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EFFECT OF ETCHING WITH GASEOUS HYDROGEN CHLORIDE ON THE QUALITY OF GLASS CAPILLARY COLUMNS

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SUMMARY

The effect of etching with gaseous HCl on the quality of glass capillary columns made of soft soda-lime glass and coated with OV-101 and Carbowax 20M has been studied. The quality of the columns was evaluated in terms of the number of theoretical plates, coating efficiency and Kováts retention indices of polychlorinated biphenyls (PCBs). The retention indices depend, *inter alia*, on the time and temperature of etching of the inner walls of the capillary. Columns coated with a thin film of OV-101 show adsorption properties resulting in an increase in Kováts retention indices and are capable of separating pairs of PCBs which, when chromatographed on columns coated with a thicker film of stationary phase, remain unresolved.

It has been found that by coupling shorter columns together, extremely efficient columns or columns of required polarity can be prepared.

INTRODUCTION

The use of glass capillary columns in gas chromatography has been of increasing interest in recent years[1,2]. Glass capillary columns are often used for the separation of complex mixtures in environmental samples and in clinical, food and flavour chemistry[3]. Prior to coating, the inner surface of glass capillary columns is most often etched with hydrogen chloride[4,5] or methyl trifluorochloroethyl ether (CH_3OCF_2CHFCl)[6]. Good results have been obtained by coating the inner wall of the column with colloidal silicic acid[7,8] and graphitized carbon black[9].

It follows from published results that soft soda-lime glass is the most suitable column material when etching with gaseous HCl is to be applied[3–5]. The etching procedure considerably improves the wettability of the glass surface with polar stationary phases, because a layer of microcrystalline sodium chloride is formed[3,4]. This layer has been studied by scanning electron microscopy (SEM), analyzed by means of EDAX (energy dispersive X-ray analyzer) elemental analysis[10], and it has been proved that crystals on the etched surface consist mainly of sodium chloride. Obviously, sodium chloride on the glass surface is formed by the reaction

The liberated free SiOH groups, which are the source of adsorptive properties of the glass, with a negative effect on the properties of capillary columns coated with non-polar stationary phases, can be eliminated by silanization[11,12], by coating the active centres with surface-active agents[11], by addition of a polar stationary phase[11,12] or by increasing the film thickness of the layer of stationary phase[13].

When coating capillary columns, the best results were obtained with non-polar stationary phases. With these stationary phases, mainly polydimethylsiloxanes (OV-1, OV-101 and SE-30), columns with 2000–4000 theoretical plates per metre for capacity ratios greater than 2 could be prepared, which is a substantially better column efficiency than that usually achieved with metal capillary columns coated with the same phases[15]. Very good results could also be obtained when glass capillary columns were coated with some polar phases[2,5,8,9,12], and very efficient and thermally stable columns were found to be those coated with Carbowax 20M (ref. 14), the efficiency being almost as good as that of polydimethylsiloxane columns.

In the analysis of polychlorinated biphenyls (PCBs), we have previously tested glass and metal capillary columns coated with OV-101. It was found that glass columns were much more efficient and showed longer lifetimes at temperatures of about 470 °K than metal columns coated with the same stationary phase[15].

The aim of the present work was to study the effect of the most important variables (temperature and the etching time of the inner surface of the column with HCl) on the properties of capillary columns coated with OV-101 and Carbowax 20M in the analysis of PCBs.

EXPERIMENTAL

Capillary columns were drawn by a machine that was a modified version of the type proposed by Desty *et al.*[16]. The drawing machine was constructed at the Institute of Analytical Chemistry, Czechoslovak Academy of Science (Brno, Czechoslovakia). The capillaries were drawn from soda-lime soft glass (Unihost and PN glasses, Jablonec Glass Works, Czechoslovakia). Prior to drawing, the glass tubing was cleaned by rinsing it with chromic acid. The acid was washed out with water, then the tubes were washed with acetone and dried using a water pump. The composition of the glass material used is summarized in Table I.

TABLE I

CHEMICAL COMPOSITIONS (%) OF THE GLASSES USED

Component	*Type of glass*	
	Unihost	*PN*
SiO_2	68.6	67.0
B_2O_3	—	2.0
Al_2O_3	3.9	3.0
CaO	5.5	6.5
MgO	2.9	—
ZrO	—	8.0
Na_2O	17.8	13.5
K_2O	1.3	—

The tubes were 0.7–1.5 m long with 7–8 mm O.D. and 2–3 mm I.D. From these, capillaries up to 75 m long with 0.8–1.1 mm O.D. and 0.20–0.35 mm I.D. were drawn.

Glass capillary column I.D. measurements

With the aid of compressed nitrogen and a burette, the capillary was filled with dichloromethane. Using the equation $d = 2\sqrt{V/(\pi L)}$, where V is the known volume of dichloromethane and L is the length of the capillary, the mean inner diameter (d) was calculated with an accuracy of $\pm 2\%$.

Etching of glass capillaries with gaseous HCl

Gaseous HCl, generated from dry sodium chloride and sulphuric acid, was forced through the capillary. After the appearance of HCl at the end of tubing (indicated by wetted reagent paper), passage of HCl through the capillary was continued for a further 2 h and then the amount of air present in the tube was determined by the test of Alexander *et al.*[4]. Usually more than 90% of the capillary volume was filled with HCl. Both ends of the filled capillary were sealed using a micro-burner and the column was heated in a thermostat with a forced air circulation for 2–42 h at 523–653 °K.

Prior to the coating procedure, the capillaries were activated, while nitrogen was passed through them, with the temperature programmed from 323 to 433 °K at 5 °K/min. The etched surfaces were studied using SEM and an X-ray microanalyzer.

Dynamic coating procedure

The capillaries were coated dynamically using 0.15–3 ml of a 10–20% solution of the stationary phase in *n*-hexane or chloroform at a flow-rate 0.3–0.5 cm/sec[17]. Ultra-thin-film capillary columns were prepared by a modified dynamic procedure as proposed by Schomburg and Husmann[14]. The solution of stationary phase (0.15–0.30 ml of 10–20% solution) was sucked into the capillary followed by a plug of mercury (2–5 cm). The vacuum was discontinued and the mercury plug was pushed through the column by means of compressed nitrogen at a rate of 0.3–0.5 cm/sec.

Column conditioning and testing

The columns were conditioned at a nitrogen flow-rate of 0.5 ml/min with the temperature programmed from 323 to 533 °K at the rate of 4 °K/min and maintained isothermally at 533 °K for 60 min. The column efficiency was characterized by separating a mixture of PCBs at a carrier gas flow-rate 0.3–0.5 ml/min. The column efficiency was measured in terms of the number of theoretical plates. The coating efficiency was calculated according to Ettre[17].

Gas chromatography

The instrument used was an Erba Science (Carlo Erba, Milan, Italy) Fractovap Model 2300 gas chromatograph equipped with a flame-ionization detector and a stream splitter. Glass capillary columns were connected to the splitter and to the detector by means of shrinkable PTFE tubing. The retention times were measured with a stop-watch. The carrier gas flow-rate was calculated from the known column

volume, V, and the retention time of methane, t_M, using the equation $F_M = V/t_M$. For determinations of Kováts retention indices, methane and alkanes were injected together with the sample of PCBs. The characteristics of the capillary columns are given in Tables II and III.

TABLE II

CHARACTERISTICS OF COLUMNS COATED WITH OV-101

The columns used were as follows. No. 1: PN glass, length 28 m, I.D. 0.25 mm, etched 4 h at 623°K, coated dynamically with 0.3 ml of 10% OV-101 solution in *n*-hexane. No. 2: PN glass, length 29 m, I.D. 0.25 mm, etched 4 h at 623°K, coated dynamically with 3.0 ml of 10% OV-101 solution in *n*-hexane. No. 3: PN glass, length 29 m, I.D. 0.25 mm, etched 4 h at 623°K, coated dynamically with 3.0 ml of 10% OV-101 solution in *n*-hexane. No. 4: Unihost glass, length 74 m, I.D. 0.25 mm, inside volume 3.5 ml, etched 1 h at 373°K and 24 h at 573°K, coated dynamically with 0.15 ml of 20% OV-101 solution in chloroform using Hg plug at a rate 0.3 cm/sec. No .5: Unihost glass, length 70 m, I.D. 0.25 mm, inside volume 3.5 ml, etched 1 h at 373°K and 24 h at 573°K, coated dynamically with 0.15 ml of 20% OV-101 solution in chloroform using Hg plug at a rate 0.3 cm/sec. No. 6: Unihost glass, length 70 m, I.D. 0.25 mm, inside volume 3.53 ml, etched 1 h at 373°K and 24 h at 573°K, coated dynamically with 0.15 ml of 20% OV-101 solution in chloroform using Hg plug at a rate 0.3 cm/sec. No. 7: Unihost glass, length 66 m, I.D. 0.25 mm, inside volume 3.38 ml, etched 2 h at 623°K, coated dynamically with 0.3 ml of 10% OV-101 solution in *n*-hexane. k = capacity ratio; n = efficiency in theoretical plates; L = column length.

Column No.	*k*	*n*	*n/L*	*Coating efficiency (%)*
1	1.80	61,100	2260	—
	3 90	57,700	2140	—
	5.98	56,900	2100	—
2	1.08	68,000	2340	—
	2.24	70,300	2420	—
	4.05	63,900	2200	—
3	1.05	119,200	4770	—
	2.00	113,800	4550	—
	3.44	89,800	3590	—
4	2.53	255,200	3420	65.5
	5.08	241,300	3230	68.6
	8.53	196,300	2630	58.4
5	0.90	320,100	4560	68.4
	1.36	307,800	4385	73.8
	2.03	249,000	3547	65.5
6	1.46	204,800	2930	50.1
	2.61	176,000	2510	48.7
7	2.48	262,900	3980	76.4
	6.36	213,500	3230	72.4
	8.28	201,800	3060	68.5

Study of etched surfaces

For the studies of the glass capillaries after etching with gaseous HCl, a JEOL JXA-5A X-ray microanalyzer and a JEOL JSM-U3 scanning electron microscope (Jeol, Tokyo, Japan) were used. The SEM instrument (Dionýz Štúr Institute of Geology, Bratislava, Czechoslovakia) was used in cooperation with Dr. Švec.

TABLE III

CHARACTERISTICS OF COLUMNS COATED WITH CARBOWAX 20M

The columns used were as follows. No. 8: Unihost glass, length 54.6 m, I.D. 0.26 mm, inside volume 2.78 ml, etched 1 h at 373°K and 24 h at 573°K, coated dynamically with 0.15 ml of 10% Carbowax 20M solution in chloroform using Hg plug at a rate 0.36 cm/sec. No. 9: Unihost glass, length 51.8 m, I.D. 0.25 mm, inside volume 2.87 ml, etched 1 h at 373°K and 24 h at 573°K, coated dynamically with 0.15 ml of 10% Carbowax 20M solution in chloroform using Hg plug at a rate 0.33 cm/sec. No. 10: Unihost glass, length 53 m, I.D. 0.19 mm, inside volume 1.50 ml, etched 1 h at 373°K and 24 h at 573°K, coated dynamically with 0.15 ml of 10% Carbowax 20M solution in chloroform using Hg plug at a rate 0.33 cm/sec. No. 11: Unihost glass, length 67.5 m, I.D. 0.24 mm, inside volume 2.90 ml, etched 1 h at 373°K and 24 h at 573°K, coated dynamically with 0.15 ml of 10% Carbowax 20M solution in chloroform using Hg plug at a rate 0.28 cm/sec. No. 12: Unihost glass, length 70 m, I.D. 0.21 mm, inside volume 2.35 ml, etched 1 h at 373°K and 24 h at 573°K, coated dynamically with 0.15 ml of 10% Carbowax 20M solution in chloroform using Hg plug at a rate 0.40 cm/sec.

Column No.	*k*	*n*	*n/L*	*Coating efficiency (%)*
8	1.96	247,200	4530	84.7
	3.58	167,700	3070	63.9
9	1.68	238,500	4600	85.5
	4.84	181,500	3500	78.5
10	2.24	161,400	3045	43.6
	4.65	140,600	2600	43.0
11	1.59	230,000	3430	55.7
	2.92	200,000	2980	54.7
12	1.51	293,100	4200	59.3
	2.67	226,100	3230	51.7

RESULTS AND DISCUSSION

We have previously demonstrated that glass capillary columns coated with OV-101 stationary phase are suitable for the analysis of PCBs[15]. The columns used were prepared by etching their surface with methyl trifluorochloroethyl ether. As it is difficult to ensure the reproducibility of the filling and the etching of the column with the ether with this technique, we have made more extensive studies of glass capillary columns prepared from capillaries etched with HCl. The etched column surface was monitored by local electron microanalysis and scanning electron microscopy. The etched capillaries were coated dynamically. The reproducibility of column preparation and the effects of several variables on the quality of the columns prepared were tested by the separation of a mixture of PCBs (by the number of theoretical plates for peaks 9, 21 and 38 in Fig. 1) and by determining the Kováts retention indices of the PCBs.

It was found that some pairs of PCBs could not be separated on columns coated with OV-101, even though the columns used showed extremely good efficiencies. Therefore, the possibility of separating chlorinated biphenyls on capillary columns coated with polar stationary phases was also studied. Of the polar stationary phases tested in preliminary experiments, the best results were obtained with Carbowax 20M.

Columns with non-polar stationary phase (OV-101)

The separation of a mixture of PCBs (Aroclor 1242) together with C_{14}–C_{22} *n*-alkanes on a capillary column coated with OV-101 stationary phase is shown in Fig. 1 (column No. 7). This column was prepared using a capillary etched with HCl for 2 h

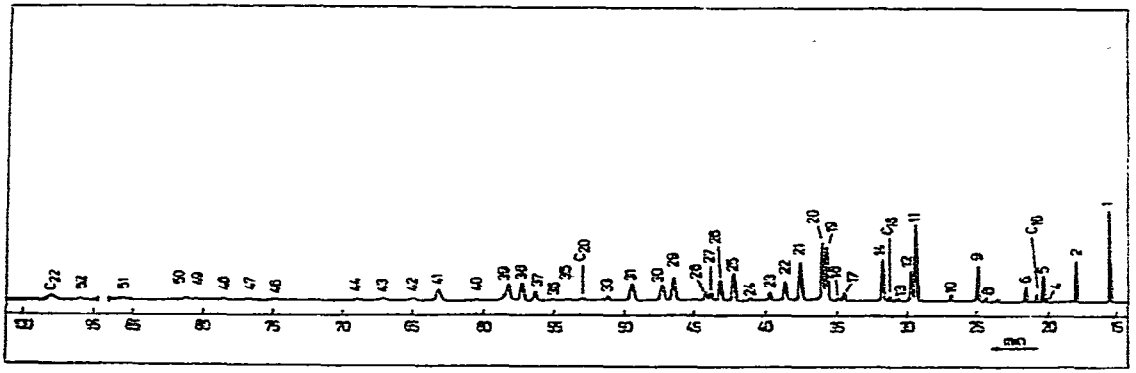

Fig. 1. Separation of components of Aroclor 1242 on a glass capillary column coated with OV-101 at 473°K (column No. 7). For peak numbering, see Table IV.

at 623 °K. It can be concluded, by comparing the results obtained by separating the same mixture of PCBs on a capillary column coated with OV-101 and having its surface etched with methyl trifluorochloroethyl ether[15] with those in Fig. 1, that the quality of the resolution of PCBs does not differ significantly.

In order to establish the effect of the variables on etching of the column surface with HCl and methyl trifluorochloroethyl ether, Kováts retention indices of PCBs on both columns were compared. Table IV gives the Kováts retention indices of PCBs found at 473 °K on column No. 7, together with published data[15]. The retention indices obtained for the column with its surface etched with gaseous HCl (column No. 7) were found to be lower than those for the column with the surface etched with methyl trifluorochloroethyl ether. It can be seen from the standard deviations (Table IV) that the fluctuations in the operating conditions during gas chromatography affects the variation of the results by less than ± 1 index unit.

Table V shows the Kováts retention indices of the main components of Aroclor 1242 found at 473 °K for columns coated with OV-101. The conditions of etching with HCl were identical. From the retention indices found for columns Nos. 1, 2 and 3 an average value $I = (I_1 + I_2 + I_3)/3$ and standard deviation (σ) were calculated. It follows from the results in Table V that the reproducibility of the preparation of the columns (expressed in terms of the retention indices of PCBs) after some standardization of the operating procedures can be better than ± 1 index unit. The last column in Table V gives the retention indices of PCBs obtained on a column made by coupling together columns Nos. 1, 2 and 3 (this coupling gave a 86-m long column having an efficiency of 261,200 theoretical plates for a capacity ratio $k = 2.19$, corresponding to about 3040 theoretical plates per metre). Moreover, the results show that by coupling individual columns together using shrinkable PTFE tubing, the retention indices were not affected significantly.

A comparison of the retention indices in Tables IV and V shows that they are also different when the process of etching the capillary surface with HCl was conducted at the same temperature but for a different period of time (the retention indices found for columns Nos. 1, 2 and 3, etched at 623 °K for 4 h, are higher than those found for column No. 7, etched at 623 °K for 2 h).

TABLE IV

KOVÁTS RETENTION INDICES (I) OF MAIN COMPONENTS OF AROCLOR 1242 MEASURED ON CAPILLARY COLUMNS COATED WITH OV-101 STATIONARY PHASE AT 473°K

Peak No.	*Structure*	*Column No. 7*		*I (ref. 15)*
		I	*Standard deviation (σ)*	
6	2,2′	1621.6	0.4	1625.8
8	2,3′	1686.0	0.7	1690.0
9	2,4′	1636.9	0.6	1700.9
10	2,2′,6	1731.8	0.4	1735.8
11	2,2′,5	1772.2	0.1	1776.2
12	4,4′ + 2,2′,3	1777.4	0.2	1781.8
14	2,2′,3	1805.8	0.6	1810.0
17	2,3′,5	1839.2	0.7	1843.6
18	2,3′,4	1844.2	0.7	1848.8
19	2,4′,5	1853.3	0.4	1858.1
20	2,4,4′	1856.7	0.6	1861.1
21	2′,3,4	1873.2	0.3	1878.1
22	—	1884.3	0.4	1890.2
23	—	1894.7	0.4	1899.7
24	—	1907.5	0.4	1912.5
25	2,2′,5,5′	1918.3	0.1	1922.7
26	2,2′,4,5′	1926.6	0.1	1931.3
27	2,2′,4,4′	1932.7	0.6	1937.1
28	—	1935.6	0.3	1939.1
29	2,2′,3,5′	1953.0	0.3	1958.1
30	2,2′,3,4′	1958.5	0.7	1965.2
31	—	1975.1	0.2	1980.1
33	2,2′,3,3′	1987.4	0.7	1992.7
37	—	2020.5	0.4	2025.7
38	2,3′,4′,5	2025.9	0.5	2031.3
39	—	2031.8	0.6	2037.4
41	—	2059.0	0.1	2065.3

As we have found that the reproducibility of the column preparation is significantly affected by the temperature at which the etching was performed, this process was carried out in a thermostat with a forced air circulation.

Table VI shows the Kováts retention indices of PCBs measured in three capillary columns coated with OV-101 at 473 °K. The conditions of etching with HCl were identical and the procedure applied was that used by Badings *et al.*[10]. It can be seen that the highest retention indices were found for column No. 5, which had the thinnest film of stationary phase ($k = 2.03$ for peak 37, Fig. 1), while the lowest retention indices were found for column No. 4, which had the thickest film ($k = 8.53$ for peak 37, Fig. 1). The data in Table VI also show that, when the surface of the glass column is etched with HCl using the procedure suggested by Badings *et al.*[10] and coated with a thin film of a non-polar stationary phase, the process of separation is governed, *inter alia*, also by the adsorption properties of the walls of the capillary columns.

TABLE V

KOVÁTS RETENTION INDICES (I) OF MAIN COMPONENTS OF AROCLOR 1242 MEASURED ON CAPILLARY COLUMNS COATED WITH OV-101 STATIONARY PHASE AT 473°K

Peak No.	*Column No.*			$\bar{I}$	σ	A^*
	1	*2*	*3*			
6	1623.7	1624.2	1624.0	1624.0	0.5	1624.0
9	1698.3	1698.7	1699.0	1698.7	0.5	1698.9
10	1733.6	1734.2	1733.9	1733.9	0.4	1733.8
11	1774.0	1774.2	1774.2	1774.1	0.1	1774.4
12	1778.8	1778.9	1779.2	1779.0	0.3	1779.5
14	1807.1	1807.5	1807.5	1807.4	0.3	1807.5
17	1840.7	1841.3	1841.3	1841.1	0.4	1841.2
18	1845.7	1845.6	1845.4	1845.6	0.2	1846.3
19	1855.6	1855.7	1855.5	1855.6	0.1	1855.2
20	1858.5	1858.4	1859.0	1858.6	0.4	1858.7
21	1875.3	1875.3	1875.2	1875.3	0.2	1874.6
22	1886.4	1886.7	1886.0	1886.4	0.5	1887.0
23	1897.0	1897.4	1896.8	1897.1	0.3	1897.0
24	1909.7	1910.4	1909.9	1910.0	0.3	1909.6
25	1920.2	1920.3	1920.0	1920.2	0.2	1920.5
26	1928.5	1928.7	1928.2	1928.5	0.4	1928.8
27	1935.1	1934.8	1934.7	1934.9	0.4	1934.4
28	1937.3	1937.8	1937.0	1937.4	0.5	1937.6
29	1955.2	1955.2	1955.7	1955.5	0.1	1955.5
30	1961.4	1961.4	1961.3	1961.4	0.1	1961.5
31	1977.1	1977.3	1976.8	1977.1	0.3	1976.5
37	2022.4	2022.5	2022.1	2022.3	0.3	2022.6
38	2028.1	2028.6	2028.2	2028.3	0.4	2028.2
39	2034.2	2034.4	2034.1	2034.2	0.3	2033.9
41	2061.5	2061.8	2061.4	2061.6	0.3	2061.5

* Retention indices with columns Nos. 1, 2 and 3 coupled together (see text).

The separation of Aroclor 1242 on capillary column No. 4 coated with OV-101 at 473 °K is shown in Fig. 2.

It follows from a comparison of Figs. 1 and 2 that on the capillary column coated with a thin film (column No. 4) of OV-101 some of the peaks were split (peaks Nos. 12, 14 and 30). The splitting disappeared when the capillary was coated with a thicker film of the stationary phase. This observation agrees with the conclusions of Franken and Rutten[13], drawn from the separation of PCBs at extremely low substance concentrations on glass capillary columns coated with SE-30.

A comparison of the surface of the capillary etched with HCl at 573 °K for 4 h (Fig. 3) with that resulting from etching of the surface for 24 h (Fig. 4) shows some changes in the crystal structure as a function of the heating time.

By coupling together columns Nos. 4 and 6, a 144.4-m long column with an efficiency of 471,290 theoretical plates (for peak 37, with a capacity ratio $k = 4.12$) was obtained. When PCBs were separated on this capillary column, peaks 12, 14 and 30 (Fig. 5) remained unresolved.

TABLE VI

KOVÁTS RETENTION INDICES OF MAIN COMPONENTS OF AROCLOR 1242 MEASURED ON CAPILLARY COLUMNS COATED WITH OV-101 STATIONARY PHASE AT 473°K

Peak No.	*Column No.*		
	4	*5*	*6*
6	1620.7	1631.4	
9	1692.9	1698.3	1698.0
10	1726.5	1732.5	1731.4
11	1765.7	1773.6	1772.5
12	1770.5	1778.6	1777.5
14	1797.6	1806.5	1805.3
17	1832.5	1842.3	1840.2
18	1837.7	1848.6	1845.9
19	1847.3	1856.2	1854.5
20	1850.4	1859.8	1858.1
21	1868.0	1875.5	1873.9
22	1879.6	1887.0	1885.5
23	1890.3	1895.7	1894.9
24	1903.5	1908.7	1907.1
25	1915.0	1922.1	1917.8
26	1923.6	1929.8	1928.0
27	1929.6	1935.4	1933.5
28	1932.7	1936.8	1935.8
29	1951.1	1956.3	1954.5
30	1957.5	1961.8	1960.5
		1965.0	1963.5
31	1973.8	1976.5	1975.6
37	2020.4	2024.6	2022.5
38	2026.0	2030.1	2029.0
39	2031.8	2036.4	2034.7
41	2059.1	2063.2	2062.0

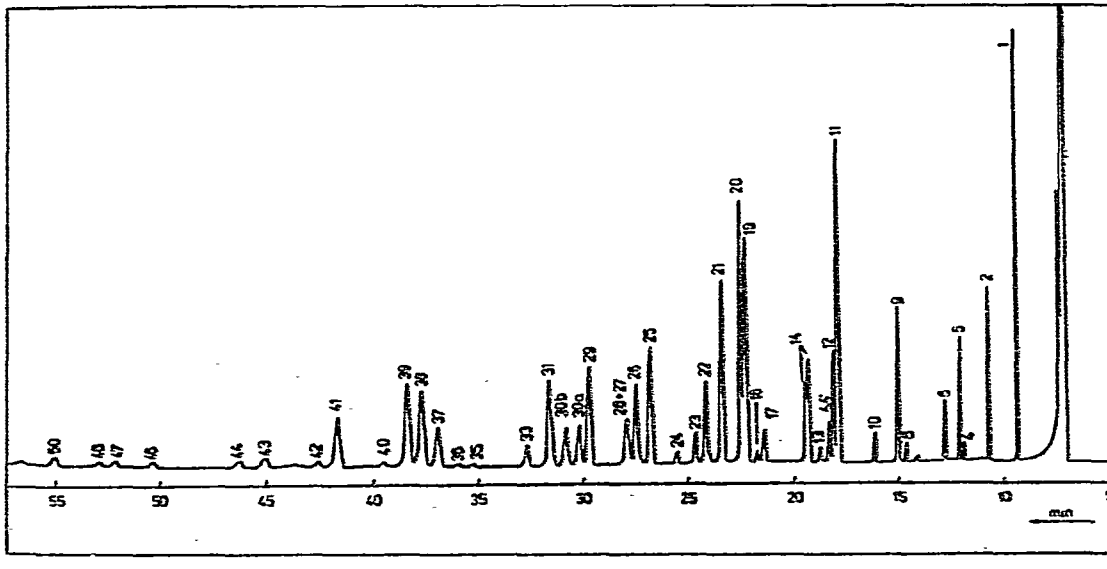

Fig. 2. Separation of components of Aroclor 1242 on a glass capillary column coated with OV-101 at 473°K (column No. 4).

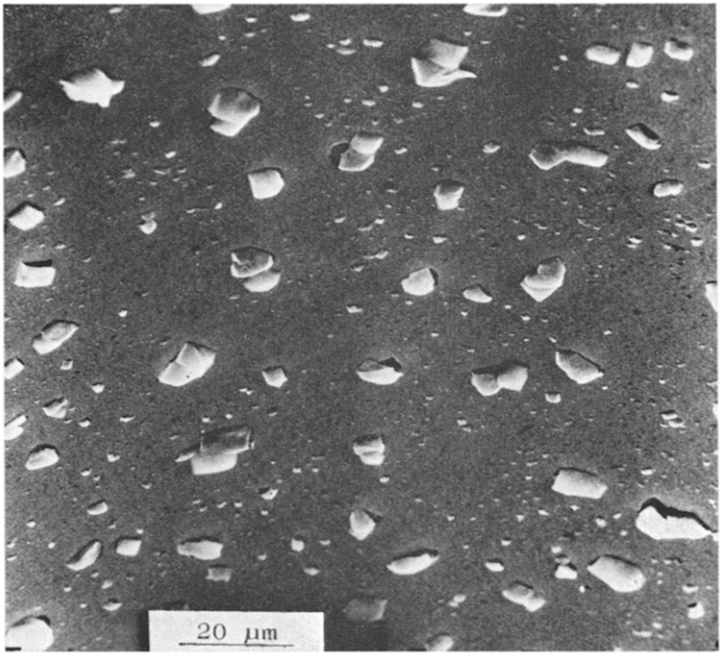

Fig. 3. Scanning electron micrograph of the inner wall of a glass capillary etched for 4 h at 573°K.

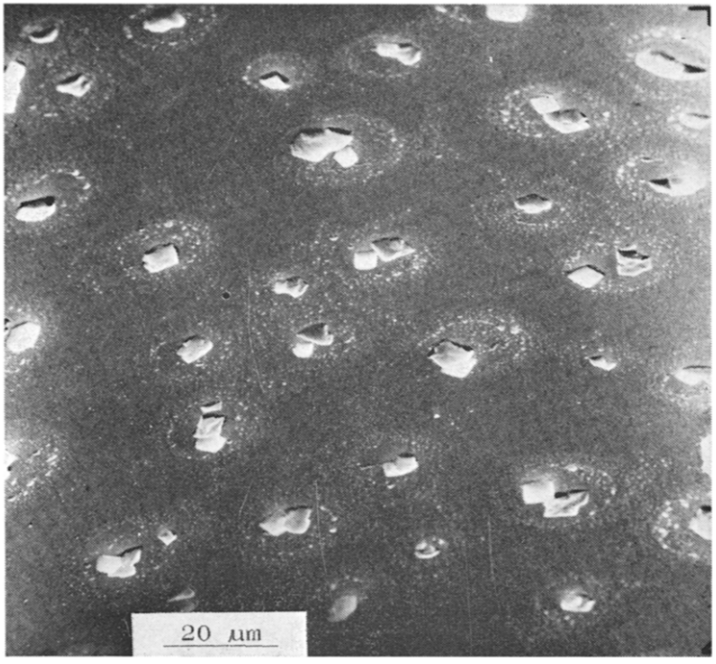

Fig. 4. Scanning electron micrograph of the inner wall of a glass capillary etched for 24 h at 573°K.

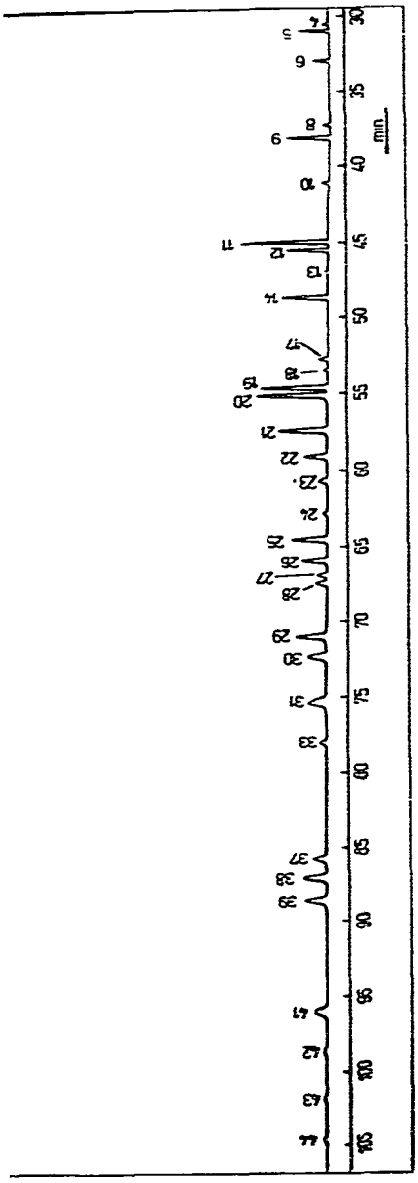

Fig. 5. Separation of components of Aroclor 1242 on a glass capillary column coated with OV-101 at 473°K (coupled columns Nos. 4 and 6).

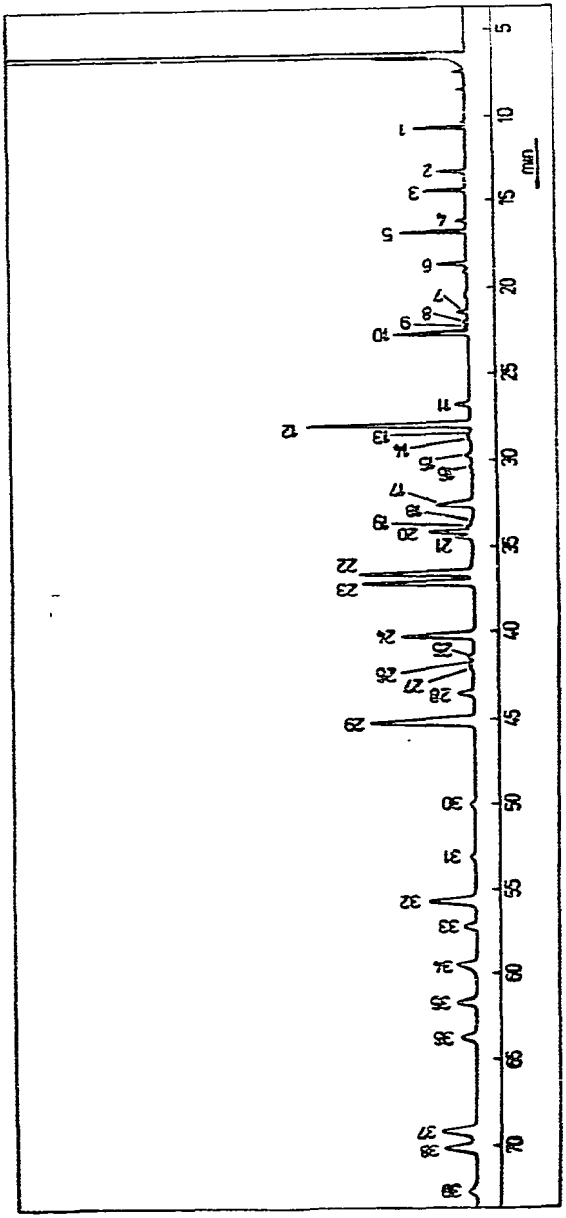

Fig. 6. Separation of components of Aroclor 1242 on a glass capillary column coated with Carbowax 20M at 473°K (column No. 8).

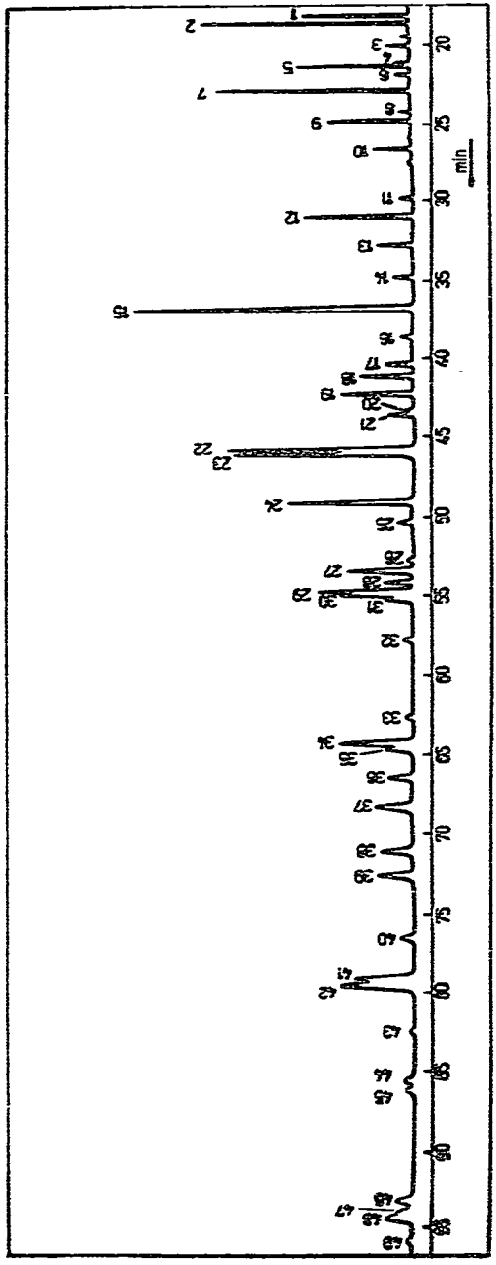

Fig. 7. Separation of components of Aroclor 1242 on a glass capillary column resulting from coupling column No. 7 (OV-101) with column No 11. (Carbowax 20M) at 473°K.

TABLE VII

KOVÁTS RETENTION INDICES OF SOME COMPONENTS OF AROCLOR 1242 MEASURED ON CAPILLARY COLUMNS COATED WITH CARBOWAX 20M STATIONARY PHASE AT 473°K

Peak No.	*Column No.*		
	8	*9*	*10*
1	2020.3	2019.3	2013.4
2	2158.7	2158.9	2152.0
3	2264.9	2255.9	2257.7
4	2282.9	2283.4	2275.7
5	2332.1	2332.5	2324.8
6	2418.6	2419.5	2411.2
7	2488.1	2489.1	2481.2
10	2529.4	2530.3	2509.9
12	2563.2	2565.4	2556.3
17	2611.3	2612.8	2604.5
20	2652.9	2653.6	2645.2
21	2658.0	2658.5	2650.1
22	2670.8	2672.1	2663.2
23	2682.4	2683.6	2674.4
24	2685.4	2686.8	2677.6
25	2720.5	2721.7	2712.4
26	2740.6	2741.6	2732.3
27	2757.0	2757.7	2748.4
28	2766.6	2767.2	2757.8
29	2780.0	2781.0	2771.3
30	2782.9	2783.7	2774.0
31	2792.7	2793.9	2783.5

Columns with polar stationary phase (Carbowax 20M)

The thermal stability of capillary columns coated with Carbowax 20M was studied by Schomburg and Husmann[14]. They found that on heating for 204 h at 473 °K, the capacity ratio of *n*-dodecane changed from the original value of $k = 1.87$ to 1.64 and the Kováts retention index of *n*-butanol at 353 °K changed from 1131 to 1116. It is thus obvious that the reproducibility of the preparation of the columns depends on the standardization of all operating procedures and that the properties of Carbowax 20M columns are also altered by ageing. In spite of this, separation of PCBs on a column coated with Carbowax 20M provides useful complementary information for the identification of PCBs in environmental analysis.

Fig. 6 shows the separation of Aroclor 1242 on a capillary column coated with Carbowax 20M at 473 °K (column No. 8). The peak numbering in Fig. 6 is different from that in Figs. 1–3.

A comparison of the data in Tables II and III shows that the efficiency of capillary columns coated with Carbowax 20M is comparable with that of columns coated with OV-101.

The Kováts retention indices found for PCBs (Table VII) differ significantly despite the fact that the etching procedure applied was identical and the film thickness of the phase does not differ significantly (the capacity ratio for peak 12 in Fig. 6 changes for the columns in Table VII from $k = 3.58$ to 4.65).

Column coupling provides a means for obtaining a column of required polarity. Fig. 7 shows the separation of Aroclor 1242 on a capillary column resulting from coupling column No. 7 (OV-101) with column No. 11 (Carbowax 20M). The column thus obtained showed for peak 15, with a capacity ratio $k = 2.14$, an efficiency of 487,000 theoretical plates.

The identification of PCBs present on chromatograms obtained using Carbowax 20M glass capillary columns is currently being studied and the results will be published later.

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