* 2400 plates/m). In other words, even after a continuous run under such severe conditions, the column still ensured 2400 plates/m, which is high enough for analyses of ordinary samples (see Fig. 11).

This column provided chromatograms of polar test mixture samples (Grob test mixture and primary amine mixture) of excellent separation and ideal shape of peaks without tailing, proving that the column still has satisfactory separating efficiency and inertness (see Fig. 11).

It may be expected from these experiments that our high-purity fused-silica capillary columns can be used quite stably at a column temperature of 280°C, and that their service life is quite long. Needless to say, the column will have a longer life at a lower column temperature.

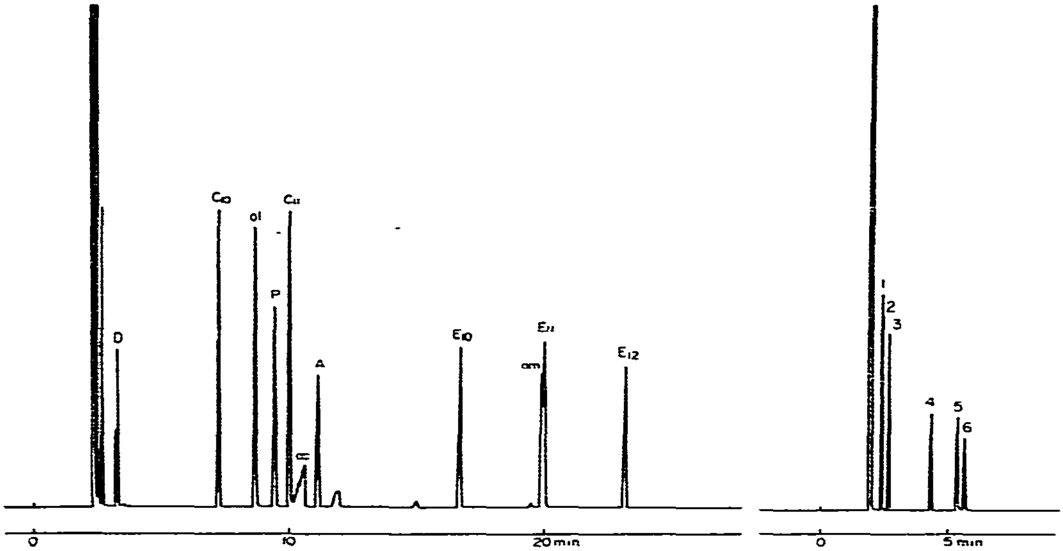


Fig. 11. Gas chromatograms of polar test mixtures on untreated fused-silica capillary column after 550 h running at 280°C. Column, see Fig. 10; conditions and peaks, see Figs. 1 and 3.

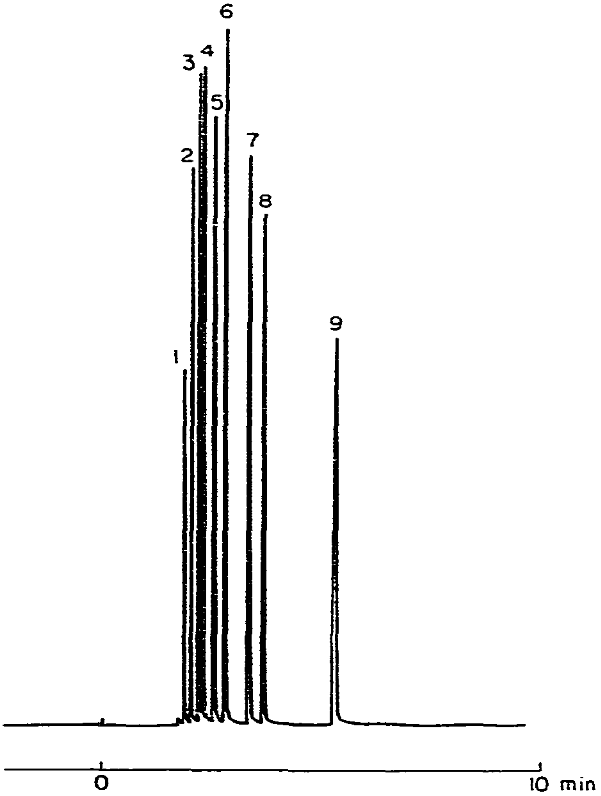


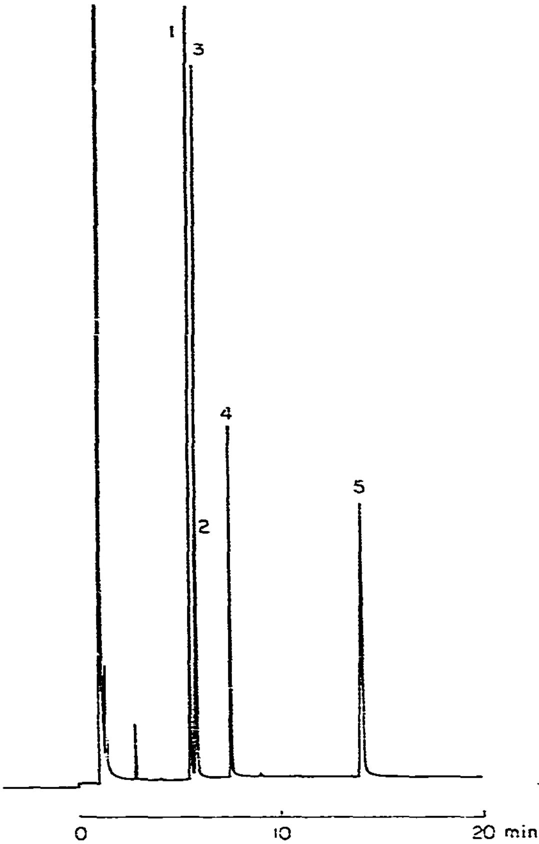
Fig. 12. Gas chromatogram of free fatty acids (aqueous solution) on an untreated fused-silica capillary column (25 m × 0.20 mm I.D.) coated with OV-101. Column temperature, 120°C; carrier gas, helium; flow-rate, 25 cm/sec. Peaks: 1 = acetic acid; 2 = propionic acid; 3 = isobutyric acid; 4 = butyric acid; 5 = isovaleric acid; 6 = valeric acid; 7 = isocaproic acid; 8 = caproic acid; 9 = heptanoic acid (*ca.* 2 ng of each component).

APPLICATIONS

Figs. 12–16 show the chromatograms of the compounds having polar functional groups, such as OH groups, COOH groups, and NH groups, which are difficult to obtain as sharp peaks.

The data in Fig. 12 show that a high-purity fused-silica capillary column coated with polymethylsiloxane (OV-101), a non-polar liquid phase, can provide sharp peaks, without tailing, of free fatty acids.

Figs. 13–16 also show that this column can provide sharp peaks in direct analysis of steroids, estrogens, anti-convulsants, and sterols in soy beans, which are generally analysed after derivatization.



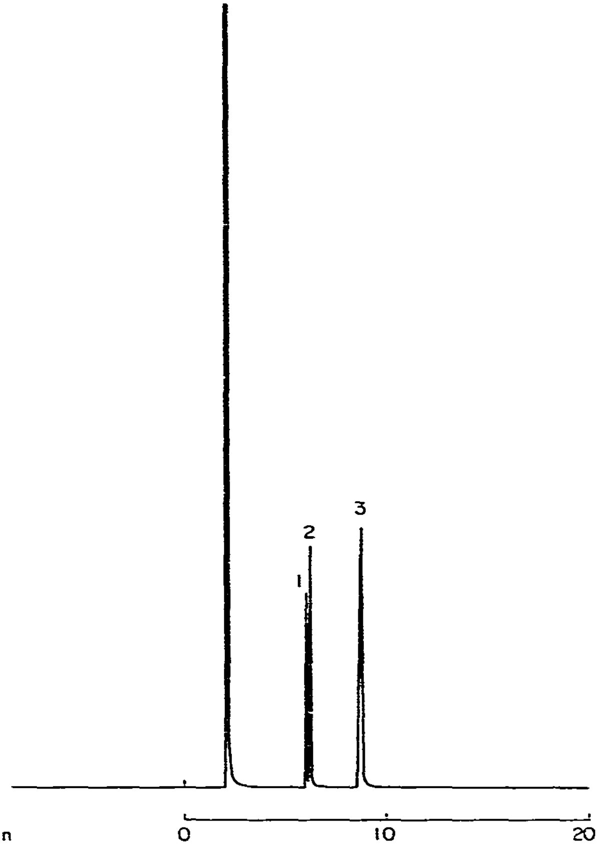
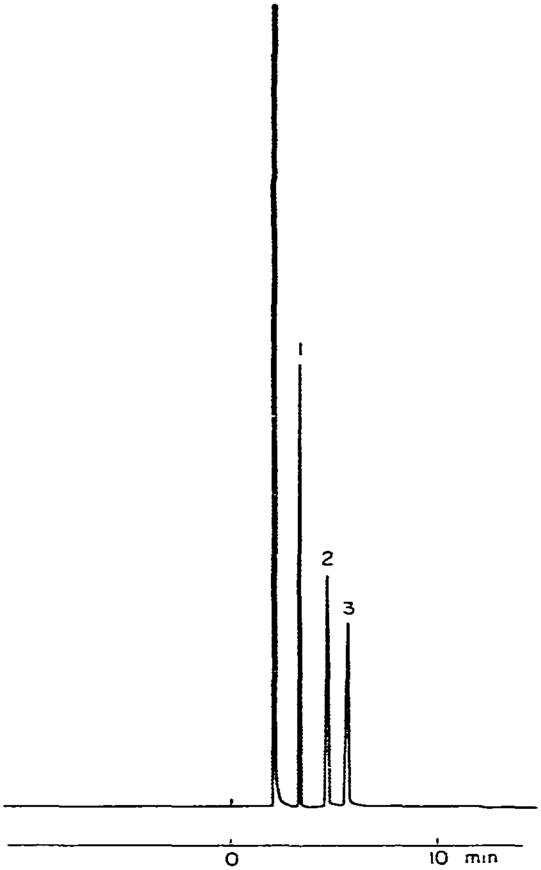


Fig. 13. Gas chromatogram of non-derivatized steroids on untreated fused-silica capillary column (25 m × 0.20 mm I.D.) coated with OV-101. Column temperature from 230 to 280°C at 4°C/min; carrier gas, helium; flow-rate, 30 cm/sec. Peaks: 1 = etiocholanolone; 2 = dehydroepiandrosterone; 3 = androsterone; 4 = pregnanediol; 5 = cholesterol.

Fig. 14. Gas chromatogram of non-derivatized estrogens on untreated fused-silica capillary column (25 m × 0.20 mm I.D.) coated with OV-101. Column temperature, 250°C; carrier gas, helium; flow-rate, 25 cm/sec. Peaks: 1 = estrone; 2 = estradiol; 3 = estriol.



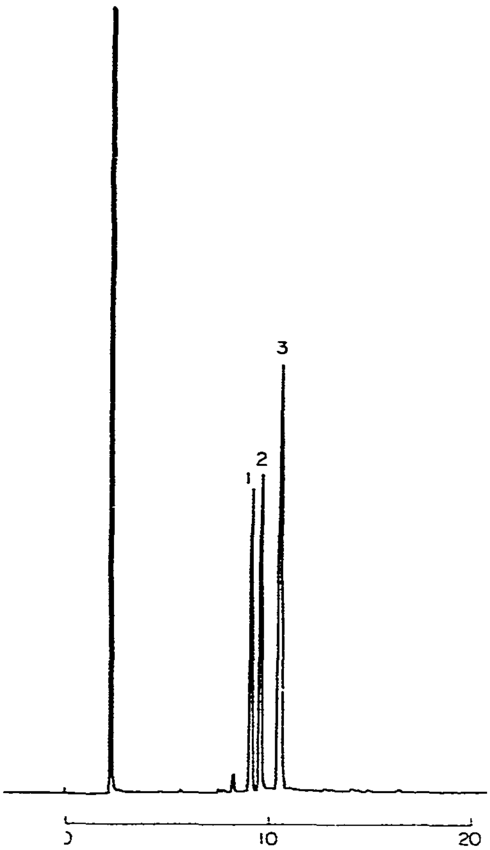


Fig. 15. Gas chromatogram of non-derivatized anticonvulsants on untreated fused-silica capillary column (25 m × 0.20 mm I.D.) coated with OV-101. Column temperature, 230°C; carrier gas, helium; flow-rate, 25 cm/sec. Peaks: 1 = phenobarbital; 2 = primidone; 3 = phenytoin.

Fig. 16. Gas chromatogram of non-derivatized sterols in soy beans on untreated fused-silica capillary column (25 m × 0.20 mm I.D.) coated with OV-101. Column temperature, 280°C; carrier gas, helium; flow-rate, 30 cm/sec. Peaks: 1 = campesterol; 2 = stigmasterol; 3 = β-sitosterol.

CONCLUSIONS

High-purity (99.9999 %) fused silica containing less than 1 ppm of metal oxides and silanol groups (OH groups), which are thought to be the cause of active sites on the inner surface of column tubings, was tested as a material for capillary columns for GC.

A capillary column made of this fused silica, which was coated with methylpolysiloxane (OV-101), a non-polar liquid phase, and conditioned in a suitable manner, ensured better thermal stability and inertness than capillary columns deactivated with PEG-20M.

It is necessary to investigate further the influence of the concentration of OH groups on the activity of the inner surface of columns.

The performance of high-purity fused-silica columns coated with a polar liquid phase will be reported in future.

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