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## POSSIBILITIES AND LIMITATIONS OF CAPILLARY GAS CHROMATOGRAPHY AND MASS SPECTROMETRY IN THE ANALYSIS OF POLYCHLORINATED BIPHENYLS

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### SUMMARY

The possibilities and limitations of analyses of polychlorinated biphenyls (PCBs) by capillary gas chromatography and capillary gas chromatography-mass spectrometry have been investigated. Metal capillary columns (WCOT) coated with Apiezon L and OV-101 were not suitable for PCB analyses. Good results were obtained in the separation of model mixtures of PCBs and of Aroclor 1242 on a glass capillary column coated with OV-101. Sources of error are indicated that may be encountered in the characterization of PCB components in Aroclor 1242 by standard additions, Kováts' retention indices and mass spectrometry.

The direct coupling of a capillary column (WCOT) to a mass spectrometer produced spectra of the main PCB components, many of which could be used in the identification of isomeric PCBs.

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### INTRODUCTION

Owing to excellent chemical and electrical properties, polychlorinated biphenyls (PCBs) are widely used in the chemical industry and electrotechnology<sup>1</sup>. Some PCBs have insecticidal and fungicidal properties. Since 1966, when some

environmental samples were shown to contain chlorinated biphenyls, numerous papers appeared, describing acute and chronic toxicological properties of these substances. Although not fully understood, it is assumed that isomers have different toxic properties.

Pure isomeric PCBs have been characterized by proton magnetic resonance (PMR), ultraviolet and infrared spectroscopy<sup>1</sup>. Mixtures of PCBs have most frequently been separated and characterized by gas chromatography, mass spectrometry and the combination thereof<sup>1</sup>. The clean-up procedure of environmental samples normally involves extraction, thin-layer chromatography and column chromatography<sup>1</sup>.

The separation power of packed columns is insufficient to separate PCBs by gas chromatography<sup>1</sup>: capillary columns are therefore preferred. The most commonly used stationary phases are those that have been found satisfactory in the analysis of chlorinated pesticides (silicone elastomers, Apiezon L and high-boiling polyesters). Stainless steel has usually been used as column material. Both wall-coated open-tubular capillary columns (WCOT) and support-coated open-tubular capillary columns (SCOT) have been used<sup>1-9</sup>.

Sissons and Welti<sup>4</sup> analyzed Aroclors on an Apiezon-coated capillary column (SCOT) and described the most probable structures of the majority of the compounds present in Aroclor 1242. Standard materials, increments of Kováts' indices and mass spectrometry were used to identify the individual substances, and some of the isolated fractions were analyzed by PMR spectroscopy. Despite the use of up-to-date analytical instrumentation, alternative structures had to be assigned to some of the elution peaks.

The results obtained by analyzing PCBs by thin-layer and column chromatography and gas chromatography-mass spectrometry (GC-MS) have been reviewed by Fishbein<sup>8</sup>. Mass spectrometric fragmentation of PCBs has been studied by Hutzinger *et al.*<sup>1</sup> and by Safe and Hutzinger<sup>10</sup>. Oswald *et al.*<sup>11</sup> investigated the isomeric structures of the substances of this class by GC-MS. <sup>13</sup>C-Labeling techniques have been applied to obtain a better understanding of the *o,o'*-interactions.

The mass spectra of PCBs are characterized by two pronounced features. (1) The spectra of most PCBs contain rather large peaks corresponding to  $[M - 70]^+$  ions, and peaks corresponding to doubly charged ions. (2) The isotopic clusters of chlorine (75.8% <sup>35</sup>Cl, 24.2% <sup>37</sup>Cl) make it possible to distinguish between substances with different numbers of chlorine atoms.

The mass spectra of monochlorobiphenyls are similar. Hence, no unambiguous conclusions about the location of chlorine atoms can be drawn from these spectra. Nor do mass spectra of the isomeric dichlorobiphenyls differ much from one another. The only exception is 2,2'-dichlorobiphenyl from which a very abundant  $[M - 70]^+$  ion is formed. Of the tetrachlorobiphenyls, the 2,2',5,5' derivative can be unequivocally identified since the relative intensity of the  $[M - 35]^+$  ion differs by an order of magnitude from that of the corresponding fragment ions from other isomers of the same class. Although the intensity of the  $[M - 70]^+$  ion produced from the 2,2',6,6' isomer differs only slightly from that produced from the 2,2',5,5' derivative, both substances can be identified because the ions  $[M - 35]^+$  and  $[M - 36]^+$  formed from them have different intensities.

With GC-MS techniques a number of isomeric PCBs present in a mixture can

be distinguished and the number of chlorine atoms corresponding with the elution peaks can be determined by MS from the molecular ions. Individual isomers however, can only be unambiguously identified when standard materials are available.

The aim of the present work is to point out the possibilities and limitations in the analysis of PCBs by capillary GC and MS. As model PCB mixtures commercial preparations containing 41–44% of chlorine were used.

## EXPERIMENTAL

### *Apparatus, working conditions and chemicals*

An Erba Science (Fractovap, Model 2300) gas chromatograph was used. Mass spectra were recorded on a Varian-MAT 111 (Gnom) GC-MS system and an AEI MS-12 mass spectrometer with a directly coupled WCOT column<sup>13</sup>. The samples were injected in the form of acetone or dichloromethane solutions from a 10- $\mu$ l Hamilton microsyringe.

The working conditions are summarized in Table I.

TABLE I  
GAS CHROMATOGRAPHY WORKING CONDITIONS

Apparatus	Erba Science	Erba Science	Erba Science
Column	stainless steel	glass	stainless steel
Length (m)	45	50 and 60	45
I.D. (mm)	0.25	0.25	0.25
Column temperature (°K)	473	450–490	473
Injector port temperature (°K)	523	523	523
Liquid phase	Apiezon L	OV-101	OV-101
Nitrogen flow-rate (ml/min)	0.5	0.3–0.7	0.5
Inlet splitter	1/100	1/60–1/100	1/70

The retention times were measured with a stop-watch or a digital integrator (Autolab, Model 6300). The dead retention time was determined with methane.

Kováts' retention indices were determined with *n*-alkanes (C<sub>12</sub>–C<sub>22</sub>). The components in the mixtures were characterized by mass spectra obtained by GC-MS techniques, the working conditions of which are summarized in Table II.

Standard isomeric PCBs were: 2-; 3-; 4-; 2,3-; 2,6-; 4,4'-; 2',3,4-; 2,2',5-; 2,3',5-; 2,4',5-; 2,2'-; 3,3'-; 2,2',3,5'-; 2,2',4,4'-; 2,2',5,5'-; 2,2',4,5'-; 2,3',4,5'-; 2,3',4',5-; 2,2',6,6'-; 3,3',4,4'-; 2,2',3,4,5'-. These PCBs were obtained from Analabs (North Haven, Conn., U.S.A.). The PCB mixtures analyzed were commercial products: Aroclor 1232, Aroclor 1242 (Monsanto, St. Louis, Mo., U.S.A.) or distillates obtained from the commercial products by rectification at reduced pressure.

Other chemicals were of reagent-grade purity. The solvents were freshly distilled.

### *Characterization of capillary columns*

Glass capillary columns coated with OV-101 were characterized by their capacity ratio (*k*) for 2,2',5-trichlorobiphenyl, relative retentions (*r*) for 4,4'-dichloro-

TABLE II  
GC-MS WORKING CONDITIONS

Apparatus	Varian-MAT Model 111	AEI MS-12*
Electron energy (eV)	80	70
Ionizing current ( $\mu$ A)	280	500
Column	stainless steel	glass
Length (m)	2	30
I.D. (mm)	2	0.25
Column temperature ( $^{\circ}$ K)	463-483 programmed 2 $^{\circ}$ /min	473
Injector port temperature ( $^{\circ}$ K)	493	493
Ion source temperature ( $^{\circ}$ K)	493	493
Liquid phase	3% SE-30 or OV-225	SE-30
Helium flow-rate (ml/min)	15	0.5
Support	Chromosorb W HP	—
Mesh size	60-80	—

\* Details on the direct coupling of a capillary column to a mass spectrometer were described by Leferink and Leclercq<sup>13</sup>.

biphenyl and 2,2',5-trichlorobiphenyl, by the number of theoretical plates ( $n$ ) for 2,2',5-trichlorobiphenyl, separation number ( $n_{sep}$ ) for octadecane and hexadecane and the calculated number of theoretical plates ( $n_l$ ) necessary to separate 4,4'-dichlorobiphenyl from 2,2',5-trichlorobiphenyl at the resolution  $R = 1.5$  (Table III).

Although the characteristics of the glass capillary columns were altered by ageing, these alterations were less pronounced than those of metal capillary columns. During a 3-months period  $k$  for 2,2',5-trichlorobiphenyl had changed from the original value of 2.26 to 1.08 (using a 60-m column) and during a period of 3 weeks from 1.41 to 1.38 (using a 50-m column). The decreased capacity ratio was a result of the bleeding

TABLE III  
CHARACTERISTICS OF THE GLASS CAPILLARY COLUMNS COATED WITH OV-101

Length (m)	50	60
Temperature ( $^{\circ}$ K)	473	473
Capacity ratio ( $k$ )*	1.38	1.27
Number of theoretical plates ( $n$ )**	186,000	173,000
Separation number ( $n_{sep}$ )***	32	34
Calculated number of theoretical plates ( $n_l$ )	280,000	300,000
Relative retention ( $r$ ) <sup>§</sup>	1.02	1.02

$$* k = t_R/t_M$$

$$** n = 5.54 \left( \frac{t_R}{W_{1/2}} \right)^2 \quad \text{where } W_{1/2} \text{ is the peak width at half height.}$$

$$*** n_{sep} = \frac{t_{R,z+2} - t_{R,z}}{W_{1/2,z+2} + W_{1/2,z}} - 1 \quad \text{where } z \text{ is the number of carbon atoms, and } W_{1/2,z+2} \text{ and } W_{1/2,z} \text{ are the widths of all peaks at half-height.}$$

$$§ r_{1,2} = t_{R,2}/t_{R,1}$$

$$R_{1,2} = \frac{t_{R,2} - t_{R,1}}{W_{1/2,1} + W_{1/2,2}}$$

out of a considerable amount of the stationary phase from the columns during the time they had been in operation. The efficiency of the columns, calculated for 2,2',5-trichlorobiphenyl, decreased during a period of three months from the original value of 227,000 to 173,000 theoretical plates (60-m column) and during a three-week period from 198,000 to 186,000 theoretical plates (50-m column).

## RESULTS AND DISCUSSION

In the first approach the components in Aroclor 1242 were characterized by GC-MS on a packed column with OV-225 as a liquid phase. Fig. 1 shows a chromatogram of this PCB mixture on 3% OV-225 using the mass spectrometer as detector. MS showed that each of several peaks corresponded to more than one component, containing different numbers of chlorine atoms. Moreover, the elution of several isomeric substances, containing the same number of chlorine atoms, in one peak cannot be excluded.

In the next approach the separation and characterization of PCBs on a capillary column (WCOT) and by capillary GC-MS techniques was investigated.

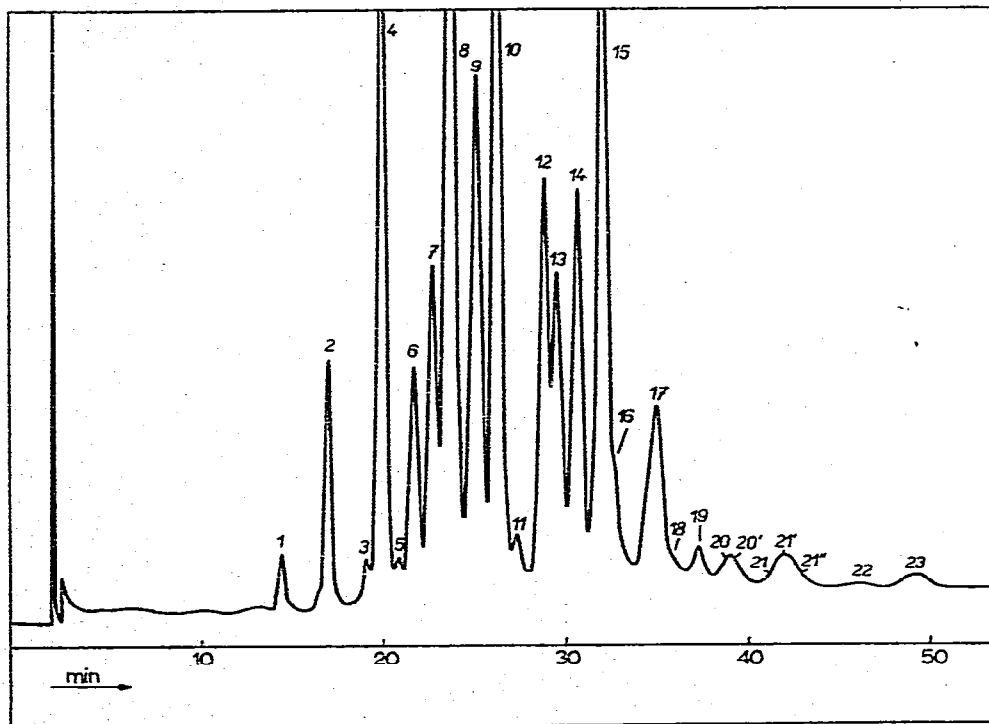


Fig. 1. Separation of Aroclor 1242 on a packed column coated with OV-225. For details see Table II. The peak numbers corresponding to number of chlorine: 1, 2Cl; 2, 2Cl; 3, 3Cl; 4, 3Cl; 5, 3Cl; 6, 2Cl; 7, 3Cl; 8, 3Cl; 9, 3Cl + spots of 4Cl; 10, 3Cl + 4Cl; 11, 3Cl + 4Cl; 12, 4Cl; 13, 4Cl; 14, 3Cl + 4Cl; 15, 4Cl + 5Cl; 16, 5Cl + 4Cl; 17, 4Cl + spots of 5Cl; 18, 4Cl + 5Cl; 19, 5Cl + 6Cl; 20, 5Cl + 6Cl; 20', 5Cl + 6Cl; 21, 5Cl + 6Cl; 21', 4Cl + 5Cl + 6Cl; 21'', 4Cl + spots of 5Cl + 6Cl; 22, 6Cl; 23, 5Cl + 6Cl.

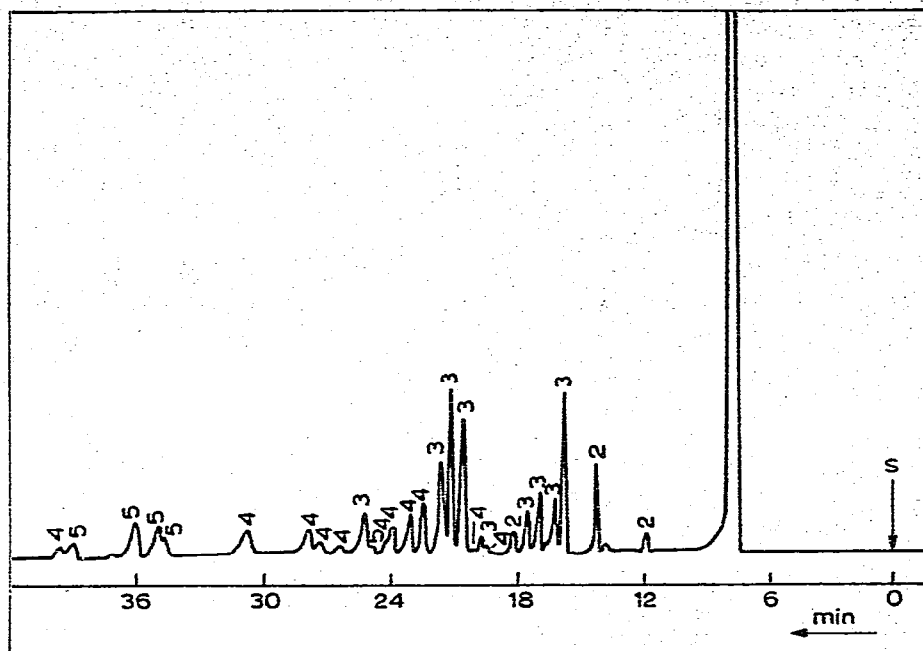


Fig. 2. Separation of Aroclor 1242 on a metal capillary column, coated with Apiezon L, at 473 °K. For details see text.

Fig. 2 shows a chromatogram of Aroclor 1242 on a metal capillary column, coated with Apiezon L, at 473 °K. The number of chlorine atoms per peak was assigned by MS<sup>12</sup>. Fig. 3 shows the separation of Aroclor 1242 on a metal capillary column, coated with OV-101, at 473 °K.

An important drawback of metal capillary columns coated with Apiezon L or OV-101 is their ageing, resulting in a decreased resolving power and the elution of asymmetric peaks of PCBs. In addition, the metal walls of the capillary may cause

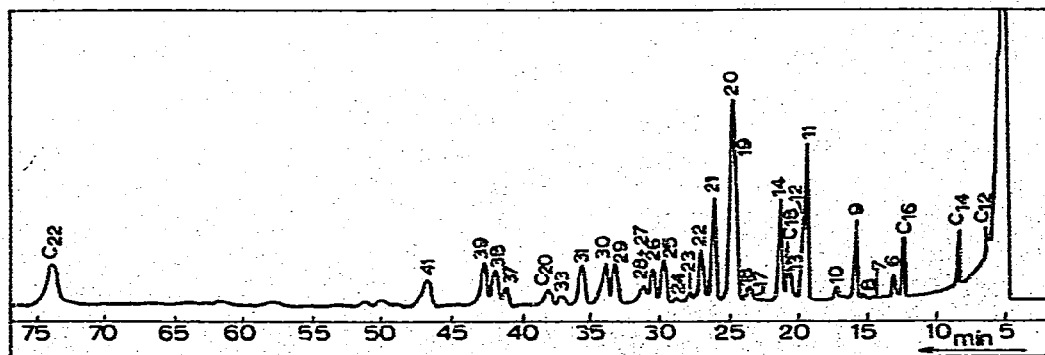


Fig. 3. Separation of Aroclor 1242 and *n*-alkanes C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub>, C<sub>18</sub>, C<sub>20</sub>, C<sub>22</sub> on a metal capillary column, coated with OV-101, at 473 °K. Peak numbers are the same as in Table V.

catalytic dechlorination and/or redistribution of the chlorine atoms in the isomeric PCBs.

Most of the drawbacks mentioned above were successfully overcome by using glass capillaries. After suitable modification of the glass surface, these columns were sufficiently inert, and capillary columns with excellent efficiency and high resolving power (Table III) were made. These properties are particularly important when environmental samples are analyzed for the presence of PCBs<sup>1</sup>. OV-101 was selected as stationary phase because very efficient capillary columns can be made with this phase and it is considerably less polar than Apiezon L. Kováts' retention indices of the corresponding PCBs determined on Apiezon L are larger by 100 units than on OV-101 (ref. 4).

Fig. 4 shows a chromatogram of a model mixture of PCBs on a glass capillary column, coated with OV-101, at 473 °K. The elution pattern gives symmetrical peaks and shows that the efficiency of the column is considerably higher than that of the comparable metal column.

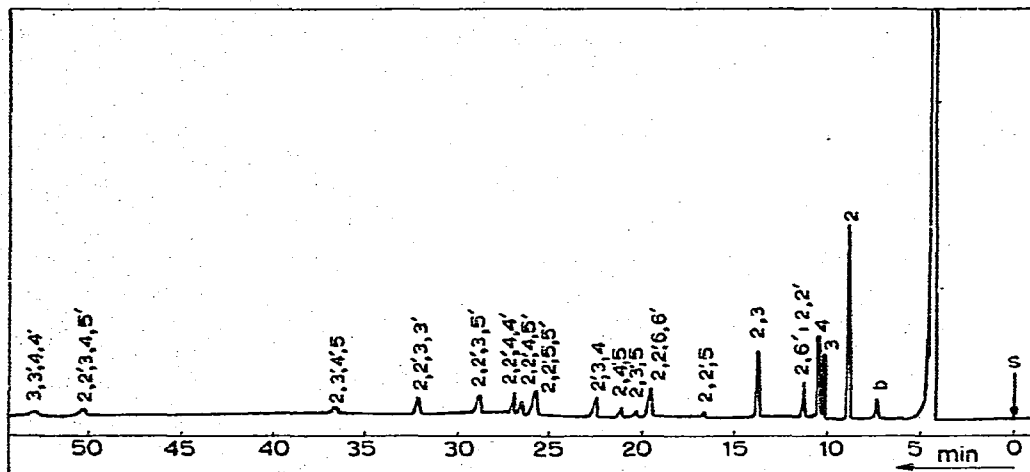


Fig. 4. Separation of a model mixture of PCBs on a glass capillary column, coated with OV-101, at 473 °K.

Fig. 5 shows a chromatogram of Aroclor 1242 on a glass capillary column, coated with OV-101, at 473 °K. The resolution of peaks 11 and 12, 19 and 20, and 27 and 28 caused some problems. Peaks 11 and 12, and 27 and 28 were much better distinguished at a lower working temperature (453 °K).

The characterization of PCBs is usually done by standard addition, Kováts' retention indices or MS. In the following the characterization of PCB mixtures by these techniques is critically analyzed.

The chromatograms of the separation of Aroclor 1242 together with standard materials on a glass capillary column, coated with OV-101, at 473 °K is shown in Fig. 6. Under the working conditions used, 2,2'- and 2,5-dichlorobiphenyl could not be distinguished, nor could 2,3- and 2,4'-dichlorobiphenyl, and 4,4'-dichlorobiphenyl could not be distinguished from 2,2',4-trichlorobiphenyl.

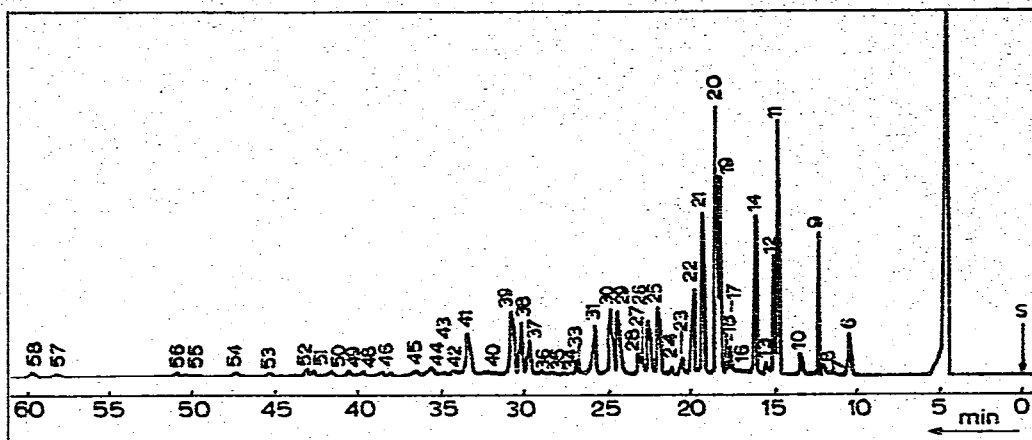


Fig. 5. Separation of Aroclor 1242 on a glass capillary column, coated with OV-101, at 473 °K.

To distinguish between 2,2'- and 2,6-dichlorobiphenyls a column with an efficiency of 600,000 theoretical plates would be required and for 2,3- and 2,4'-dichlorobiphenyls and 4,4'-dichloro- and 2,2',4-trichlorobiphenyls an efficiency of 350,000 theoretical plates would be necessary (provided that the capacity ratio remained unaltered and  $R_{1,2} = 1.5$ ; Table III). It follows that the identification, from a standard addition, even when highly efficient columns are used, may lead to erroneous conclusions. Under the given conditions (commercial instrument, column, etc.) the characterization of PCB components in a mixture is much more precisely done by the comparison of their Kováts' indices with those of the standard materials. It is necessary, however, that the corresponding indices agree within the limits of the experimental error. Repeatability of the Kováts' index measurements, when expressed in terms of the standard deviation, as a rule allows more accurate information about the mixture than is obtained with the standard addition method. Thus, for instance, retention indices found for 2,2'-dichlorobiphenyl and 2,6-dichlorobiphenyl were  $1625.8 \pm 0.3$  and  $1627.9 \pm 0.6$ , respectively. It is evident that peak 6 (Fig. 5), for which the index was  $1625.6 \pm 0.2$ , unquestionably corresponds to 2,2'-dichlorobiphenyl and not to the other isomer although these two could not be separated under the conditions used (Fig. 6).

The repeatability of the retention index measurements of the standard PCBs was ascertained at three different temperatures. Table IV shows the retention indices, standard deviations and temperature increments for the standard isomers as found on a 60-m glass capillary column coated with OV-101. Table IV shows that the standard deviation from the arithmetic mean value is less than 0.5 index unit.

Under our conditions of measurement, the Kováts' indices calculated from the retention times measured with a stop-watch (accuracy  $\pm 0.1$  sec) and from those measured with a digital integrator (accuracy  $\pm 0.5$  sec) were, within experimental error, virtually the same. Table IV shows that  $\Delta I/10^\circ$  depends on the number of chlorine atoms and their location in the molecule of biphenyl. The use of temperature increments for identification purposes, however, would require more accurate retention index measurements.





The retention indices measured during the period of three months on one column remained virtually unaltered, although a portion of the liquid phase had bled out (Table III).

Table V contains the peak numbers of the main Aroclor 1242 components (Fig. 5) and the number of chlorine atoms determined by GC-MS, Kováts' retention indices of the main Aroclor 1242 components measured at 473 °K, their standard deviations, temperature increments ( $\Delta I/10^\circ$ ) and the structures as found by standard additions, and the comparison of the indices found for the standard materials and Aroclor components.

TABLE V

KOVÁTS' RETENTION INDICES, THEIR STANDARD DEVIATIONS AND TEMPERATURE INCREMENTS FOR PCB STANDARD MATERIALS, AND THE MAIN COMPONENTS IN AROCLOR 1242 MEASURED ON A 50-m GLASS CAPILLARY COLUMN

Peak No.	Cl	$I^*$	$\sigma$	$\Delta I/10^\circ$	Found structure
6	2	1625.8	0.3	8.8	2,2'
7	2	1671.4	0.4	5.5	2,4
8	2	1690.0	0.3	8.3	2,3'***
9	2	1700.9	0.2	8.6	2,4'
10	3	1735.8	0.2	9.2	2,2',6**
11	3	1776.2	0.1	9.4	2,2',5
12	2	1781.8	0.1	9.5	4,4' + 2,2',4
13	—	1795.6	0.3	9.3	—
14	3	1810.0	0.1	9.8	2,2',3**
17	3	1843.6	0.2	9.0	2,3',5
18	3	1848.8	0.2	9.4	2,3',4**
19	3	1858.1	0.1	9.3	2,4',5
20	3	1861.1	0.2	9.3	2,4,4'
21	3 + 4	1878.1	0.1	9.7	2',3,4
22	3	1890.2	0.4	10.8	—
23	4	1899.7	0.1	10.8	—
24	4	1912.5	0.2	10.8	—
25	4	1922.7	0.2	9.4	2,2',5,5'
26	4	1931.3	0.1	9.9	2,2',4,5'
27	4	1937.1	0.1	10.0	2,2',4,4'
28	4	1939.1	0.1	10.1	—
29	4	1958.1	0.1	10.3	2,2',3,5'
30	4	1965.2	0.2	10.9	2,2',3,4'***
31	4	1980.1	0.1	10.8	—
33	4	1992.7	0.1	11.3	2,2',3,3'
35	—	2009.9	0.5	12.4	—
37	4	2025.7	0.1	10.8	—
38	4	2031.3	0.1	10.6	2,3',4',5
39	5	2037.4	0.1	11.0	—
40	5	2048.8	0.4	11.1	—
41	4	2065.3	0.1	11.9	—
42	5	2074.0	0.1	11.6	—
44	5	2084.6	0.2	10.6	—
49	5	2128.2	0.5	11.1	2,2',3,4,5'
51	4	2146.6	0.5	11.5	3,3',4,4'

\* Indices measured at 473 °K.

\*\* Assumed structure based on structural interpretation of Kováts' indices.

The numbers of chlorine atoms represented in the individual peaks were determined by GC-MS analysis of Aroclor 1242 on a glass capillary column coated with SE-30 (Fig. 7). The column was directly coupled to the mass spectrometer<sup>13</sup>. In this way excellent mass spectra were obtained from nanogram quantities of material. We found, in disagreement with data from the literature<sup>1</sup>, that many of the components containing the same number of chlorine atoms differed significantly in the intensity ratio of the peaks produced  $[M]^+$ ,  $[M-35]^+$ ,  $[M-70]^+$  and  $[M-105]^+$ .

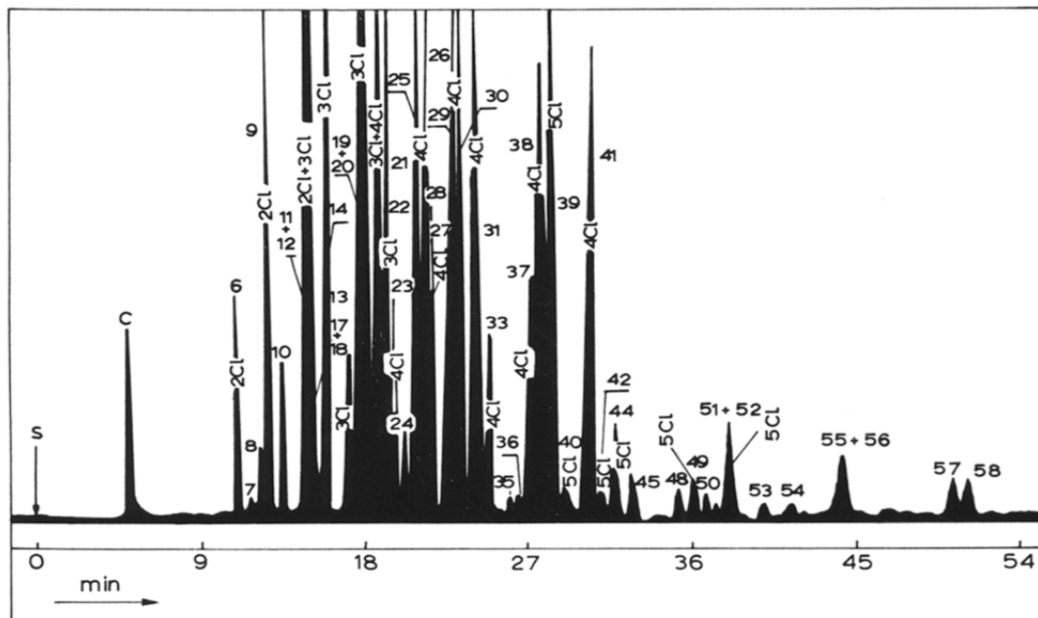


Fig. 7. GC-MS analysis of Aroclor 1242: total ion current chromatogram. For details see text and Table II.

As examples, Figs. 8 and 9 show the mass spectra of 2,2',3- and 2,4',5-trichlorobiphenyl in which the intensity ratios of the ions  $[M]^+$ ,  $[M-35]^+$ , and  $[M-70]^+$  are different. Generally, however, the correlation of the spectra with the PCB structures is difficult and the routine characterization should be done by capillary GC data.

In inter-laboratory retention data exchange, Kováts' indices are most often used<sup>1,4</sup>. To be able to take advantage of the published retention indices for the identification of PCBs in mixtures it is necessary to evaluate the reproducibility of the retention index determination.

Kováts' retention indices of some isomeric PCBs were, at 473 °K, determined on three capillary columns coated with OV-101. The index reproducibility was an order of magnitude worse than their repeatability.

The temperature of the stationary phase (which, for a capillary column may differ significantly from that in the thermostat), column material, modification of the column inner surface and the chemical composition of the stationary phase are parameters that may be responsible for the errors and may significantly affect the reproducibility of the retention index measurements.

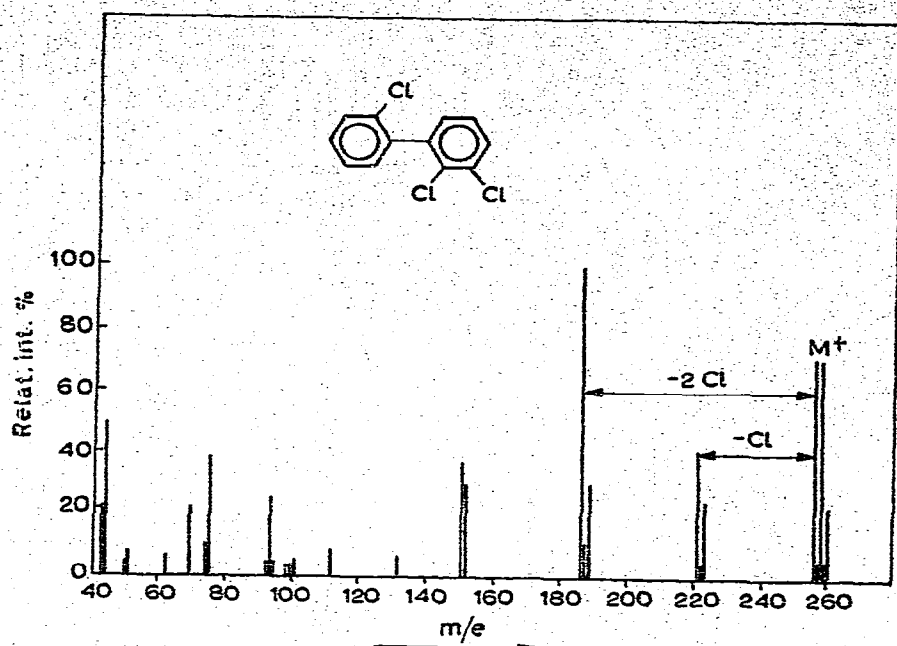


Fig. 8. Mass spectrum of 2,2',3-trichlorobiphenyl.

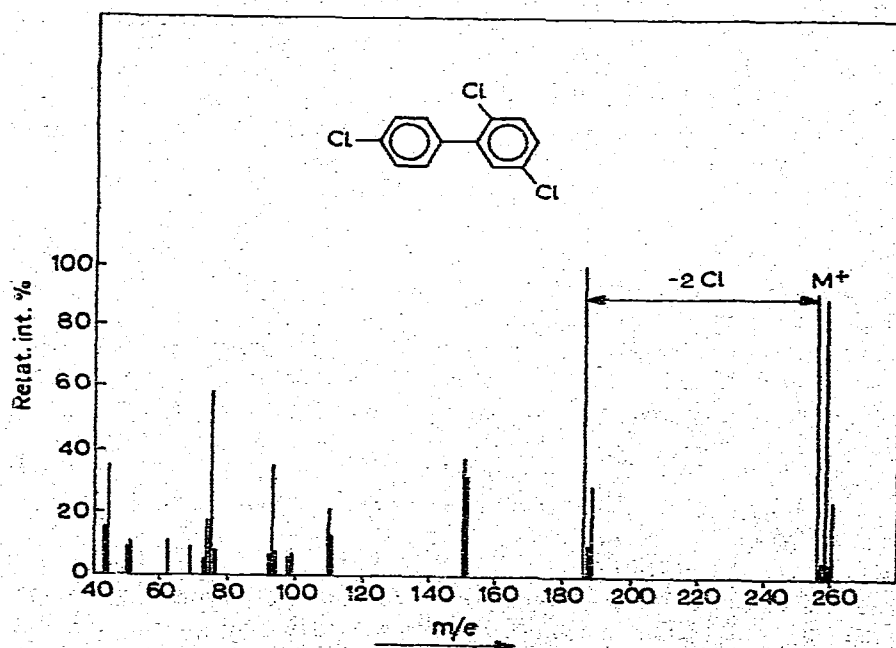


Fig. 9. Mass spectrum of 2,4',5-trichlorobiphenyl.

Recalculation of the indices  $I_2$  and  $I_3$  to 475.5 °K and 478.6 °K, respectively, gives  $I_1$ ,  $I_2$  and  $I_3$  with a deviation of less than  $\pm 1$  index unit, from which it can be deduced that the main limiting factor of the improved reproducibility is the different temperature of the liquid phase.

## CONCLUSIONS

The following conclusions may be drawn from the results obtained by analyzing PCBs in Aroclor 1242 by capillary GC and MS.

Metal capillary columns coated with OV-101 or Apiezon L are not suitable for PCB analysis.

The characterization of the components in a PCB mixture by Kováts' retention indices is more precise than that based on standard addition.

The repeatability of the Kováts' index measurements of PCBs using a commercial instrument is comparable with that of hydrocarbons.

The reproducibility of Kováts' retention indices obtained with a commercial instrument is insufficient for inter-laboratory data exchange.

By direct coupling of a glass capillary column to a mass spectrometer, good mass spectra can be obtained from nanogram quantities of substances, and the spectra can be used for the identification of isomeric PCBs.

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