

CHROM. 11,289

IN SITU SYNTHESIS OF HIGHLY THERMOSTABLE, NON-EXTRACTABLE, METHYLSILICONE GUM PHASES FOR GLASS CAPILLARY GAS CHROMATOGRAPHY

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(Received June 16th, 1978)

SUMMARY

The high thermal stability of crosslinked poly(methylsiloxane) gums, as compared with linear polysiloxanes, makes them especially suitable as stationary phase for glass capillary columns. Because such gums have a very limited solubility in commonly used solvents, it is necessary to develop a method for their formation within the column. To further increase the stability of the gum films, conditions have been chosen which facilitate chemical bonding to the glass surface. On temperature programming to 300°, such columns show good efficiency, low bleeding and good durability. The columns have been successfully used for the routine analysis of polyaromatic hydrocarbons.

INTRODUCTION

In recent years, the use of chemically bonded stationary phases in chromatography has been of considerable interest^{1,2}. Attempts to prepare glass capillary columns containing chemically bonded silicones as the stationary phase have been reported³⁻⁵. However, it was not until recently that detailed descriptions for the preparation of such columns appeared in the literature⁶⁻⁹, thus making it possible to reproduce the results reported. Chemical bonding has been shown to increase the stability of the stationary phase film as compared with a conventionally coated film¹. Another method of increasing film stability is to use silicones that contain some degree of crosslinking¹⁰.

The use of capillary columns having firmly established stationary phase films is a necessary condition for the successful performance of many analyses. A conventionally applied stationary phase film is inclined to rearrangement. This implies that the column efficiency tends to decline after heating or after being used for some time. Further, the use of conventional, non-bonded, thin films is not possible at higher temperatures since minor rearrangement of the film might expose areas of the glass surface. This can lead to adsorption of the sample.

Based on experience in our search for a type of capillary column suitable for

the separation of samples containing polyaromatic hydrocarbons (PAHs), we concluded that columns having a highly stable stationary phase film would be required¹¹. In this paper, we describe the preparation of such columns utilizing a combination of two approaches to the problem: the use of crosslinked silicone gums as stationary phase and the use of chemically bonded silicone phases.

EXPERIMENTAL

Capillaries

Pyrex and AR-glass capillaries were drawn as described earlier¹². The AR-glass capillaries were double-etched with HCl according to the method of Parker and Marshall¹³. The Pyrex capillaries were treated with tetrachlorosilane. A 2-m long plug of tetrachlorosilane was thus drawn into the glass capillary and then transferred by dry nitrogen along the capillary at a rate of 100 mm/sec. The capillaries were sealed, placed in an oven at 300° for 15 h and then flushed with dry nitrogen for 1 h at 200°.

Coating materials

An α,ω -hydroxypoly(methylsiloxane) pre-polymer was prepared by hydrolysis of mixtures of dimethyldichlorosilane (DMCS) and methyltrichlorosilane (MTCS) according to Andrianov¹⁴. In this method, butanol and methylchlorosilanes (181:139, w/w) were heated under reflux for 1.5 h until the evolution of HCl ceased. After cooling, 325 parts by weight of water were added and the mixture refluxed for 3 h. The mixture was extracted with water until the aqueous phase was neutral, and the butanol phase was distilled off at 20 mmHg, gradually increasing the temperature of the distillation flask to 100°. For polymers having a CH₃/Si ratio of 1.4 and 1.6, the residue in the distillation flask is used as pre-polymer. With a CH₃/Si ratio of 1.8, the low viscosity of these polymers does not allow a satisfactory coating of the column. Further distillation of the pre-polymer up to 200° at 20 mmHg, where another 15% is distilled over, gives a residue suitable for column coating.

Preparation and testing of the columns

All the columns were coated by the dynamic method using a solution of the coating materials in chloroform¹². Capillaries with a CH₃/Si ratio of <2 were filled with dry nitrogen, sealed and placed in the oven of a gas chromatograph. Polymerization was attempted by programming the temperature to 320° at 5°/min and maintaining this temperature at 320° for 20 h. Before making a preliminary test, the columns were conditioned for 30 min at 300°. The columns were then conditioned for 48 h at 300° and tested again.

The capillaries were tested in a Carlo Erba 2350 gas chromatograph, using hydrogen as carrier gas. The capacity ratio, *k*, was measured for dodecane at 100° and tetradecane at 220°. Kováts' indices for octanol and naphthalene were determined at 100°. The shapes of the octanol and naphthalene peaks indicated the degree of adsorption taking place on the columns. Further, the HETP was measured for C₂₄ for comparison of the efficiencies of the different columns used within this investigation. Analyses of PAH samples were performed on a Carlo Erba 2350 gas chromatograph and the identification studies on a Finnegan 3200 mass spectrometer.

RESULTS AND DISCUSSION

We synthesize the methylsilicone gums in two steps: first a pre-polymer is prepared by hydrolysis of a suitable mixture of chlorosilanes; a glass capillary is then coated with the pre-polymer and final polymerization is accomplished by thermo-setting *in situ*.

The hydrolysis can be performed under basic conditions^{14,15}, by direct addition of aqueous ammonia to DMCS; this method was utilized by Madani and co-workers^{6,7,9}. For the preparation of polymers containing crosslinks, it is more convenient to work with a less reactive system¹⁴. The chlorosilanes are thus first treated with butanol and, after reaction, water is added. This method presumably prevents cyclization and precipitation of polymer in this first step of the polymer preparation¹⁴.

The purity of the starting material is of decisive importance for the final polymer properties¹⁶. Monofunctional chlorosilanes act as endblockers and their presence in the reaction mixture will result in the formation of short polymer chains; the concentration of trimethylchlorosilane should thus not exceed 0.95%¹⁴. Linear polysiloxanes, having a CH₃/Si ratio of 2, can be prepared from pure DMCS, resulting in soft and elastic polymers. Trifunctional chlorosilanes act as crosslinkers; polymers with different degrees of crosslinking can be prepared by addition of different amounts of MTCS to the starting material. Highly crosslinked polymers, having a CH₃/Si ratio of <1.2, are hard, brittle and glassy; softer and more elastic polymers are obtained¹⁴ when the CH₃/Si ratio approaches 2. The phase polarity is also affected by the CH₃/Si ratio; from the Kováts' indices in Table I it is evident that a higher silicone content increases the polarity of the stationary phase.

TABLE I
CHARACTERISTICS OF SOME TYPICAL 20 m GLASS CAPILLARY COLUMNS

Column No.	Glass type	Pre-treatment	Concn. of coating solution (%v/v)	Coating velocity (mm/sec)	CH ₃ /Si ratio	Capacity ratio for C ₂₄	HETP for C ₂₄ (mm)	Kováts' index	
								1-Octanol	Naphthalene
1	P	SiCl ₄	20	20	1.4	7.3	0.41	1086	1195
2	P	SiCl ₄	20	20	1.6	5.3	0.48	1075	1187
3	P	SiCl ₄	20	20	1.8	5.8	0.51	1069	1176
4	P	SiCl ₄	30	15	1.8	9.4	0.40	1062	1173
5	P	SiCl ₄	30	20	1.6	9.7	0.54	1072	1186
6	AR	HCl	30	20	1.6	12.7	0.56	—	1188

A prerequisite for high column efficiencies is that the stationary phase is present as an even, uniform film along the entire length of the column. The quality of such a film is greatly dependent on the technique used for its deposition and we stress that the coating must be performed very carefully. Further, for good film formation, the glass surface must be easily wetted by the stationary phase and some kind of surface etching seems to be necessary. For our purposes, surface treatment also serves to facilitate chemical bonding of the siloxanes to the glass. We have obtained the best results when using Pyrex glass treated with SiCl₄. Etching with thionyl chloride was also tried but this was found to be insufficiently reactive. Even etching with HCl was

tested; this greatly improves glass wettability and thus coating with more polar silicones is made feasible. For methylsilicones, however, we consider the treatment to be unnecessarily drastic, leading to adsorption of hydroxylated sample compounds in the coated column.

The final thermosetting of the polymer is favoured by a high degree of cross-linking in the polymer, *i.e.*, polymers with a CH_3/Si ratio of 1.8 require higher temperatures and longer times for polymerization than, for example, a polymer having a CH_3/Si ratio of 1.4 (ref. 14). For linear polymers we found it necessary to use ammonia to promote the final polymerization.

After conditioning for 30 min at 300° , columns 1–5 (Table I) were well deactivated but the rate of bleeding was too high (Figs. 1 and 2); further conditioning, for 48 h at 300° , was necessary to reduce the bleeding to tolerable levels (Fig. 1). After such a rigorous treatment, the activity increased for all the columns, and, as might be expected, the increase was most pronounced for columns with a low degree of cross-linking (Fig. 2). The activity level was however stabilized after such a severe conditioning. A further consequence of the conditioning was a reduction of the k values for C_{24} by *ca.* 5%. HCl-etched AR-glass columns showed high bleeding rates and the activity was high (the alcohol was not even eluted), Figs. 1 and 2. To depress the activity, we tried to silanize the columns after polymerization using a method we have previously utilized¹⁷, but this did not result in improved deactivation.

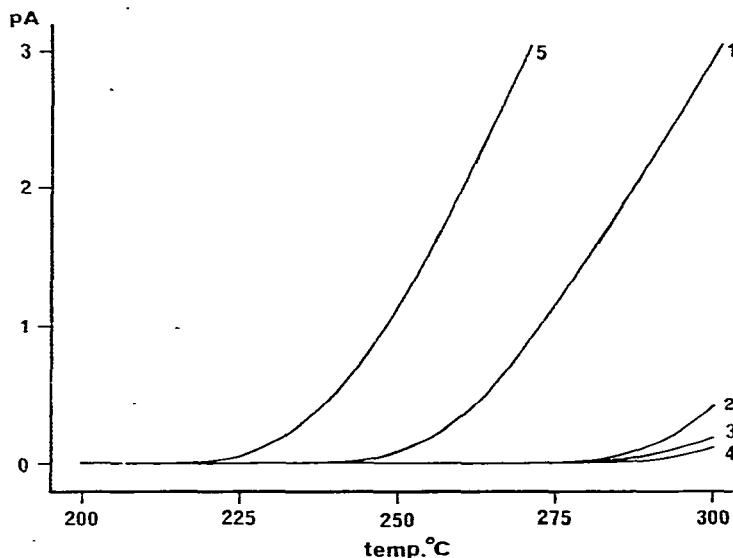


Fig. 1. Relative bleeding rates of 20-m glass capillary columns during a temperature programme of $5^\circ/\text{min}$, flame ionization detector. Column types: 1 = Pyrex glass coated with methylsiloxane polymer, CH_3/Si ratio of 1.8, after conditioning for 30 min at 300° ; 2 = column 1 after further conditioning for 48 h at 300° ; 3 = Pyrex glass coated with methylsiloxane polymer, CH_3/Si ratio of 1.6, after conditioning for 48 h at 300° ; 4 = Pyrex glass coated with methylsiloxane polymer, CH_3/Si ratio of 1.4, after conditioning for 48 h at 300° ; 5 = AR-glass coated with methylsiloxane polymer, CH_3/Si ratio of 1.6, after conditioning for 48 h at 300° .

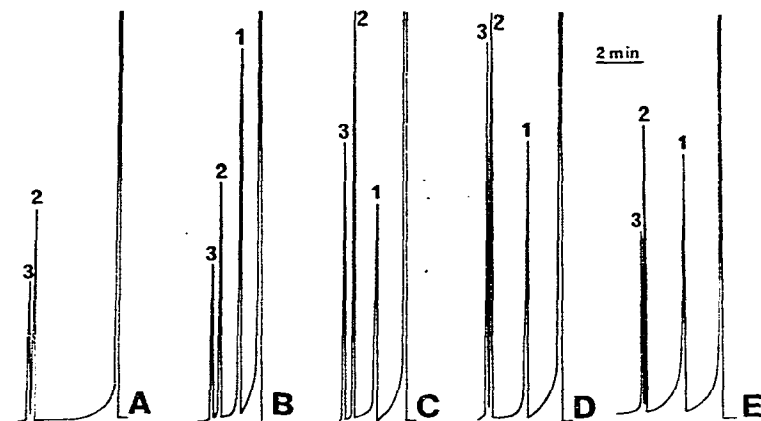


Fig. 2. Gas chromatograms (flame ionisation detector, FID) of a polarity mixture on different 20-m capillary columns. A = AR-glass coated with methylsiloxane polymer, CH_3/Si ratio of 1.6, column conditioned for 48 h at 300° ; B = Pyrex glass coated with methylsiloxane polymer, CH_3/Si ratio of 1.8, column conditioned for 30 min at 300° ; C = column B after further conditioning for 48 h at 300° ; D = Pyrex glass coated with methylsiloxane polymer, CH_3/Si ratio of 1.6, column conditioned for 48 h at 300° ; E = Pyrex glass coated with methylsiloxane polymer, CH_3/Si ratio of 1.4, column conditioned for 48 h at 300° . Temperature, 100° . Carrier gas (hydrogen) flow-rate, 70 cm/sec. Peaks: 1 = 1-octanol; 2 = naphthalene and 3 = dodecane. Sample size, ca. 1 ng of each test substance.

A fairly good estimation of the film thickness in a smooth Pyrex capillary column¹² can be obtained from the equation presented by Fairbrother and Stubbs¹⁸

$$d_f = cr/200 (u \cdot \eta/\gamma)^{\frac{1}{2}}$$

where d_f is the film thickness, c the coating solution concentration, r the column radius, u the coating velocity, η the viscosity and γ the surface tension of the coating solution. We thus measured η and γ for the 30 and 20% solutions of the polymer having a CH_3/Si ratio of 1.6 (Table II). Using these data, the average film thickness of columns 2 and 5 (Table I) were estimated as 0.34 and 0.63 μm , respectively. The values of the activity and bleeding rate were similar for these two types of columns.

The non-extractability of the film is a characteristic feature of our columns. According to our tests, rinsing of conditioned columns with 20 ml of dichloromethane had no effect on column properties such as k , adsorption, bleeding, Kováts' index or HETP.

TABLE II

PROPERTIES OF SOLUTIONS OF POLY(METHYLSILOXANE), CH_3/Si RATIO OF 1.6, IN CHLOROFORM AT 25°

Concentration (% v/v)	Viscosity (η) (10^{-3} kg/m·sec)	Surface tension (γ) (10^{-2} N/m)
20	1.04	2.66
30	1.45	2.48

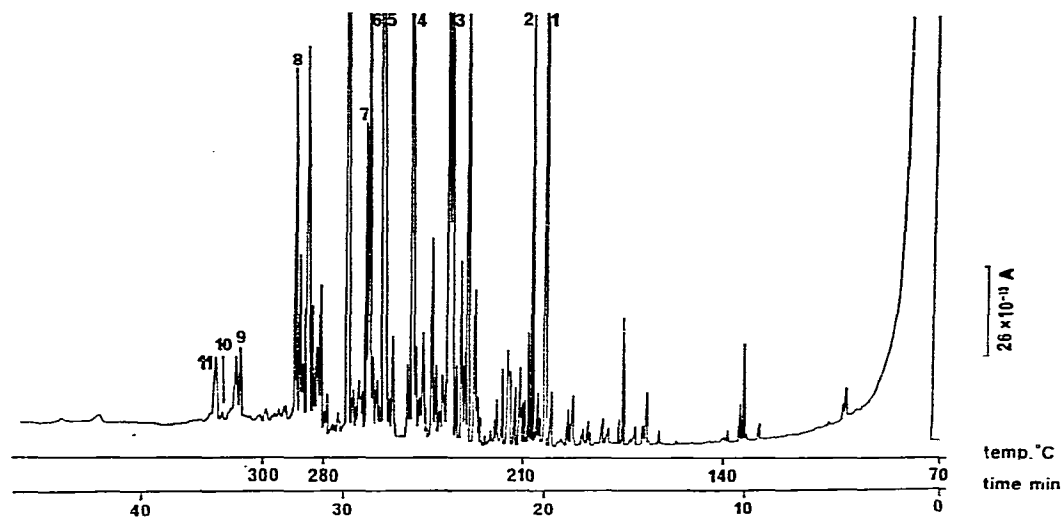


Fig. 3. Gas chromatogram (FID) of a sample containing polycyclic aromatic hydrocarbons derived from cyclon dust collected at an aluminium plant. Pyrex glass capillary column (20 m \times 0.20 mm I.D.), coated with a crosslinked methylsiloxane polymer, CH₃/Si ratio of 1.6. Initial temperature on injection, 70°; after 1 min, programmed to 300° at 7°/min, then isothermal for 12 min. Carrier gas (hydrogen) velocity at 70°, 70 cm/sec. Inlet splitter opened 1 min after injection. Peaks: 1 = fluoranthene; 2 = pyrene; 3 = benz[*a*]anthracene; 4 = β,β' -binaphthyl (I.S.); 5 = benzo[*b*]fluoranthene + benzo[*k*]fluoranthene; 6 = benzo[*e*]pyrene; 7 = benzo[*a*]pyrene; 8 = benzo[*ghi*]perylene; 9 = di-benzo[*a,h*]pyrene; 10 = mol. wt. 300; 11 = dibenzo[*ac*]pyrene + coronene.

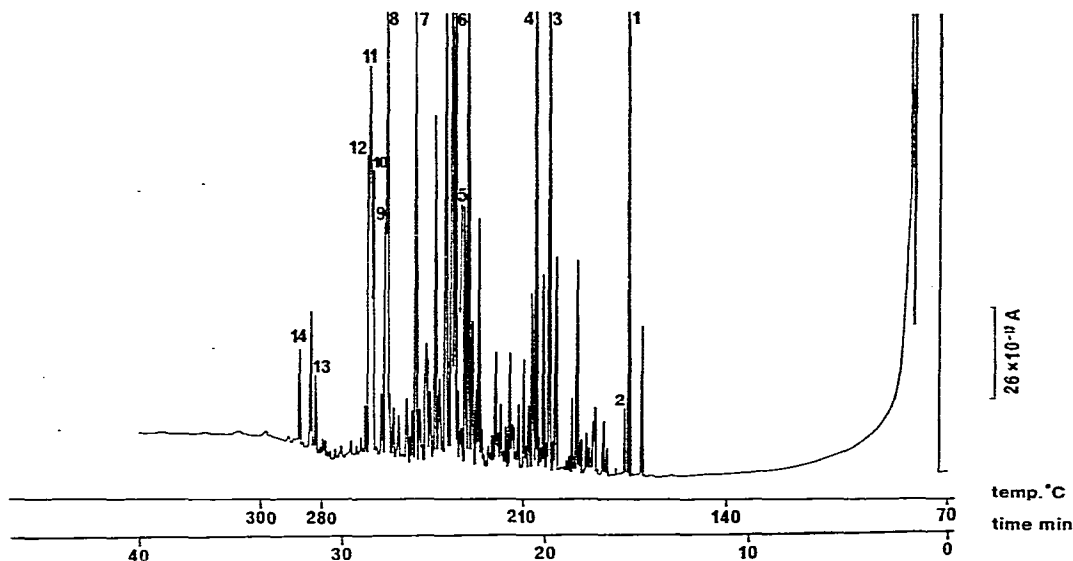


Fig. 4. Gas chromatogram (FID) of a sample obtained from the combustion of wood chippings. Column and conditions as in Fig. 3. Peaks: 1 = phenanthrene; 2 = anthracene; 3 = fluoranthene; 4 = pyrene; 5 = cyclopenta[*cd*]pyrene; 6 = benzo[*a*]anthracene; 7 = β,β' -binaphthyl (I.S.); 8 = benzo[*b*]fluoranthene; 9 = benzo[*k*]fluoranthene; 10 = benzo[*e*]pyrene; 11 = compound of molecular weight 254; 12 = benzo[*a*]pyrene; 13 = indeno[1,2,3-*cd*]fluoranthene; 14 = benzo[*ghi*]perylene.

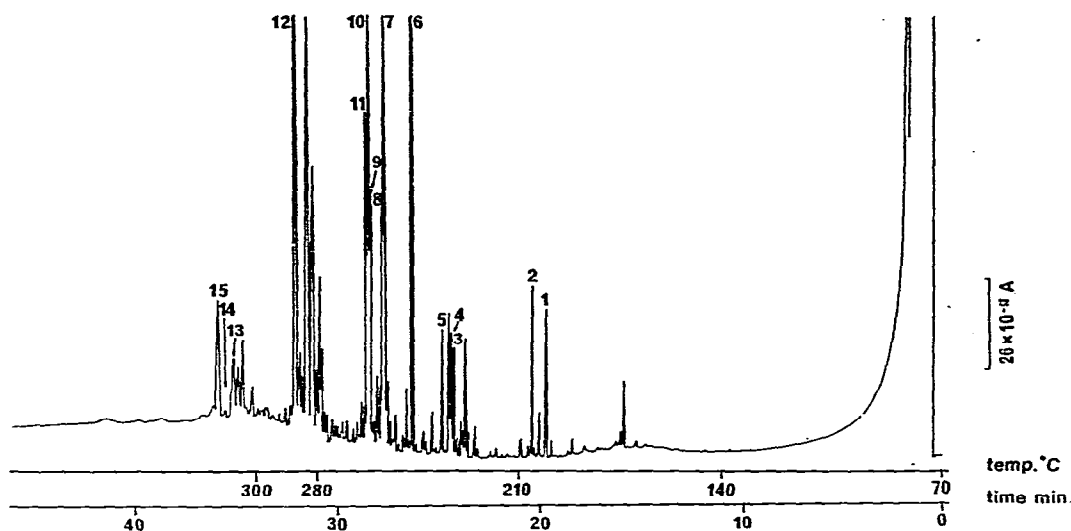


Fig. 5. Gas chromatogram (FID) of a sample obtained from the combustion of peat. Column and conditions as in Fig. 3. Peaks: 1 = fluoranthene; 2 = pyrene; 3 = cyclopenta[*cd*]pyrene; 4 = benzo[*a*]anthracene; 5 = naphthacene; 6 = β,β' -binaphthyl (I.S.); 7 = benzo[*b*]fluoranthene; 8 = benzo[*k*]fluoranthene; 9 = benzo[*e*]pyrene; 10 = compound of molecular weight 254; 11 = benzo[*a*]pyrene; 12 = benzo[*ghi*]perylene; 13 = dibenzo[*ah*]pyrene; 14 = mol. wt. 300; 15 = dibenzo[*ac*]pyrene + coronene.

The capillary columns presented here are primarily designed for routine analyses of PAHs (Figs. 3–5). The demands placed on such columns are in some ways related to the stability of the stationary phase film. The sample contains high-boiling isomers such as dibenzopyrenes and this calls for columns having not only low bleeding rates at elevated temperatures but also films which maintain efficiency up to 300°. Further, it is desirable to use thin films of stationary phase in order to obtain a more rapid elution of the sample¹⁹. This must however be balanced against the necessity for deactivation, since very thin films might involve activity problems. Most typical polyaromatic hydrocarbons are not inclined to adsorption. Adsorptive components are however usually present in samples from natural sources. The column lifetime is also an important factor, and our experience is that columns with bonded gum phases can be used for at least half a year for these analyses. Capillaries coated with polymers having a CH₃/Si ratio of 1.4 show very good chromatographic properties at 300° but they are less useful at lower temperatures. Most PAH samples contain components covering a wide range of boiling points, and this makes polymers having a CH₃/Si ratio of 1.4 less suitable if the analysis of low-boiling PAHs is of interest; polymers having a ratio of 1.8 are useful at lower temperatures but not at 300°. We find that columns with a CH₃/Si ratio of 1.6 are most suitable over the temperature range, 70–300°, utilized in this investigation. One of the most prominent applications of our low-bleed columns is realized in connection with mass spectrometry where the low column bleed rate facilitates identification of the most high-boiling components in PAH samples²⁰.

Some isomers, *e.g.*, chrysene and triphenylene or benzo[*b*]fluoranthene and benzo[*k*]fluoranthene, are difficult to separate on a non-polar column. These isomers can be separated on a Carbowax¹¹ or a bonded phenylsilicone gum column²¹. Due to

the somewhat greater durability of the methylsilicone gum columns, we use them for routine analyses. The more specific columns are employed for confirmatory purposes.

We have prepared capillary columns coated with stable films of stationary phase. A further extension of this work could involve the preparation of phases of a range of different polarities. For high-temperature analyses, methyl and phenyl substituents appear to be most useful¹⁴. Other functional groups such as cyanoalkyl can be incorporated to give more polar columns applicable to analysis at somewhat lower temperatures. Further, we believe that the procedure for gum preparation described here might be feasible also for the preparation of packing material for micropacked gas chromatographic columns, high-performance thin-layer chromatographic plates and liquid chromatographic columns.

ACKNOWLEDGEMENTS

This investigation was kindly supported by Professor G. Widmark and the Department of Analytical Chemistry. We are pleased to acknowledge Mr. U. Stenberg for supplying PAH standards and samples and for carrying out the mass spectrometric studies. Further, we thank Mr. B. O. Lundmark for technical assistance and Mrs. B. Holm for reviewing the manuscript.

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