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Preparation of deactivated metal capillary for gas chromatography

Y. Takayama*, T. Takeichi

School of Materials Science, Toyohashi University of Technology, Toyohashi 441, Japan

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Abstract

Research was conducted to prepare a deactivated metal (stainless-steel) capillary that is physically tough and thermally stable compared with a fused-silica capillary. A key step in the preparation is the formation of a silicon layer by the thermal decomposition of monosilane. The silicon formed on the metal surface is assumed to exist as large grains compared with that on the glass surface. Activation of metal capillary was observed, which is assumed to be due to the migration of silicon grains on the metal surface during the heating test of the capillary, thus exposing the metal surface. Such a phenomenon was not found with a glass capillary treated with monosilane. These observations suggest that the problem comes from the wettability of the metal surface with silicon. The problem was solved by oxidizing the metal surface prior to the monosilane treatment. As a consequence, it became possible to prepare a deactivated metal capillary (DMC) thermally stable even above 400°C. A column coated with a commercially available gum-like liquid phase could not withstand continuous heating at 280°C. On the other hand, a column coated with dimethylpolysiloxane by the in situ (in the capillary) condensation of oligomer prepared from dimethyldichlorosilane showed excellent thermal stability: the column withstood continuous heating above 400°C and also repeated heating by programming up to 450°C. Various advantages of DMC over a fused-silica capillary (FSC) were also made clear. Hence DMC, as a metal capillary of the second generation, should replace FSC.

1. Introduction

Capillary column (capillary column signifies, in this article, a tube coated with liquid stationary phase to differentiate it from a capillary that signifies a tube that is not coated) was invented by Golay in 1957 [1]. At first, a metal was used as the material for the capillary. Handling was easy, but the application range was very limited because of the highly active inner surface.

Metal capillaries as columns for GC were

given up in 1960, and glass capillaries became used. It was found, however, that glass capillaries also possess considerable activity and that homogeneous coating of a medium-polarity or polar liquid phase is difficult. These problems were overcome with great effort and, at the end of 1970s, capillary GC finally came into bloom with the use of deactivated glass capillaries.

Just at this time, fused-silica capillaries (FSC) were reported [2]. FSC are as inert as deactivated glass capillaries and, further, they are flexible. Therefore, FSC completely replaced glass capillaries, which were no longer consid-

* Corresponding author.

ered. As an FSC is covered with a polyimide thin film, we thought that FSC could not be used at high temperatures (above 350°C), and that, even when used below 350°C, FSC is unexpectedly easily damaged owing to the polyimide, which forms cracks and becomes brittle by losing small amounts of volatiles, which cause a notch effect.

In 1980, we started a project to develop a metal capillary of the second generation that is as inert as FSC. With the same purpose, Pretorius's group [3–7] reported results on this aspect for several years after 1981. They started with a stainless-steel capillary and subsequently shifted to a nickel capillary, with which they reported that they succeeded in the preparation of a deactivated metal capillary. As they did not report on the application of the capillary, we doubt if they accomplished the technology successfully. Our methodology is similar to theirs in that thermal decomposition of monosilane is used, but the decomposition conditions are very different. Our conditions are superior, from the industrial point of view, in that the productivity is much better. Further, we introduced an oxidation process of the inner surface of the metal capillary prior to the monosilane treatment, with which it became possible to make a metal capillary that is thermally stable for continuous use above 400°C. We found that *in situ* (in the capillary) synthesis [8,9] of liquid phase by thermal condensation of a diol-type oligomer enabled us to realize columns that withstand repeated use by programming up to 450°C and holding at that temperature for 10 min. We applied the metal capillary or the column where FSC or glass capillaries are difficult to use [10–15]. We also prepared enantiomer separation columns where breakage of the columns is costly [16].

In the 5-year period since 1986, we asked a company to produce and sell the deactivated metal capillary columns (DMCC), and checked possible problems in manufacturing and claims against quality. As a result, it was found out that, although the production of DMC takes time, the productivity is good enough for industrial use, and we received no claim against ca. commercialized 150 columns. Hence it was made

clear that our DMC, taking advantage of the excellent thermal stability and the lack of fear of breakage, is more useful than FSC. Although the manufacturing technology of our DMC needs to be studied further, theoretically, we considered it useful to present the results of our efforts so far.

2. Preparation of deactivated metal capillary

The following description is for a commercial stainless-steel capillary of 0.25 mm I.D. and 0.6–0.7 mm O.D.

2.1. Acid washing of metal capillary

Per 25 m of capillary, 10 ml of chloroform, 10 ml of methanol and then 10 ml of distilled water were passed through at the rate of 1 ml/min. The capillary was filled with concentrated HNO₃ and kept standing at 80°C for 1 h. After cooling, HNO₃ was removed from the capillary, which was then washed by passing 10 ml of distilled water, 10 ml of methanol and then 10 ml of chloroform at the rate of 1 ml/min. Chloroform was removed by a flow of nitrogen gas. The flow-rate was then adjusted to 10–20 ml/min, and the capillary was dried at 200°C for 1 h.

2.2. Oxidation of capillary

Under a continuous oxygen flow at 98.6 kPa, the above-treated capillary was heated to 250°C and then maintained at that temperature for 1 h.

2.3. Treatment with monosilane

Using the apparatus shown in Fig. 1, treatment of the inner surface of the capillary with monosilane (SiH₄), was performed. Monosilane was sealed in the capillary (14) at 295.7 kPa (3 kg/cm²) and valves V1 and V2 were shut. Thermal decomposition of the sealed monosilane was conducted at 530°C for 15 min, after which the capillary was evacuated. Monosilane was sealed again at 295.7 kPa and thermally de-

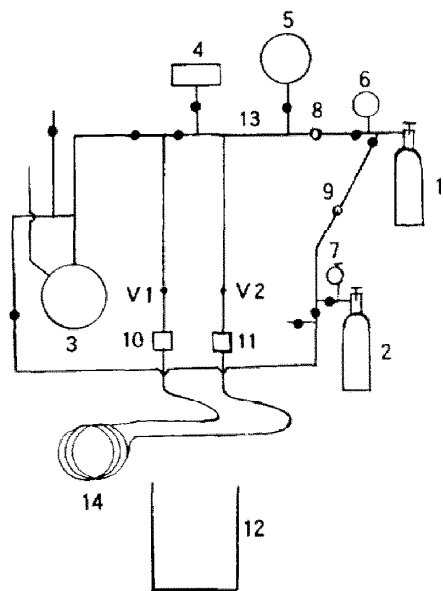


Fig. 1. Apparatus for treating capillary with monosilane. 1 = Monosilane gas cylinder; 2 = nitrogen gas cylinder; 3 = vacuum pump; 4 = Pirani gauge; 5–7 = pressure gauges; 8, 9 = needle valves; 10, 11 = joints; 12 = electric furnace; 13 = stainless-steel manifold line (I.D. 2 mm); 14 = metal capillary; ● = stop valve.

composed similarly. The capillary was evacuated and removed from the apparatus.

2.4. Polarity test for the capillary treated with monosilane

A polarity test was performed following the Grob's polarity test [17,18]. As a precolumn we employed a deactivated non-polar capillary column such as OV-1, $d_f = 0.2$ mm, 20 m \times 0.25 mm I.D. The test mixture was a heptane solution of 0.5 mg/ml of each solute shown in Table 1. The test parameters were as follows: nitrogen flow-rate; 40 cm/s; initial temperature, 60°C; pro-

gramming rate, 3°C/min; sample volume, 1 ml; and splitting ratio, 1:100.

We can use the following two criteria to evaluate the capillary treated with monosilane: (1) the shape of tailing for each peak of hydrocarbon should be the same as that obtained with the precolumn alone, and (2) tailing of 2,6-dimethylphenol should be only slightly larger than that obtained with the precolumn alone. In this case, 1-decanol generally does not appear, and the peak height of 2,6-dimethylaniline is low.

2.5. Treatment with octamethyltetrasiloxane or other compounds to deactivate the capillary treated with monosilane

For preparation of non-polar column

Prior to the coating of a liquid phase, treatment with octamethyltetrasiloxane was performed. When the oligomer of a non-polar liquid phase terminated with hydroxyl groups is to be coated, octamethyltetrasiloxane treatment can often be omitted. For the easily tailing solutes, octamethyltetrasiloxane treatment should be done prior to the coating.

Octamethyltetrasiloxane treatment was performed as follows. A plug of 100% octamethyltetrasiloxane was inserted into the capillary treated with monosilane so that the length of the plug was ca. 10% of the capillary, and dynamic coating was conducted. The rate of movement of the plug was ca. 2 cm/s. After passing the plug, the capillary was dried with a nitrogen flow for 1 h. Both ends of the capillary were sealed under vacuum. The capillary was treated at 400°C for 10 h in an oven. After being

Table 1
Test mixture

Solute	Abbreviation	Solute	Abbreviation
2,3-Butanediol	D	1-Decanol	ol
<i>n</i> -Butyric acid	Ba	<i>n</i> -Tridecane	C ₁₃
2,6-Dimethylphenol	P	<i>n</i> -Tetradecane	C ₁₄
2,6-Dimethylaniline	A	<i>n</i> -Heptadecane	C ₁₇

cooled, the capillary was opened and rinsed with dichloromethane [19].

For preparation of polar column

Although treatment depends on the liquid phase to be coated later, 1,3-diphenyl-1,1,3,3-tetramethyldisilazane (DPTMDS) [20] was generally used instead of octamethyltetrasiloxane. The procedure was similar to that with octamethyltetrasiloxane. When Carbowax (CW) is to be used as a liquid phase, Auc et al.'s ageing method [21] was conducted as a further treatment of the capillary treated with monosilane. That is, a plug of a 5% dichloromethane solution of CW was inserted into the capillary so that the length of the plug was ca. 20% of the capillary, and dynamically coated at the rate of 2 cm/s. After drying with a nitrogen flow, both ends were sealed and heated at 280°C for 3 h. The seal was opened and the capillary was rinsed with dichloromethane. For the coating of Silar 5CP as a liquid phase, a plug of a 7% solution of 5CP in dichloromethane was used as further treatment of the capillary instead of CW mentioned above. Other details can be found elsewhere [20,22–25].

2.6. Polarity test for the capillary treated with the process in Section 2.5

Quality evaluation was performed under the same test parameters as mentioned in Section 2.4, using a precolumn coated with the liquid phase intended to be coated, and at a programming rate of 1°C/min if necessary. The aim is to obtain a chromatogram the same as that with the precolumn, except for retention time.

3. Results and discussion

3.1. Research on treatment of glass capillary with monosilane

A study was conducted to obtain operating parameters for monosilane (SiH_4) treatment. A Pyrex glass capillary with an untreated inner surface was submitted to monosilane treatment

using the apparatus shown in Fig. 1, and a chromatogram of the monosilane-treated capillary was obtained to evaluate the degree of deactivation following the procedure in Section 2.4. In Sections 3.1 and 3.2, columns coated dynamically with CW20M or 40M were used as precolumns unless mentioned otherwise. The test mixture often did not include 2,6-dimethylphenol and 2,6-dimethylaniline. Although the amounts of solutes in the test mixture are not perfectly accurate, they are sufficient as the relative retention and shape of each peak are discussed in this paper. The following results were obtained.

(i) When ca. 10 m of capillary was used, it is difficult to recognize the difference in the relative retention of solutes between the chromatogram and that using the precolumn alone. When a longer capillary is used, however, the late elution of hydrocarbons compared with other solutes becomes substantial (Figs. 2–4).

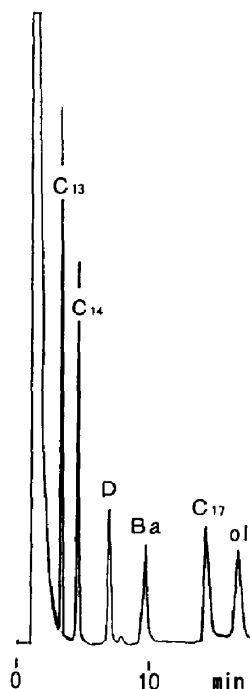


Fig. 2. Chromatogram of test mixture on precolumn coated with CW20M alone. Precolumn, 30 m \times 0.28 mm I.D. Test parameters: initial oven temperature, 80°C; programming rate, 1°C/min; N_2 flow-rate, 0.5 m/s. Test mixture and abbreviations: see Table 1, but not containing P and A.

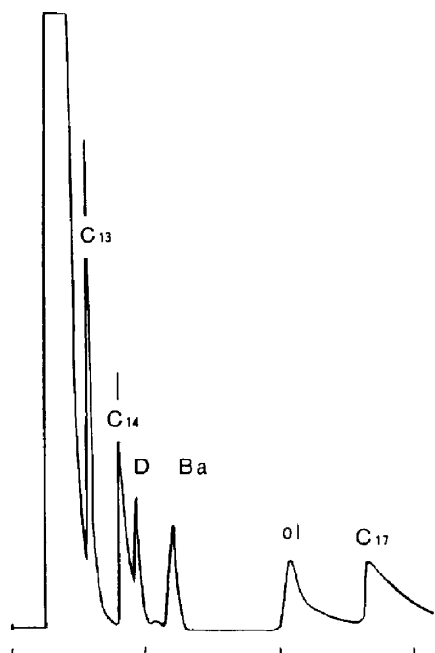


Fig. 3. Polarity test chromatogram of monosilane-treated glass capillary with precolumn of CW20M. Capillary size, 60 m \times 0.28 mm I.D. Parameters for monosilane treatment: monosilane seal pressure, 98.6 kPa; thermal decomposition, 375°C for 15 min. Test parameters: see Fig. 2.

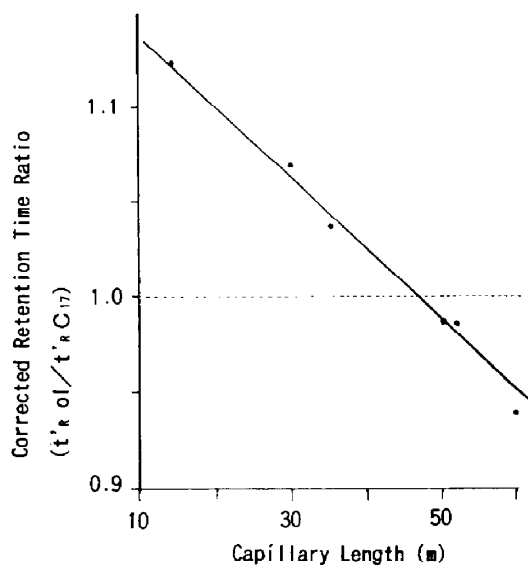


Fig. 4. Elution order of 1-decanol and C_{17} , depending on capillary length. Glass capillary, I.D. 0.28 mm. Parameters for monosilane treatment: 98.6 kPa, 400°C, 15 min. Test parameters: see Fig. 2.

(ii) As the decomposition temperature of monosilane is elevated from 375 to 550°C (softening temperature of the capillary), the peaks of hydrocarbons become narrower, keeping a triangular shape with sharp front, and tend to show leading in shape at 500–550°C (Fig. 5). The retention times of solutes, however, are almost constant independent of the decomposition temperature.

(iii) The peak of 1-decanol is higher when the decomposition temperature of monosilane is low than when the decomposition temperature is high, as shown in Figs. 3 and 5. When the decomposition temperature exceeds 500°C, the peak of 1-decanol becomes very small or is absent.

(iv) At decomposition temperatures between 400 and 550°C, the chromatograms obtained were independent of the decomposition time period during 5–60 min at each temperature.

(v) For the capillary of 0.28 mm I.D., the seal pressure of monosilane should be above ca. 50

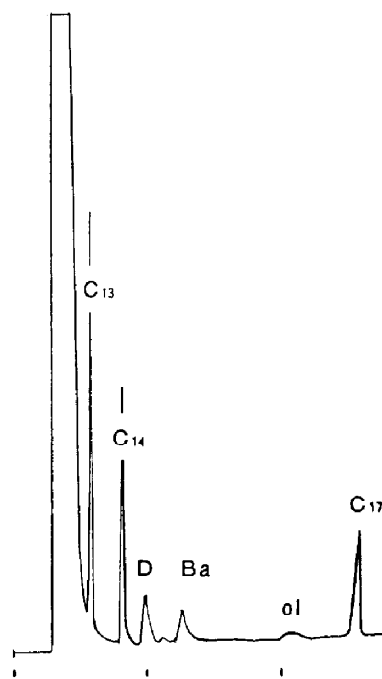


Fig. 5. Polarity test chromatogram on monosilane-treated glass capillary with precolumn of CW20M. Capillary size as in Fig. 3. Parameters for monosilane treatment: 98.6 kPa, 550°C, 15 min. Test parameters: see Fig. 2.

kPa, which corresponds to a thickness of silicon of 178 Å. The capillary treated in that way, when further treated with octamethyltetrasiloxane, gives a chromatogram the same as that in Fig. 2, except for the time needed for each solute to pass through the capillary.

The results in (i) suggest that the silicon is formed inside the glass capillary not as a homogeneous film but as piled small grains. Piled grains have small cavities, and linear hydrocarbons that have a small cross-section are assumed to be retained there temporarily, thus delaying elution. On the other hand, other solutes such as 2,3-butanediol, *n*-butyric acid, 1-decanol and also 2,6-dimethylphenol and 2,6-dimethylaniline, as will be shown later in Fig. 7, do not enter the cavity and elute without delay. As seen from the shapes of the peaks, gas–solid chromatography is assumed to be working with hydrocarbons. The effect of octamethyltetrasiloxane treatment in (v) is that octamethyltetrasiloxane reacted with silanol on the grains to block the cavities, thus acting as a so-called tailing reducer. The liquid phase also should play a role as a tailing reducer [26]. Hence it was clear that broad operation conditions are effective for monosilane treatment as described in (iv) and (v).

3.2. Research on treatment of metal capillary with monosilane

The stainless-steel (SUS 316) capillary washed with water and then with acetone was treated with monosilane as was done with the glass capillary. Evaluation was also conducted similarly. The results are described below.

(i) When the metal capillary was used, even as short as 10 m, an extraordinary chromatogram (Fig. 7a) compared with that of the precolumn (Fig. 6) was obtained. When the metal capillary was replaced with a glass capillary having the same silicon thickness, the chromatogram shown in Fig. 7b was obtained. Even when the metal capillary was used, after the octamethyltetrasiloxane treatment, the chromatogram obtained was same as that in Fig. 6.

(ii) When a column coated with OV-1 was used

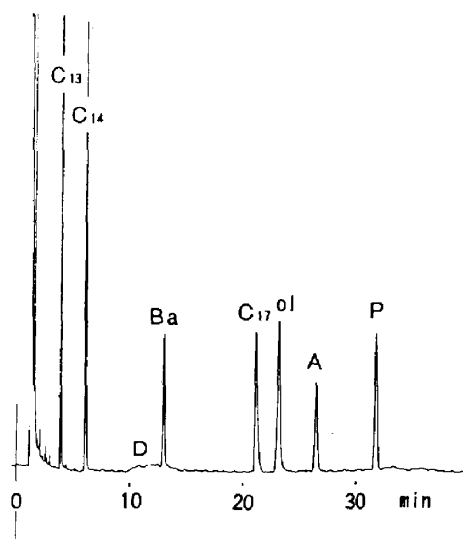


Fig. 6. Chromatogram of test mixture on precolumn of CW40M alone. Precolumn, 20 m \times 0.25 mm I.D. Test parameters: initial oven temperature, 60°C; programming rate, 1°C/min; N₂ flow-rate, 0.28 m/s. Test mixture: see Table 1.

as a precolumn, even with the metal capillary, an extraordinary elution order in the chromatogram was not observed (Figs. 8 and 9)

(iii) Aspects (ii)–(iv) in Section 3.1 was also observed in the case of a 10-m metal capillary.

The results in (i) are considered to arise from the difference in the state of deposited silicon grains depending on the capillary material. With glass, the silicon grains are small and there are few cavities to capture hydrocarbons. With a metal (in this instance stainless covered with very thin layer of naturally grown oxide), the wettability with the silicon is poor and the grains become large, thus increasing the cavities to trap hydrocarbons.

Concerning (ii), taking C₁₇ as an example, as seen from Figs. 6 and 8, C₁₇ enters the capillary at 81 and 144°C in the case of CW40M and OV-1 as precolumns, respectively. The temperature difference is assumed to determine the degree of capture of hydrocarbons.

The requirement of silicon thickness, (v) in Section 3.1, was not ascertained with the metal capillary. When octamethyltetrasiloxane was

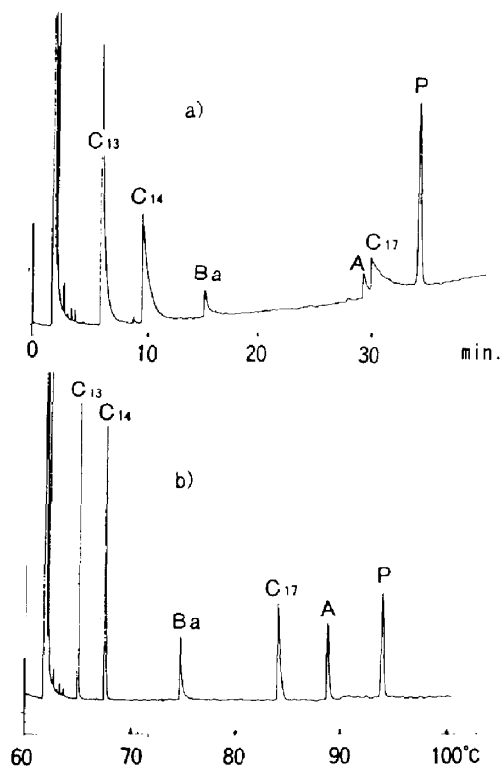


Fig. 7. Polarity test chromatograms on monosilane-treated capillaries with precolumn of CW40M. (a) Metal capillary, 10 m \times 0.25 mm I.D. Parameters for monosilane treatment: 98.6 kPa, 530°C, 15 min. (b) Glass capillary, 10 m \times 0.28 mm I.D. Parameters for monosilane treatment: 98.6 kPa, 500°C, 15 min. Test parameters: see Fig. 6.

used to treat the capillary used for the measurements in Fig. 9, and subjected to the same measurements as in Figs. 7a and 9, the chromatograms were almost the same as that with the precolumn alone. The thickness of silicon at that time was calculated to be ca. 320 Å. Hence, in the case of metal capillary, it seems that there is no necessity to deposit silicon as thick as ca. 3000 Å [4].

The inner surface of the metal capillary is uneven, however. Therefore, to obtain a reliable metal capillary treated with monosilane, the silicon layer should be sufficiently thick. For the purpose of increasing the thickness of silicon, the seal pressure of monosilane was increased and monosilane treatment was repeated three times.

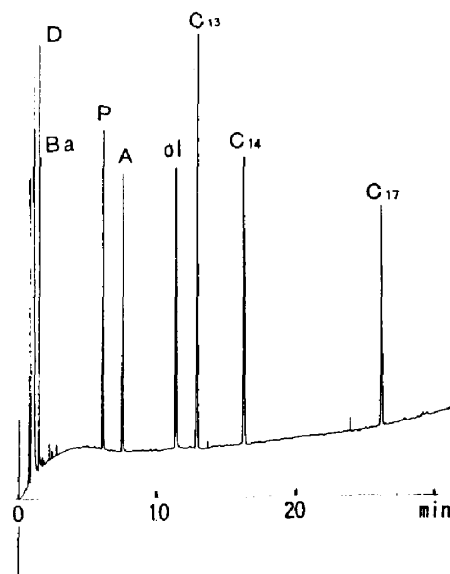


Fig. 8. Chromatogram of test mixture on precolumn of OV-1 alone. Precolumn, 25 m \times 0.25 mm I.D., OV-1, $d_t = 0.4 \mu\text{m}$. Test parameters: initial oven temperature, 60°C; programming rate, 3°C/min; N_2 flow-rate, 0.49 m/s. Test mixture: see Table 1.

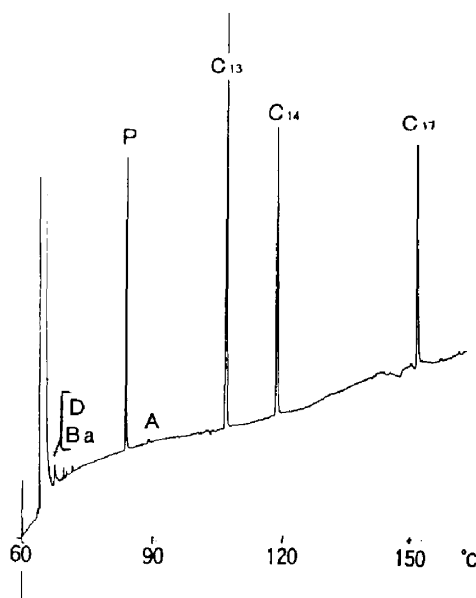


Fig. 9. Polarity test chromatogram on monosilane-treated metal capillary shown in Fig. 7a with precolumn of OV-1. Test parameters: see Fig. 8.

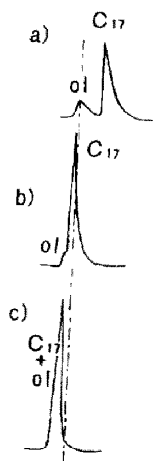


Fig. 10. Influence of repeated monosilane treatment. Column: precolumn of CW20M + metal capillary (6 m \times 0.35 mm I.D.) treated with monosilane. Parameters for monosilane treatment: 197.2 kPa, 450°C, 15 min. Number of repetitions of monosilane treatment: (a) 1, (b) 2, (c) 3. Test parameters: N₂ flow-rate, 0.4 m/s; for other parameters see Fig. 2.

When the capillary was connected to a precolumn of CW20M, as shown in Fig. 10, the reversed peak order of 1-decanol and C₁₇ was gradually improved. The thickness of the silicon layer was 890 Å/cycle. Fig. 10 shows that, although the wettability between the silicon grains and the newly deposited silicon is better than that between the metal capillary and silicon, the cavity of grains does not become sufficiently small so as not to trap hydrocarbons owing to the geometry formed by the initial silicon grains. As the uneven inner surface of the capillary can cause a smaller column plate number, it is preferable to lessen the roughness, and also to lessen the degree of capture of hydrocarbons by the cavity of grains before the octamethyltetrasiloxane treatment. Therefore, we set the standard conditions for monosilane treatment of the capillary of 0.25 mm I.D. as follows: the monosilane seal pressure was 295.3 kPa (3 kg/cm²), thermal decomposition was applied at 530°C for 15 min and the process was repeated twice. The calculated thickness of the silicon layer was 1914 Å.

3.3. Thermal stability of metal capillary column coated with commercial dimethylpolysiloxane gum

It was found out that a metal capillary column that was treated with monosilane and octamethyltetrasiloxane after washing with water and acetone was, contrary to expectation, thermally very unstable. Details are described below.

From a metal capillary treated with monosilane and octamethyltetrasiloxane, column (1) was prepared by coating with extensively used commercial dimethylpolysiloxane (DMPS) gum, X1. A cross-linked column (2) was also prepared by coating X1 with 1% of dicumyl peroxide (DCUP) [27]. A glass capillary column X1 (3) and cross-linked X1 column (4) were prepared for comparison. The thermal stability of the columns was tested at a column temperature of 250–260°C under a nitrogen flow of 0.45–0.48 m/s. The test was performed at each time period under the conditions described in Fig. 8 except for the flow-rate of carrier gas. We observed peak tailing of 1-decanol and C₁₇ as representatives for an easily tailing solute and a hardly tailing solute. The results are summarized in Table 2.

The column made by cross-linking with DCUP, as seen with column (4), showed slight tailing of 1-decanol. As the degree of the tailing does not change during the heat treatment, the glass capillary columns (4) and (3) are good enough for this kind of thermal test. On the other hand, column (1) degraded with heat treatment until not only 1-decanol but also C₁₇ started to show tailing (Fig. 11). Column (2) was not good enough from the time it was made, and showed severe degradation even after 12 h of heating. It is not clear why the column cross-linked with DCUP tend to degrade severely. The same was true with a column crosslinked with AZO [28]. It should be noted that column (1) showed tailing with hydrocarbons. The poor wettability of metal with silicon in the metal capillary has been mentioned before. If the assumption is correct, on continuous heating part of the silicon grains move from the surface and migrate or grow into larger grains, thus exposing

Table 2

Thermal stability test of metal and glass capillary columns coated with commercial dimethylpolysiloxane gum, X1

No.	Column ^a	Heating time (h)										Heating temperature (°C)
		0		12		24		50		74		
		ol	C ₁₇	ol	C ₁₇	ol	C ₁₇	ol	C ₁₇	ol	C ₁₇	
1	Metal, 10 m, NC	○	○ ^b	△	○	×	△	×	×	×	○ ^c	250
2	Metal, 15 m, C	×	△	×	×	×						260
3	Glass, 15 m, NC	○	○	○	○	○	○	○	○	○	○	260
4	Glass, 15 m, C	△	○	△	○	△	○	△	○	△	○	260

Symbols: ○ = no tailing, △ = slight tailing, × = tailing, × × = severe tailing.

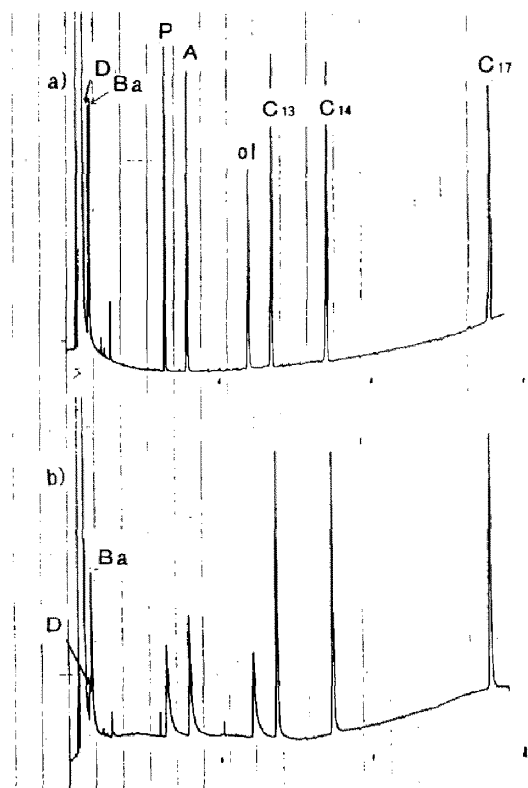
^a NC, non-cross-linked; C, cross-linked. I.D. of the columns is 0.25 mm.^b See Fig. 11a.^c See Fig. 11b.

Fig. 11. Heat treatment of metal capillary column of X1: (a) before heat treatment; (b) after heat treatment at 250°C for 50 h. Column, 10 m × 0.25 mm I.D., X1, $d_p = 0.4 \mu\text{m}$. Parameters for monosilane treatment: 197.2 kPa, 530°C, 15 min, twice. Test parameters: N_2 flow-rate, 0.25 ml/min; for other parameters see Fig. 8.

the metal surface and adsorbing hydrocarbons to show tailing. Polar solutes are assumed to show tailing ahead of hydrocarbons, as polar solutes are susceptible to the polarizing field [4] of a metal. Hence the tailing of polar solutes in columns (1) and (2) is due to the foregoing phenomenon of tailing of hydrocarbons, and different from the often observed tailing due to the hydroxyl groups on the surface of the support phase.

How to improve the wettability between the inner surface of the metal capillary and silicon is made clear in the following section.

3.4. Properties of the metal capillary treated with monosilane after acid washing of the inner surface

A commercially available metal capillary can, in many instances, be successfully processed into metal capillary as shown in Fig. 9. Consistency of the quality, however, was not expected, and often resulted in a capillary of poor quality. Therefore, the inner surface was acid washed as described in Section 2.1 to give a constant state for monosilane treatment. A green or black liquid results from acid washing, but it changes to a clear, colourless liquid after washing with distilled water. The capillary was then treated

with monosilane and was evaluated under the same condition as in Fig. 9.

As a result, an extremely poor chromatogram was obtained, as shown in Fig. 12a. It is similar to that with an untreated metal capillary. The reason is considered to be as follows. Acid washing of the inner surface exposed the bare metal surface, which made the wettability with silicon worse. As a consequence, silicon was deposited as larger grains and metal was exposed between the grains, thus giving a poor chromatogram. The phenomenon must be the same as that which Bertsch and Pretorius [4] experienced using a copper capillary. This experiment made

it clear that the oxide layer on the metal surface plays an important role in the wettability between the metal surface and silicon.

3.5. Oxidation of inner surface of acid-washed metal capillary

Oxygen oxidation was conducted on the inner surface of the metal capillary acid washed using the procedure in Section 2.1. It was then treated with monosilane and subjected to the evaluation. An excellent chromatogram, as a capillary prior to the octamethyltetrasiloxane procedure, in which tailing was a minimum not only with hydrocarbons but also with 2,6-dimethylphenol, was obtained, as shown in Fig. 12b. The result suggests that the troublesome acid washing procedure can be omitted because the oxidation procedure follows. However, from the point of view of quality control, we considered it necessary to start each procedure at a constant state of the inner surface of the capillary, and did not omit the procedure.

3.6. Thermal stability of deactivated metal capillary

Thermal stability was examined for the metal capillary prepared following the procedure in Section 3.5 and then treating with octamethyltetrasiloxane and also for the glass capillary treated with monosilane and octamethyltetrasiloxane. The capillaries were thermally treated in an oven as described in Table 3, under a nitrogen flow of 1 ml/min (linear velocity 0.34 m/s). After each thermal treatment, they were evaluated using a precolumn of OV-1. As shown in Table 3, the thermal stability of the metal capillary before the coating of a non-polar liquid phase, the so-called pretreated capillary, is, although slightly less than that of the glass capillary, excellent at 400°C for 50 h, and it survives heating at 450°C for several hours. This suggests that the column coated with dimethylpolysiloxane whose thermal stability is estimated to be ca. 400°C [29] from thermo-

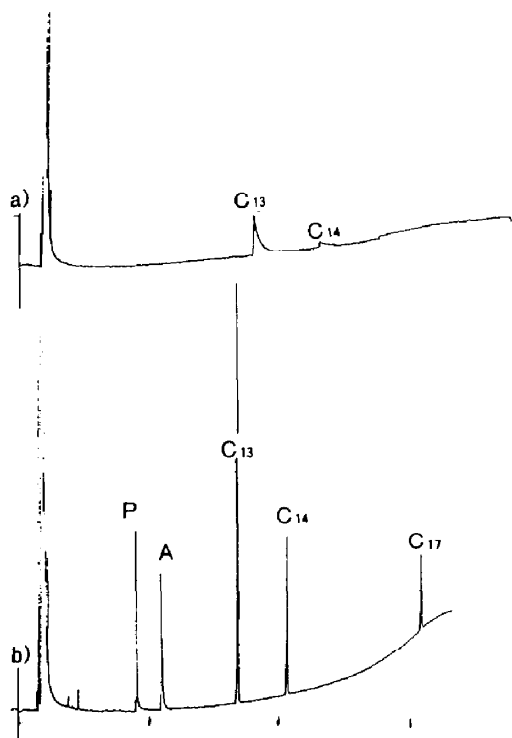


Fig. 12. Polarity test chromatograms on monosilane-treated metal capillaries (10 m \times 0.25 mm I.D.) with precolumn of OV-1. (a) Capillary acid washed followed by monosilane treatment; (b) capillary acid washed and oxidized followed by monosilane treatment. Oxidation parameters: oxygen stream, 500°C, 1 h. Parameters for monosilane treatment: 295.3 kPa, 530°C, 15 min. Test parameters: N₂ flow-rate, 0.4 m/s; for other parameters see Fig. 8. Test mixture: see Table 1, except C₁₃ concentration was increased.

Table 3
Thermal stability test of deactivated metal and glass capillaries

No.	Capillary ^a	Heat treatment									
		280°C, 50 h		400°C, 50 h		450°C, 12.5 h		450°C, 25 h		450°C, 50 h	
		ol	C ₁₇	ol	C ₁₇	ol	C ₁₇	ol	C ₁₇	ol	C ₁₇
1	Metal ^b , 30 m	○	○	△	○	×	○	— ^d	○ ^e		
2	Glass ^c , 10 m	○	○	○	○	○	○	○	○	○	○

Symbols as in Table 2: ol and C₁₇: see Table 1.

^a I.D. of capillaries is 0.25 mm.

^b Capillary was prepared under conditions described in Section 2, but oxidation was conducted at 250°C for 0.5 h.

^c Parameters for monosilane treatment: 98.6 kPa, 530°C, 15 min.

^d No peak observed.

^e See Fig. 13a.

gravimetric analysis can be used with a programming mode such as heating to 450°C and holding that temperature for a while. It also shows that inertness of the pretreated surface is maintained until the liquid phase breaks down. Hence the thermal stability of the capillary showed a remarkable improvement on introducing an oxidation process prior to the monosilane treatment, and the highly thermally stable nature of the material, metal, has come to be fully utilized. Now, for the first time, we can call such a prepared capillary a deactivated metal capillary (DMC).

What should be noted in Table 3 is that, after the heat treatment of the metal capillary at 450°C for 25 h, a peak of ol did not appear but the peak shape of C₁₇ did not change at all. This suggests that, during the heat treatment, hydroxyl groups are formed on the surface of the silicon grains, and metal is not exposed between the grains. Hence, after the heat treatment, the capillary that gave the chromatogram shown in Fig. 13a was treated with octamethyltetrasiloxane again. The chromatogram, as shown in Fig. 13b, was restored to that before the heat treatment. Although it is possible to consider that the chromatogram in Fig. 13a is due to the dispersion of octamethyltetrasiloxane from the silicon layer, this possibility is denied by the fact that thermal degradation is not recognized from capillary (2) in Table 3.

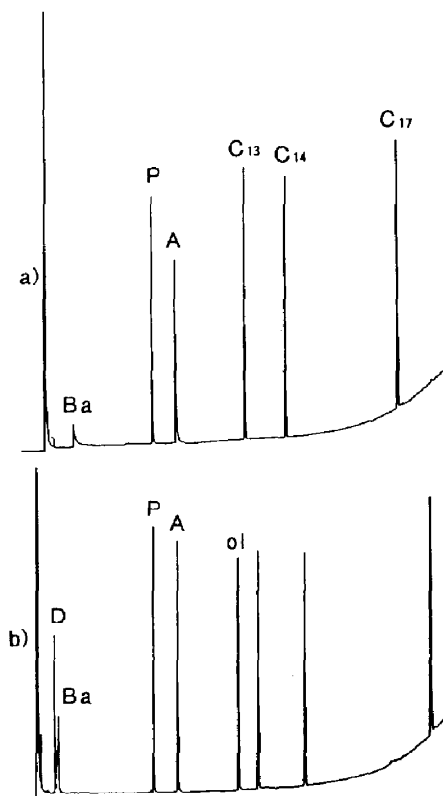


Fig. 13. Effect of repeated octamethyltetrasiloxane treatment on 1-decanol peaks: (a) before and (b) after octamethyltetrasiloxane treatment on DMC that was heated at 450°C for 25 h. Precolumn: as in Fig. 8. Metal capillary: see Table 3. Test parameters: N₂ flow-rate, 0.34 m/s; for other parameters see Fig. 8.

3.7. Thermal stability of deactivated metal capillary column: part 1

As it is clear from Table 3 that the thermal stability of DMC is above 400°C, X1 columns (Nos. 11–15) were prepared and were tested along with the reference columns 21–31 in a similar way to that shown in Table 2. As shown in Table 4, the difference between metal and glass was not appreciable, and the thermal stability even at 280°C was not satisfactory. The major difference is that C₁₇ did not show tailing in Table 4 compared with the tailing in Table 2. With the metal capillary column that was cross-linked with peroxide, although tailing of 1-decanol was observed before the heat treatment, the degree of change in the chromatogram was almost the same as that with the non-cross-linked column. It is clear that these effects are due to the oxidation process prior to the monosilane treatment. The reason for the poor performance of the X1 columns is not clear. As there is no difference in the degradation between the metal and glass columns in Table 4, it was estimated that degradation of the columns is due to X1.

Table 4

Thermal stability test of deactivated metal capillary columns coated with X1 (see Table 2) compared with glass capillary columns coated with the same liquid phase

No.	Column ^a	Carrier gas		Heating time at 280°C (h)							
				0		25		50		75	
				ol	C ₁₇	ol	C ₁₇	ol	C ₁₇	ol	C ₁₇
11	Metal ^b , 30 m, $d_t = 0.1 \mu\text{m}$	C	N ₂	△	○	△	○	×	○	×	○
12	Metal ^b , 30 m, $d_t = 0.4 \mu\text{m}$	C	N ₂	△	○	△	○	×	○		
13	Metal ^b , 30 m, $d_t = 0.25 \mu\text{m}$	NC	N ₂	○	○	△	○	×	○		
14	Metal ^b , 30 m, $d_t = 0.4 \mu\text{m}$	NC	H ₂	○	○	○	○	△	○	△	○
15	Metal ^b , 30 m, $d_t = 0.4 \mu\text{m}$	C	H ₂	△	○	△	○	×	○		
21	Glass ^c , 25 m, $d_t = 0.25 \mu\text{m}$	C	N ₂	△	○	△	○	×	○		
22	Glass ^c , 25 m, $d_t = 0.25 \mu\text{m}$	NC	N ₂	○	○	○	○	△	○	△	○
23	Glass ^c , 30 m, $d_t = 0.25 \mu\text{m}$	C	N ₂	△	○	△	○	×	○		
31	FSCC ^d , 30 m, $d_t = 0.25 \mu\text{m}$	C	N ₂	○	○	○	○	×	○	×	○

Abbreviations and symbols as in Table 2; ol and C₁₇: see Table 1.

^a I.D. of columns is 0.25 mm.

^b These were prepared under conditions described in Section 2.

^c Parameters for monosilane treatment: see Table 3.

^d Commercial column coated with liquid phase X2 corresponding to X1.

According to column 31 in Table 4, FSCC cannot withstand continuous heating at 280°C and begins to show activity towards polar solutes. This FSCC is a commercial column coated with a gum-like liquid phase X2 corresponding to X1. Although it is not yet clear whether the poor performance is due to the gum-like liquid phase, the results show that the columns coated with it acquire activity even in a moderate temperature range such as 250–350°C.

3.8. Thermal stability of deactivated metal capillary column: part 2

Thermal stability was tested again by preparing a column coated with characterized dimethylpolysiloxane (DMPS) instead of the commercially available X1. A DMPS column was prepared by thermally condensing, in a capillary, the liquid oligomer that was prepared by hydrolysing dimethyldichlorosilane with aqueous ammonia [8,9]. A 20% solution of oligomer in dichloromethane was dynamically coated in a metal capillary treated with the procedure in Sections 2.1–2.3. At the stage of condensation,

the carrier gas flow-rate was maintained at ca. 0.1 m/s so as not to disperse the oligomer. The column was maintained at 250°C for 20 h, then at 300, 330, 350 and 370°C each for 15 h and finally at 390°C for 10 h. The results of the thermal test of the obtained DMCC at 440°C for 20 h are shown in Fig. 14. The chromatogram seems reasonable considering the results in Table 3. Although 1-decanol shows slight tailing, it must be due to the ring opening of siloxane, as will be mentioned in Section 3.9.

A column was prepared similarly to that mentioned above, except that it was coated statically with a 2% solution of the oligomer. Assuming programming up to a high temperature range, the column was heat treated twelve times by heating, holding and then cooling. A Grob test [18] was conducted with the column, and it was further confirmed from the chromatogram

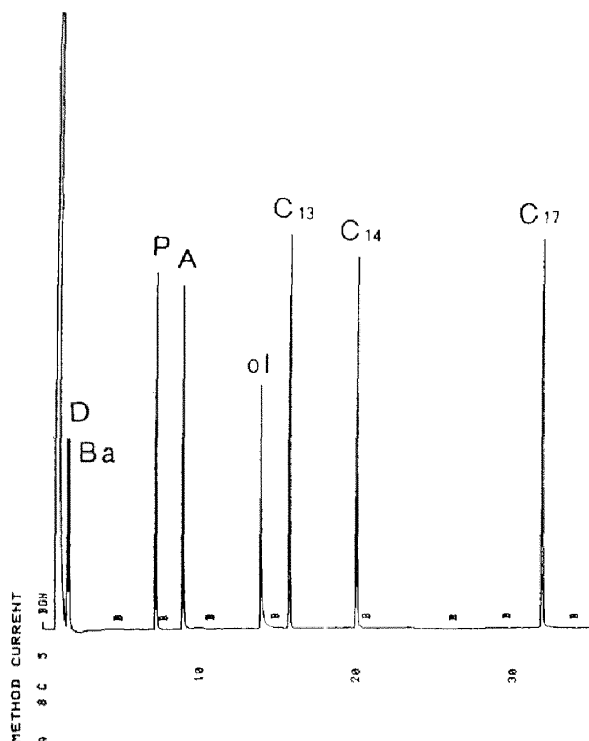


Fig. 14. Thermal test of deactivated dimethylpolysiloxane [8.9] metal capillary column. Thermal test: 440°C, 20 h, N_2 flow-rate, 0.34 m/s. Column, 15 m \times 0.25 mm I.D., $d_f = 0.25 \mu\text{m}$. Original metal capillary: as in Table 3. Test parameters: as in Fig. 13.

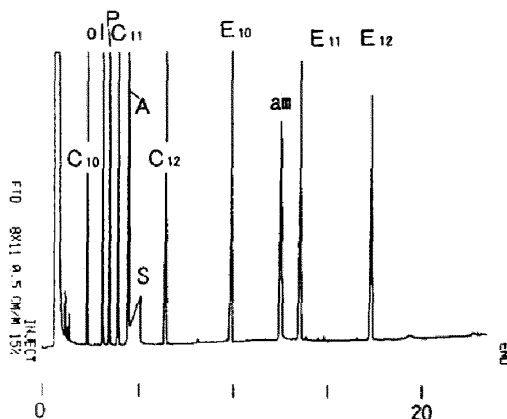


Fig. 15. Grob's test of deactivated dimethylpolysiloxane [8.9] metal capillary column after a total time of 120 min at 450°C in heat cycle test. Heat cycle test: 250–450°C at a programming rate of 10°C/min, held for 10 min at 450°C; N_2 flow-rate, 0.34 m/s. Column, 15 m \times 0.25 mm I.D., $d_f = 0.13 \mu\text{m}$, metal capillary oxidized at 250°C, 1 h. Parameters for monosilane treatment: 295.3 kPa, 530°C, 15 min, twice. Test parameters: as in Fig. 13. Sample: P = 2,6-dimethylphenol; A = 2,6-dimethylaniline; ol = 1-octanol; s = ethylhexanoic acid; am = dicyclohexylamine; C_{10} = *n*-decane; C_{11} = *n*-undecane; C_{12} = *n*-dodecane; E_{10} = methyl caprate; E_{11} = methyl undecanoate; E_{12} = methyl laurate.

gram (Fig. 15) that an extremely thermally stable column was prepared using the DMC and thermally stable liquid phase. The capacity factor (k') of C_{13} after the test was 8.68, which is 88.6% of that before the test. The theoretical plate number (N) was 23 878, which means that 87.3% of the initial performance was maintained.

3.9. Silanol and siloxane groups on the surface of the deactivated metal capillary

From Fig. 12b, a large number of silanol groups are assumed to be present on the metal capillary treated with oxidation and monosilane. From this supposition and also from the above-mentioned effectiveness of the repeated octamethyltetrasiloxane treatment, the presence of siloxane is also assumed. This is supported from the changes in a series of chromatograms, shown in Fig. 16a–c, after leaching and also after further treatment with octamethyltetrasiloxane. From the above results, it was concluded that,

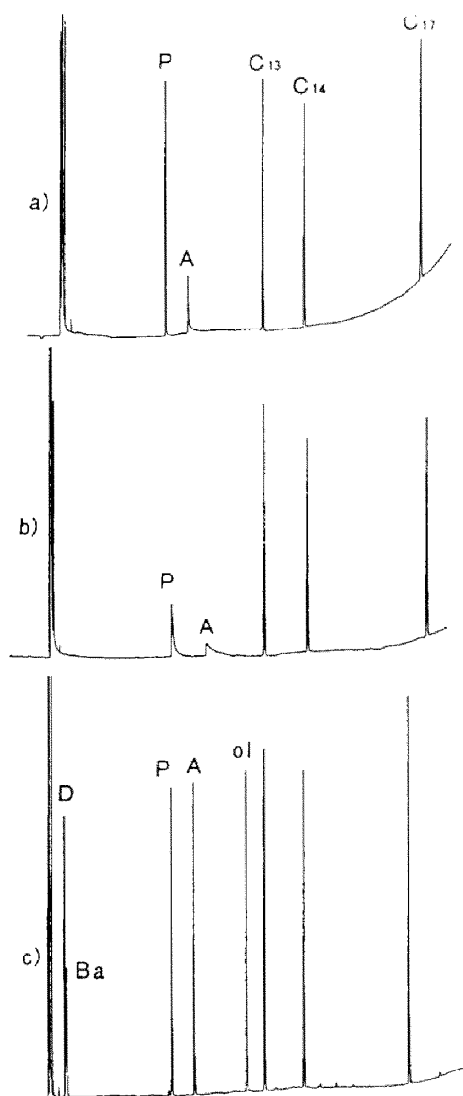


Fig. 16. Chromatogram of test mixture on metal capillary: (a) before leaching; (b) after leaching with 1% aqueous HCl for 1 h; (c) octamethyltetrasiloxane treated after leaching. Precolumn: as in Fig. 8. Metal capillary: as in Table 3. Test parameters: as in Fig. 13.

during the deactivation of the metal capillary, it is preferable to adopt a leaching process between monosilane treatment and octamethyltetrasiloxane or the corresponding treatment. Such a leaching process is considered also to be preferable from the point of view of increasing the sites for the direct reaction between an oligomeric liquid phase having hydroxyl end-groups and

the inner surface of the capillary, or for the indirect reaction through octamethyltetrasiloxane or 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane (TMTPCTS). The process can be neglected if the columns are operated in the isothermal mode below 400°C or in the temperature-programmed mode up to 450°C (see Table 3 and Fig. 15).

In the monosilane treatment described in Section 2, silicon is assumed to take oxygen away from the undercoated oxide to become silanol or siloxane. The reaction looks similar to the reduction of iron oxide with carbon. Undercoated oxide, however, is estimated not to be reduced completely to the oxygen-free state. Preparation of a glass capillary does not include an oxidation process. Hence oxygen is not abundant at the stage of monosilane treatment, and the formation of siloxane is almost negligible. It was confirmed that the chromatogram does not change before and after the leaching process.

3.10. Advantages of deactivated metal capillary (DMC) over fused-silica capillary (FSC)

The degree of deactivation of DMC is the same as that of FSC, as shown in Figs. 14 and 15. Naturally, DMC is easier to handle, has no problems of degradation and breakage and shows excellent thermal stability. There are some other advantages, as follows.

(i) It is easy to coat. As already pointed out, even polar liquid phases are easy to coat [3] owing to the silicon's high surface free energy. DMC has an uneven inner surface corresponding to the uneven original surface. Silicon is assumed to exist as fine grains on the uneven surface, which helps to make coating easy, as was found with PLOT columns. Hence, in addition to CW and OV-17, a highly polar liquid phase such as 5CP can be easily coated. In contrast, the inner surfaces of FSC and glass capillary are extremely flat, and it is very difficult to coat polar liquid phases without some treatment. With FSC, even if the coating looks successful, the liquid phases tend to aggregate to oily droplets during use.

(ii) The thermal stability of liquid phase can be fully utilized without worrying about degra-

dation of the physical and chemical performances of capillary during high-temperature use. An example is shown in Fig. 17. The baseline shifts upwards at around 400°C, which means that partial thermal degradation [29] of DMPS is occurring. When thermally stable liquid phases are used, DMCC can be used continuously at or above 450°C.

(iii) DMCC can be prepared by thermally condensing oligomers having hydroxyl end-groups in the capillary. In the case of cyano-silicon, FSC can be used [24] because the liquid phase can be prepared below 300°C. In other cases, however, FSC cannot be used. In such cases, glass capillaries have been used [20,22,23,25]. We have already shown in Section 3.8 that DMC can be used in those cases. Especially, thus prepared DMCC coated with DMPS keeps a superior deactivated state to the

FSCC coated with a gum-like liquid phase such as X2 even at moderate temperatures.

(iv) Capillaries of large bore can be prepared. FSC exceeding 0.6 mm I.D. cannot be wound into a coil shape. A metal capillary even with 1 mm I.D. can be coiled easily. Hence a capillary column that can replace the ordinarily used packed column can be prepared. As capillary columns of wide bore can be prepared and used without problems by utilizing DMC, the age of capillary gas chromatography with thermal conductivity detection can at last begin. An example is shown in Fig. 18.

(v) The time necessary to remove the solvent with static coating is short. This is probably due to the better heat conductivity of the metal capillary over the polyimide-coated FSC. The time needed for evaporation is about 70% of that for the FSC.

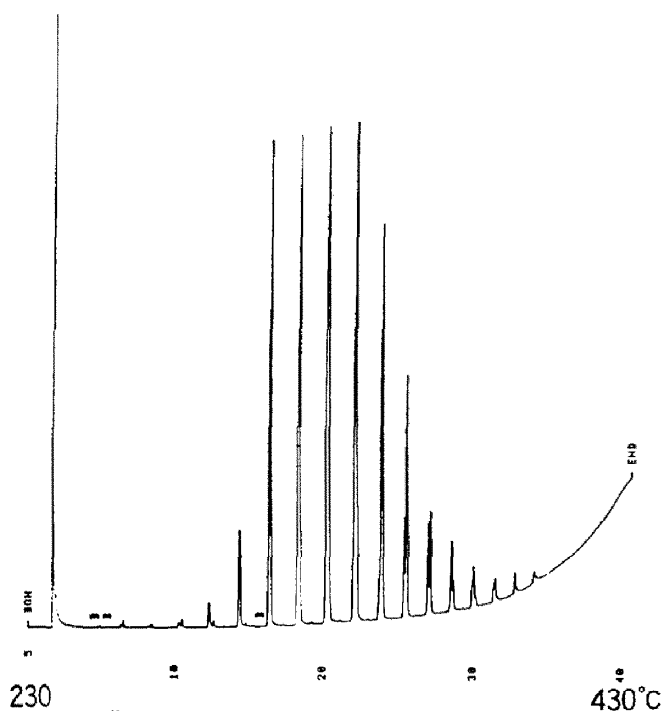


Fig. 17. High-temperature chromatogram on deactivated metal capillary column. Column, 30 m \times 0.25 mm I.D., dimethylpolysiloxane, $d_f = 0.3 \mu\text{m}$. Sample, palm oil. Test parameters: 230–430°C; programming rate, 5°C/min; N_2 flow-rate, 0.34 m/s.

3.11. Auger depth profile of deactivated metal capillary

It was difficult to prepare a sample of stainless-steel capillary of 0.25 mm I.D. whose inner surface is exposed for Auger analysis. Therefore, a stainless-steel capillary of 2 mm I.D. was treated with monosilane and was cut vertically for Auger measurement. The seal pressure of monosilane for 0.25 and 2 mm I.D. capillaries was set to give a silicon layer of the same thickness; 295.3 kPa (3 kg/cm²) and 36.5 kPa for 0.25 and 2 mm I.D., respectively, to give a 950 Å thick silicon layer.

Fig. 19a is a profile pattern of a capillary corresponding to the capillary that gave Fig. 12b. Assuming all the oxygen atoms present at the surface of silicon are bonded with silicon, the Si:O atomic ratio is 1:1.3. When monosilane was applied twice, the ratio was 1:0.8. The corresponding capillary of 0.25 mm I.D. was treated with octamethyltetrasiloxane and the chromatogram obtained was the same as that with the precolumn alone. Hence it was concluded that it is not necessary for the silicon surface to become SiO_2 [7]. The characteristic of the profile pattern of the capillary treated with monosilane after the

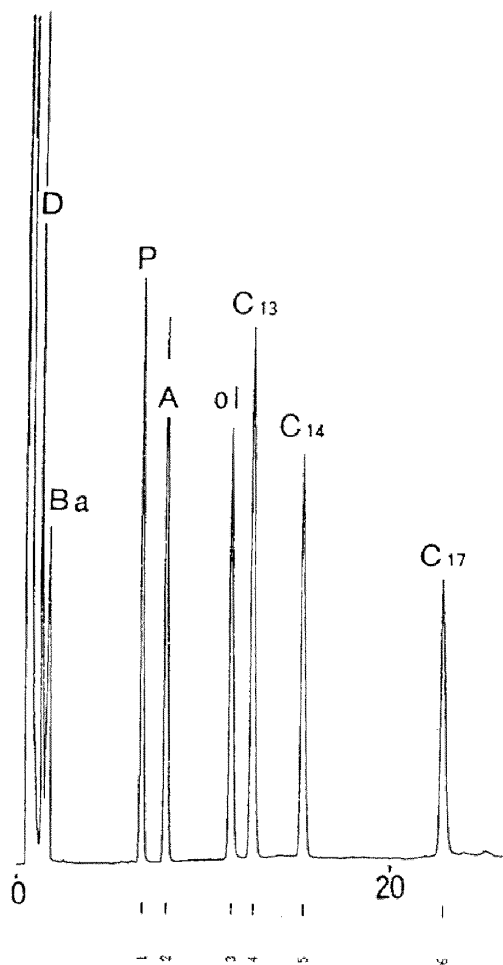


Fig. 18. Chromatogram of test mixture on large-bore deactivated metal capillary column. Column, 20 m \times 0.8 mm I.D., cross-linked X1, $d_i = 1 \mu\text{m}$. Test parameters: initial oven temperature, 60°C; programming rate, 5°C/min; N_2 flow-rate, 20 ml/min. Test mixture: see Table 1.

oxidation process is that a clear peak appears showing oxygen at the interface of the stainless steel and silicon layer. A capillary that was oxidized at 250°C for 1 h showed a smaller peak of oxygen, ca. one third in width and ca. half in height, but significantly larger than that in Fig. 19b, which omitted the oxidation process. Fig. 19b is a profile pattern of a capillary corresponding to the capillary that gave Fig. 12a. It

was not concluded that the capillary that gave Fig. 19b gives an unsatisfactory chromatogram. If we assume that the reason for Fig. 12a is partial exposure of stainless steel beneath the silicon layer, it is impossible to estimate the quality of the capillary from one Auger analysis.

4. Conclusions

The key procedure necessary to obtain a capillary that retains its inertness at moderate and high temperatures for long periods is to perform an oxidation process prior to the monosilane treatment of the capillary. Fairly broad conditions can be used for oxidation and monosilane treatment. The conditions described in Section 2 are some that we have used frequently, and it is only a recommended example. The oxidation of the metal capillary plays an important role in stabilizing and preventing coagulation of the silicon grains formed from monosilane on the metal capillary. This is the key point for the successful development of DMC. Treatment such as with octamethyltetrasiloxane prior to the coating of liquid phase to DMC can be done with various procedures being carried out with FSC or glass capillaries.

Thermal condensation in the capillary using the oligomer with hydroxyl end-groups at above 300°C has been used only in the case of glass capillaries. The know-how thus obtained can be fully used for DMC. It is of great significance that a high-performance flexible column for medium- to high-temperature gas chromatography is possible for the first time. The quality of the liquid phase is important, and the quality has to be checked when a commercially available liquid phase is to be used. With a high-quality liquid phase, column preparation does not need such a long period as described in Section 3.8.

DMC has the merit of both glass capillary and FSC, and has no problems of breakage. We believe that DMC is the metal capillary of the second generation, and it is unnecessary to predict the future of the competition with FSC.

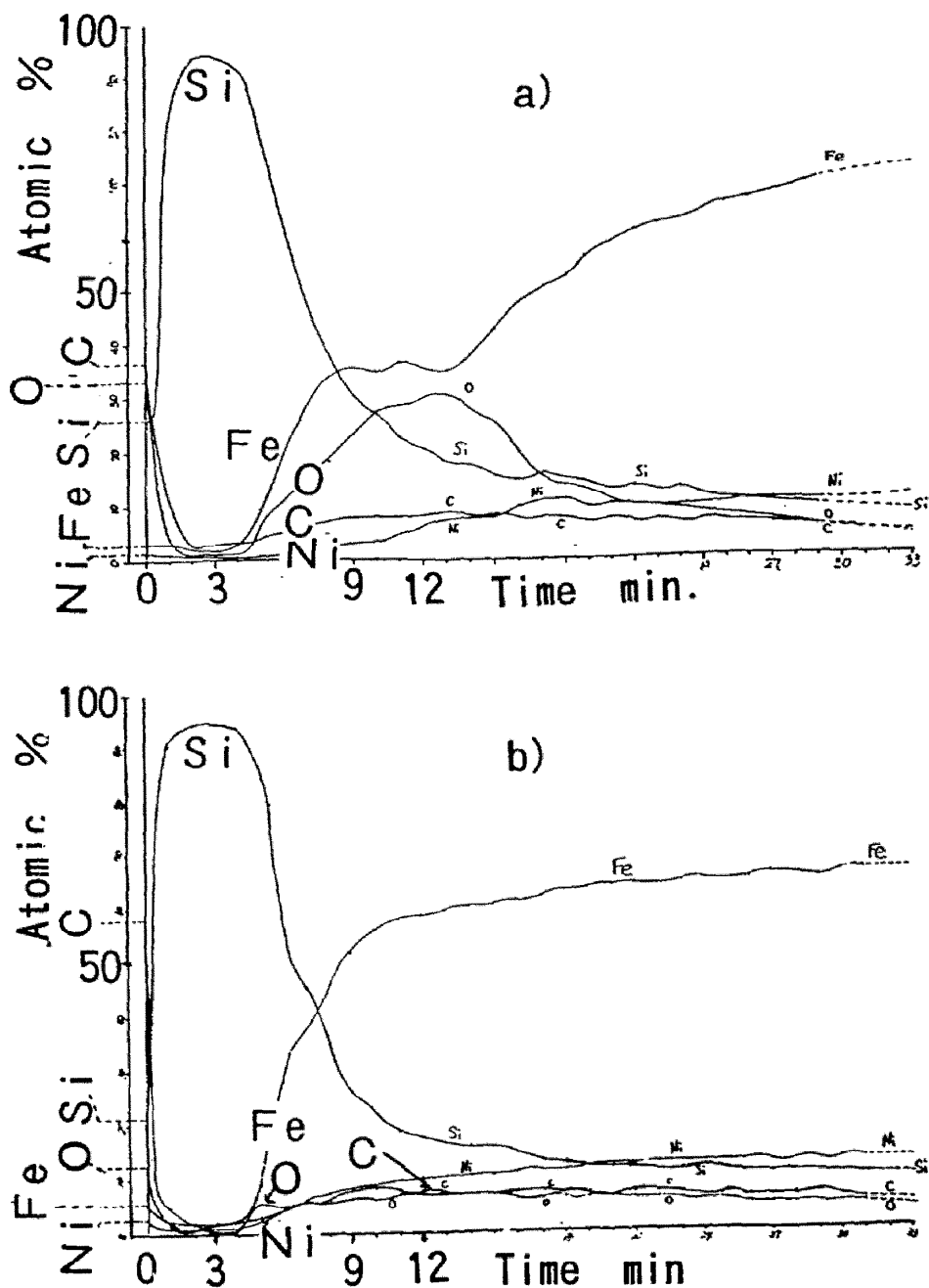


Fig. 19. Auger depth profile analysis of inner surface of metal (stainless-steel) capillaries. (a) Deactivated metal capillary, I.D. 2 mm, equivalent to that shown in Fig. 12b; (b) metal capillary, I.D. 2 mm, equivalent to that shown in Fig. 12a.

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