

## Quantitative Analysis of Biphenyl, Terphenyls and Polyphenyls by Programmed Temperature Gas—Solid Chromatography

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The authors studied the separation of biphenyl, terphenyls and several polyphenyls on a caesium chloride modified support, isothermally and at programmed column temperature. The quantitative determination of the individual constituents has been treated statistically and the determinations by IR spectroscopy and gas—solid chromatography have been compared as to their correctness. Lack of suitable organic stationary liquids which could be employed at temperatures above 280 °C is due to the limited thermal stability of organic compounds and to their high vapour pressure at such temperatures.

Great attention has been paid to the separation of polyphenyls by gas—liquid chromatography [1—6] and also modified adsorbents have been described [7—20]. The separation described in the present paper has been achieved on a short column containing a relatively small amount of an inorganic salt, i. e. caesium chloride.

### Experimental

The determination of mixed polyphenyls was performed in a Carlo Erba gas chromatograph (Milano, Italy) fitted with a dual flame ionization detector, Leed—Northrup (USA) and a Speedomax G recorder having a range of 2.5 mV. The record was evaluated by means of a Carlo Erba model 72 integrator and the results printed in a Kienzle printer (West Germany).

The samples were injected with a Hamilton 1  $\mu$ l syringe (Whittier, California, USA). The carrier gas was nitrogen (Chemlon, N. E., Humenné), the combustible gas was electrolytical hydrogen (Chemical Works W. P., Nováky) and the air was as supplied by Technoplyn (Poprad).

### *Column characteristics*

length of column	100 cm
column I. D.	5 mm
column volume	19.5 ml
weight of Chromosorb P	8.332 g
weight of caesium chloride	0.920 g
adsorbent particle size	100—120 mesh
column temperature — isothermal	230, 251, 270 and 300 °C, respectively

temperature programme	125—360 °C; 12.5 °C/min
detector temperature	340 °C
injection block temperature	335 °C
nitrogen flow rate	48.8 ml/min
hydrogen flow rate	50.0 ml/min
air flow rate	350.0 ml/min

The pure components were prepared in our laboratories and their purity was better than 99.99 %, except for *m*-terphenyl. The purity of standards was checked by measuring their physical constants and by comparing their absorption spectra. The column packing was prepared according to ref. [15].

### Infrared spectra of polyphenyls

The sample was dissolved in carbon disulfide. The cells were of NaCl, 1.01 mm thick, or of KBr, 1.036 mm thick. The measurements with the KBr cell were against the compensating window. The apparatus was an UR-10, Zeiss spectrometer. The quantitative determination was made by evaluating the following bands: 542  $\text{cm}^{-1}$  for diphenyl, 557  $\text{cm}^{-1}$  for *o*-terphenyl, 799  $\text{cm}^{-1}$  for *m*-terphenyl and 840  $\text{cm}^{-1}$  for *p*-terphenyl.

### Isothermal chromatography

A mixture of biphenyl and the isomeric terphenyls was separated at the above stated column temperatures ranging between 230—300 °C. A typical separation is shown in the chromatogram of Fig. 1. The specific retention volumes of the individual polyphenyls are listed in Tab. 1.

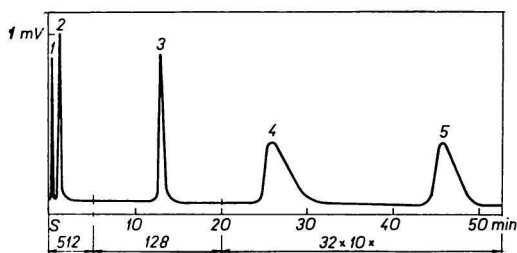


Fig. 1. Chromatogram of an isothermal separation at 230 °C of biphenyl and terphenyls.

1. benzene; 2. biphenyl; 3. *o*-terphenyl;  
4. *m*-terphenyl; 5. *p*-terphenyl.

Table 1

Specific retention volumes of several polyphenyls at various temperatures on chromosorb P modified with 10 % CsCl

Component	$V_g$			
	230 °C	251 °C	270 °C	300 °C
biphenyl	45.0	20.9	11.52	4.91
<i>o</i> -terphenyl	86.0	38.9	20.60	8.10
<i>m</i> -terphenyl	196.5	99.8	42.80	13.50
<i>p</i> -terphenyl	336.0	132.8	54.40	15.65

The data obtained were used for plotting  $\log V_g$  against  $1/T$  over the employed temperature range, as shown in Fig. 2.

### Column temperature programming

The isothermal runs show that the isothermal analysis gives peaks of poor symmetry and that the retention times are excessively long, particularly at the lower temperatures. The separation was therefore studied by programmed-temperature gas—solid chromatography. The sample was injected at 125 °C. Good separation of all components including the quaterphenyls present in the mixture has been achieved at a temperature programme from 125 °C to 360 °C. A chromatogram of an artificial mixture is shown in Fig. 3.

A column packed with Chromosorb P coated with 10 % caesium chloride has a great advantage over packing materials containing some GLC stationary phase in that there is no column bleeding at the temperature programmed run and the base line is steady even at the maximal column temperature, provided that the carrier gas flow rate in both branches is kept constant over the whole temperature range. The retention times and temperatures of the individual components are listed in Tab. 2.

### Qualitative analysis

The qualitative analysis of a technical grade product illustrated in Fig. 4 was performed

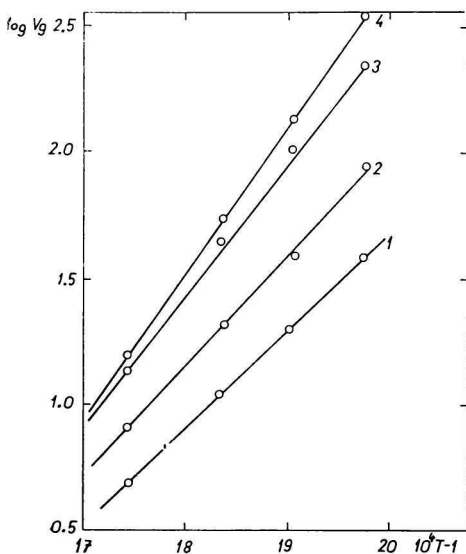


Fig. 2. The plot of  $\log V_g$  against  $T^{-1}$  for biphenyl and terphenyls.

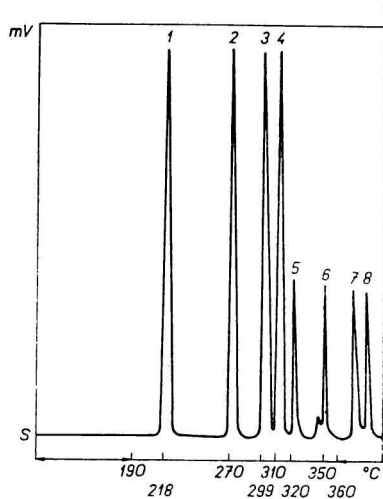


Fig. 3. Chromatogram of the separation of polyphenyls at a linear temperature programme (125–360 °C) run at a rate of 12.5 °C/min.

1. biphenyl; 2. *o*-terphenyl; 3. *m*-terphenyl; 4. *p*-terphenyl; 5. triphenylene; 6. *o,m*-quaterphenyl; 7. *m,p*-quaterphenyl; 8. *p,p'*-quaterphenyl.

by direct introduction of the particular component i. e. for biphenyl, *o*-, *m*-, *p*-terphenyl, *o,m*- and *p,p'*-quaterphenyls by infrared spectra (*o,o'*- and *m,m'*-quaterphenyls) and by the retention data [14] (1,2,3-triphenylbenzene and 1,3,5-triphenylbenzene) (Fig. 4).

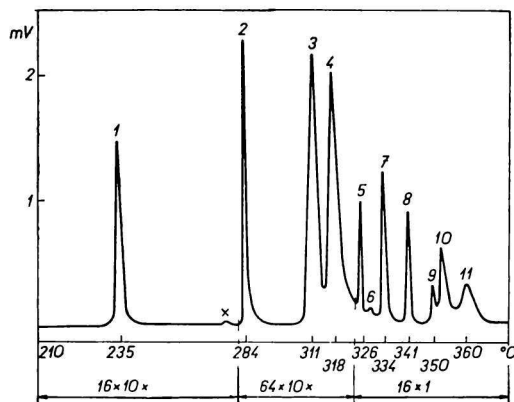


Fig. 4. Chromatogram of the separation of polyphenyls in a technical grade sample at a linear temperature programme over the 210–360 °C range at a rate of 12.5 °C/min.

1. biphenyl; 2. *o*-terphenyl; 3. *m*-terphenyl; 4. *p*-terphenyl; 5. triphenylene; 6. 1,2,3-triphenylbenzene; 7. *o,m*-quaterphenyl; 8. *o,p*-quaterphenyl; 9. 1,3,5-triphenylbenzene; 10. *m,m'*-quaterphenyl; 11. *p,p'*-quaterphenyl.

Table 2

Retention times and temperatures of polyphenyls at a programme rate of 12.5 °C/min.

Component	$T_R$ °C	$t_R$ min
biphenyl	218	7.44
<i>o</i> -terphenyl	275	12.00
<i>m</i> -terphenyl	303	14.24
<i>p</i> -terphenyl	309	14.73
triphenylene	321	15.28
1,2,3-triphenylbenzene	333	16.64
<i>o,m</i> -quaterphenyl	337	16.96
<i>o,p</i> -quaterphenyl	344	17.52
1,3,5-triphenylbenzene	357	18.56
<i>m,m'</i> -quaterphenyl	360	18.80
<i>m,p</i> -quaterphenyl*	360	20.00
<i>p,p'</i> -quaterphenyl	360	20.79

\* The peak is not shown in Figure.

### Quantitative analysis

For the quantitative analysis of biphenyl and terphenyls, a mixture containing the components in known proportions was prepared from specimens whose purity was better than 99.99 % except for *m*-terphenyl which contained 3.1 % of *p*-terphenyl (as determined by IR spectrometry). The components were weighed on a semimicro balance. The quantitative results were obtained by means of calibration graphs for the individual components.

For a statistical evaluation of the accuracy of the determination, a 1 % solution of

an artificial mixture was prepared and kept as stock solution which was injected in the chromatograph. The concentrations of the individual components were evaluated from calibration graphs and from the integrator printout for eight parallel runs. The results are summarized in Tab. 3.

The evaluation was made according to ref. [21]. The figures of the Student test furnished evidence for the reliability of the method. Only the value for *m*-terphenyl is larger than the critical value ( $t_c = 2.365$ ) which is due to the contamination of *m*-terphenyl by *p*-terphenyl.

The quantitative results were also checked by making analyses of various specimens of Santowax, a commercial product of Monsanto Chem. Co. (St. Louis, Missouri). The

Table 3

Statistical evaluation of the results of gas chromatography

Component	Actual concn. weight %	Concn. found weight %	R.	100 · R · $K_n/u$ %
biphenyl	0.122	0.145 ± 0.29 × 0.11	0.11	26.00
<i>o</i> -terphenyl	22.72	22.80 ± 0.29 × 1.80	1.80	2.30
<i>m</i> -terphenyl	43.14	42.20 ± 0.29 × 0.14	1.31	1.20
<i>p</i> -terphenyl	28.74	28.73 ± 0.29 × 0.14	0.14	0.14
polyphenyls	5.11	5.11 ± 0.29 × 0.89	0.89	5.05

Table 4

Comparison of the results of analysis of a mixture of SANTOWAXES by IR<sub>1</sub> and GC

	Biphenyl		<i>o</i> -Terphenyl		<i>m</i> -Terphenyl		<i>p</i> -Terphenyl		Polyphenyl	
	IR	GC	IR	GC	IR	GC	IR	GC	IR	GC
R	1	1.46	7.5	7.1	52.5	54.2	31.5	22.7	6.7	14.55
OMP	—	0.24	7.0	10.6	53.6	54.1	30.7	33.1	—	1.96
OM	1	2.00	72.1	78.0	14.0	18.75	7.3	1.25	—	0.10

Table 5

Composition of Delowax S, a mixture of terphenyls containing higher polyphenyls

Sample	Colour	1	2	3	4	5	6	7	8	9
R <sub>1</sub>	yellow	90.56	0.76	0.09	3.02	2.82	0.99	1.06	0.70	9.44
R <sub>2</sub>	brown	85.36	1.82	0.12	5.20	4.97	1.10	0.80	0.60	14.78

Legend: 1. biphenyl + terphenyls; 2. triphenylene; 3. 1,2,3-triphenylbenzene; 4. *o*,*m*-quaterphenyl; 5. *o*,*p*-quaterphenyl; 6. 1,3,5-triphenylbenzene; 7. *m*,*p*-quaterphenyl; 8. *p*,*p'*-quaterphenyl; 9. total of higher polyphenyls.

quantitative results of the two methods differ considerably. The cause may be that the standards employed for the preparation of IR calibration graphs differed in quality. The quantitative results as calculated from the IR spectra of the polyphenyls were computed to make 100 % (Tab. 4).

Adoption of gas chromatography permits to carry out the analysis of polyphenyls in a shorter time than by IR spectrometry. The flame ionization detector permits the determination of all components in a microgram sample of the mixture. The percentages of the individual components obtained by evaluating the respective peak areas and comparing them with the calibration graphs provide ready information about the individual components.

An analysis for the content of the higher polyphenyls present in Delowax S (Chemko, N. E., Strážske) is shown in Tab. 5.

*The authors wish to thank Ing. J. Guoth for the preparation and interpretation of IR spectra.*

## KVANTITATÍVNA ANALÝZA BIFENYLU, TERFENYLOV A POLYFENYLOV CHROMATOGRAFIOU V SYSTÉME PLYN—ADSORBENT S PROGRAMOVANOU TEPLOTOU KOLÓNKY

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Chromatografiou v systéme plyn—adsorbent na Chromosorbe P, ktorý bol pokrytý 10 % chloridu cézneho, oddeľoval sa bifenyl, terfenyly a vyššie polyfenyly izotermickou technikou a programovaním teploty chromatografickej kolónky. Kvantitatívne výsledky sa vyhodnocovali matematicko-štatistickými metódami a správnosť stanovenia sa porovnala metódou infračervenej spektrofotometrie a plynovej chromatografie.

## КОЛИЧЕСТВЕННЫЙ АНАЛИЗ ДИФЕНИЛА, ТЕРФЕНИЛОВ И ПОЛИФЕНИЛОВ ХРОМАТОГРАФИЕЙ В СИСТЕМЕ ГАЗ—АДСОРБЕНТ С ПРОГРАМИРОВАННОЙ ТЕМПЕРАТУРОЙ КОЛОНКИ

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Хроматографией в системе газ—адсорбент на Хромосорбе П, который был покрыт 10 % хлорида цезия, с програмированием температуры хроматографической колонки были отделены дифенил, терфенил и полифенилы. Количественные результаты обрабатывались методами статистической математики и сравнивалась правильность определения методом инфракрасной спектрофотометрии и газовой хроматографии.

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