USE OF RETENTION TEMPERATURES FOR THE IDENTIFICATION OF PHENOLS SEPARATED ON OV-1701 CAPILLARY COLUMNS USING LINEAR TEMPERATURE-PROGRAMMED GAS CHROMATOGRAPHY

J. KRUPČÍK*, D. REPKA, E. BENICKÁ and T. HEVESI

Department of Analytical Chemistry, Chemical Faculty, Slovak Technical University, Radlinského 9, 812 37 Bratislava (Czechoslovakia)

and

J. NOLTE, B. PASCHOLD and H. MAYER

Institut für Spektrochemie und angewandte Spektroskopie, Dortmund 1, (F.R.G.)

(First received April 7th, 1988; revised manuscript received May 17th, 1988)

SUMMARY

   A procedure is described by means of which linear temperature-programmed gas chromatographic (LTPGC) retention data can be predicted from isothermal Kováts retention indices of substituted phenols separated on capillary columns coated with OV-1701 under LTPGC conditions. The identification algorithm included the comparison of retention temperatures predicted from isothermal data ($T_{R,P}$) with retention temperatures obtained experimentally under LTPGC conditions ($T_{R,E}$) in a window which was within 1.5°C. The identification of phenol sample constituents based on the comparison of retention data was checked using spectra obtained by gas chromatography–mass spectrometry because in the identification window several sample constituents overlapped.

INTRODUCTION

   Substituted phenols are often used as disinfectants and gas chromatography (GC) is a very suitable method for their analysis. The separation of the constituents of a complex phenol sample requires capillary columns. As phenols containing electronegative substituents are strong acids, the inner surface of capillary columns for their analysis must be very inactive. In previous studies we have established conditions in which glass or fused-silica capillary columns coated with OV-1701 can be successfully used for the separation of phenols[1,2]. Further, we have shown that when separating phenol samples by linear temperature-programmed GC (LTPGC), the elution order of phenols depends on the programme mode, which complicates the qualitative analysis[2]. In subsequent studies we developed a procedure that allows the prediction of the retention temperatures ($T_{R,i}$) of solutes chromatographed by LTPGC from isothermal Kováts retention indices (I) and the retention temperatures of n-alkanes ($T_{R,z}$, $T_{R,z+1}$) found by LTPGC[3,4]. The proposed procedure was tested on hydrocarbons separated

in capillary columns coated with polydimethylsiloxane (OV-101) stationary phase. The predicted retention temperatures allowed us to predict Van den Dool and Kratz indices (I_{progr})[4]. The comparison of predicted retention temperatures and/or retention indices with the data obtained experimentally allowed us to identify the hydrocarbons in complex mixtures separated by LTPGC[5].

The aim of this paper is to show the precision by means of which the LTPGC retention data can be predicted from isothermal Kováts retention indices of substituted phenols separated in capillary columns coated with polyphenylsilicone OV-1701 under LTPGC conditions.

EXPERIMENTAL

Two capillary columns used in this work were prepared by Grob[6]. Capillary tubes of length 25 m and I.D. 0.25 mm were drawn from Duran glass tubes. The inner surface of the capillary tubes was leached with 20% hydrochloric acid for 12 h (overnight) at 150°C, then rinsed with 1% hydrochloric acid. The inner surface was further dried for 2 h at 300°C using a water pump vacuum and then silanized using 1,3-diphenyl-1,1,3,3-tetramethyldisilazane overnight at 360°C. Free silanes were removed from the surface by rinsing the column with dichloromethane. The capillaries were then coated statically using a 0.5% solution of OV-1701 in dichloromethane, this stationary phase contained 1% (w/w) dicumyl peroxide. Two columns (1/1 and 1/2) were prepared. Further details on the preparation of the columns can be found in a booklet published on the occasion of a Summer School in Bratislava, Czecho-slovakia[6].

A model sample of phenols containing 65 constituents was prepared by mixing the pure compounds. This mixture was analysed simultaneously with C_{12}–C_{20} *n*-alkanes by GC under isothermal conditions in an OV-1701 capillary column placed in a Fractovap 2350 gas chromatograph (Carlo Erba, Milan, Italy). The chromato-graph was equipped with a flame ionization detector and an all-glass inlet splitter, operating with a splitting ratio of 1:100. Hydrogen was used as the carrier gas at a velocity of 30 cm/s in isothermal operations.

The LTPGC measurements on a model phenol sample were carried out in a Fractovap 4180 gas chromatograph (Carlo Erba) equipped with a flame ionization detector and a Grob on-column injector. Hydrogen with an inlet pressure of 250 kPa, corresponding to $\bar{u} \approx 30$ cm/s at 60°C, was used as the carrier gas. The temperature programme starting at 80°C with an increase of 1, 2, 3 and 4°C/min or at 70, 80, 90, 100, 110 and 120°C with an increase of 2°C/min.

The temperature in the thermostat oven was controlled by an LT 410 digital temperature programmer (Carlo Erba). Retention temperatures (T_{RE}) were calculated from the rates of temperature increase (r) and retention times (t_R) according to the equation

$$T_{RE} = T_0 + rt_R \tag{1}$$

where T_0 is the initial temperature of LTPGC. Retention times were measured with a Chromatopack C-R3A computing integrator (Shimadzu, Kyoto, Japan).

For identification of the individual peaks on a chromatogram, mass spectra obtained by combination of GC and mass spectrometry (GC–MS) were evaluated.

Mass spectra were measured in an HP 5995 GC–MS instrument (Hewlett Packard, Avondale, PA, U.S.A.) using the OV-1701 capillary column (column No. 1/1) under similar conditions to those used in GC.

The dead time was estimated both by analysing methane (t_{ME}) and calculation (t_{MC}) from the retention times (t_R) of n-alkanes:

$$t_{MC} = \frac{t_{R,z}^2 - t_{R,z+1} \cdot t_{R,z-1}}{2t_{R,z} - t_{R,z+1} - t_{R,z-1}} \tag{2}$$

where z denotes the number of carbon atoms in the n-alkane.

As the solubility of methane in the stationary phase varies with temperature, all adjusted relative retention data are based on the dead time calculated from retention times of dodecane (C_{12}), tridecane (C_{13}) and tetradecane (C_{14}).

RESULTS AND DISCUSSION

Isothermal gas chromatography

A model phenol sample was analysed by capillary GC on OV-1701 at temperatures from 70 to 170°C with a 5°C step (isothermal). From the retention data, Kováts retention indices were calculated for each experimental temperature $[I(T)]$[7]. The values obtained were correlated with temperature and coefficients of the following linear equation were found:

$$I(T) = I(0°C) + \frac{dI}{dT} \cdot T \tag{3}$$

where $I(0°C)$ is the Kováts retention index of a given compound at 0°C and dI/dT is the temperature coefficient of the Kováts retention index.

In Table I values of $I(0°C)$ and dI/dT are given together with the correlation coefficients (r) and the temperature regions in which the data were measured (ΔT). It is surprising that the dI/dT values for most alkylphenols are negative. Relatively good correlation coefficients were obtained for compounds with relatively high dI/dT values (positive or negative) whereas compounds with very low dI/dT values were considerably influenced by the reproducibility of the measurements and therefore the correlation coefficients were poor. Deviations of the Kováts retention indices calculated for a given temperature on a given column ranged within 0.6 index unit. Deviations of the corresponding data obtained experimentally on the columns 1/1 and 1/2 (corresponding to the Kováts retention index reproducibility) were within 1.5 index unit.

Compounds corresponding to peaks on a chromatogram were identified via mass spectra obtained by GC–MS under similar conditions to those used during GC analysis. As the retention order of the peaks on a chromatogram changes dramatically with temperature, the mass spectra were compared by analysing a model phenol sample by GC/MS at 70, 90, 110, 130 and 170°C.

When the mass spectra did not give an unambiguous identification, the retention data were correlated with the proposed structure by considering chromatograms

TABLE I

KOVÁTS RETENTION INDICES (*I*) AND THEIR TEMPERATURE COEFFICIENTS (d*I*/d*T*) FOUND BY LINEAR REGRESSION ANALYSIS FOR PHENOL SAMPLE CONSTITUENTS ANALYSED ISOTHERMALLY ON OV-1701

r is the correlation coefficient and Δ*T* is the temperature range in which the retention indices were measured.

Peak No.	Compound	I (0°C)	dI/dT	r	T (°C)
1	2-Chlorophenol	1133.8	0.228	0.9857	90–150
2	Phenol	1247.2	−0.162	−0.9705	90–170
3	6-Chlorotrimethylphenol	1212.1	0.391	0.9854	90–170
4	2,6-Dimethylphenol	1269.4	0.192	0.9701	90–170
5	2-Methylphenol	1288.2	−0.088	−0.8912	90–170
6	2-Nitrophenol	1197.9	0.730	0.9952	90–170
7	4-Methylphenol	1329.1	−0.112	−0.9123	90–170
8	3-Methylphenol	1333.5	−0.134	−0.9637	90–170
9	2-Methylphenol	1380.8	−0.205	−0.9693	90–130
10	2,5-Dimethylphenol	1378.6	−0.140	−0.9608	90–130
11	2,4-Dichlorophenol	1324.2	0.425	0.9998	130–150
12	2,3-Dichlorophenol	1319.1	0.505	0.9992	130–150
13	2,5-Dichlorophenol	1327.9	0.420	0.9999	130–150
14	2,6-Dichlorophenol	1308.3	0.610	0.9984	130–150
15	2,4,6-Trimethylphenol	1361.4	0.154	0.9968	90–150
16	2,3-Dimethylphenol	1412.0	−0.092	–	90–130
17	3,5-Dimethylphenol	1440.9	−0.308	−0.9969	90–150
18	4,6-Dichloro-2-methylphenol	1333.3	0.640	0.9996	130–150
19	4-Ethylphenol	1415.5	−0.076	−0.9876	90–150
20	3-Ethylphenol	1427.1	−0.142	−0.9507	90–150
21	2,3,6-Trimethylphenol	1367.5	0.355	0.9997	130–150
22	2-Isopropylphenol	1439.8	−0.211	−0.9677	130–150
23	3,4-Dimethylphenol	1441.7	−0.068	−0.8621	130–150
24	3-Isopropylphenol	1482.4	−0.141	−0.9592	90–150
25	4-Isopropylphenol	1486.5	−0.164	−0.9783	90–150
26	2,3,5-Trimethylphenol	1490.4	−0.060	–	90–130
27	Diphenyl	1398.8	0.758	0.9990	90–130

28	2-Methylphenol	1518.1	-0.186	-0.972	90-150
29	4-Chlorophenol	1520.6	-0.068	-0.9780	90-150
30	3-Chlorophenol	1520.6	-0.068	-0.9780	90-150
31	2-Methyl-5-isopropylphenol	1522.6	-0.118	-0.9874	90-130
32	2,3,5,6-Tetramethylphenol	1485.2	0.365	0.9997	110-150
33	2,4,6-Trichlorophenol	1500.2	0.410	0.9980	110-150
34	4-Chloro-2-methylphenol	1545.1	0.085	0.9729	110-150
35	2-tert.-Butyl-4-methylphenol	1573.7	-0.182	-0.9676	110-150
36	2,3,5-Trichlorophenol	1507.1	0.485	0.9975	110-150
37	2-tert.-Butyl-5-methylphenol	1560.2	-0.017	-0.8478	110-170
38	4-tert.-Butyl-2-methylphenol	1571.3	-0.028	-0.4593	110-170
39	4-Chloro-3-methylphenol	1576.0	0.0925	0.9989	130-170
40	2,3,6-Trichlorophenol	1504.9	0.638	0.9993	130-170
41	2,3,4-Trichlorophenol	1529.7	0.585	0.9985	130-150
42	2,4,5-Trichlorophenol	1547.5	0.472	0.9930	130-170
43	4-Bromophenol	1592.8	0.162	0.9996	130-170
44	3-Bromophenol	1592.8	0.162	0.9960	130-170
45	4-Chloro-3,5-dimethylphenol	1651.2	0.125	0.9380	130-170
46	2,4,6-Trichlorophenol	1625.2	0.570	0.9944	130-170
47	2-Phenylphenol	1616.4	0.702	0.9996	130-170
49	4-Chloro-2-isopropyl-5-methylphenol	1736.8	0.128	0.9677	130-170
50	4-Bromo-3,5-dimethylphenol	1718.2	0.365	—	150-170
52	3,4-Dichlorophenol	1741.6	0.148	0.9996	150-170
53	2,3,4,5-Tetrachlorophenol	1726.2	0.680	—	170-190
54	Methyl 4-hydroxybenzoate	1823.6	0.060	—	170-190
55	Ethyl 4-hydroxybenzoate	1885.8	0.080	—	170-190
56	3-Nitrophenol	1887.3	0.350	—	170-190
57	2-Benzylphenol	1873.4	0.475	—	170-190
58	n-Propyl-4-hydroxybenzoate	1973.4	0.080	—	170-190
59	Pentachlorophenol	1936.4	0.335	—	170-190
60	4-Nitrophenol	1975.1	0.410	—	170-190
61	4-Phenylphenol	1996.0	0.300	—	170-190
62	3,4,5-Trichlorophenol	1999.2	0.370	—	170-190
63	4-Benzylphenol	1988.8	0.395	—	170-190
64	n-Butyl 4-hydroxybenzoate	2096.8	0.03	—	170-190
65	4-Hexylresorcinol*	—	—	—	—

* The retention index was not measured as C_{22} n-alkane was not present in the sample.

already published for this sample[2]. The compounds with peak numbers 11–15 and 16–22 were identified by analysing the individual compounds separately.

Temperature-programmed gas chromatography

As the retention order of phenols on a chromatogram also changes dramatically with changes in the LTPGC parameters (initial temperature T_0 and rate of temperature increase r), separations were performed gradually using different temperature rates, ranging from 0 to,4°C with a step of 0.5°C/min, and starting from various initial temperatures, from 70 to 120°C with a step of 10°C.

Fig. 1 shows a chromatogram obtained by analysing the model phenol sample with addition of C_{12}–C_{20} n-alkanes by LTPGC starting from 70°C at a rate of 2°C/min in the OV-1701 capillary column No. 1/1.

The peaks obtained on the chromatogram under LTPGC conditions were characterized by retention temperature (T_{RE}) calculated by employing eqn. 1. In the process of identification in LTPGC, experimental retention temperatures (T_{RE}) were compared with the predicted retention temperatures (T_{RP}) calculated from the following equation, published recently[3]:

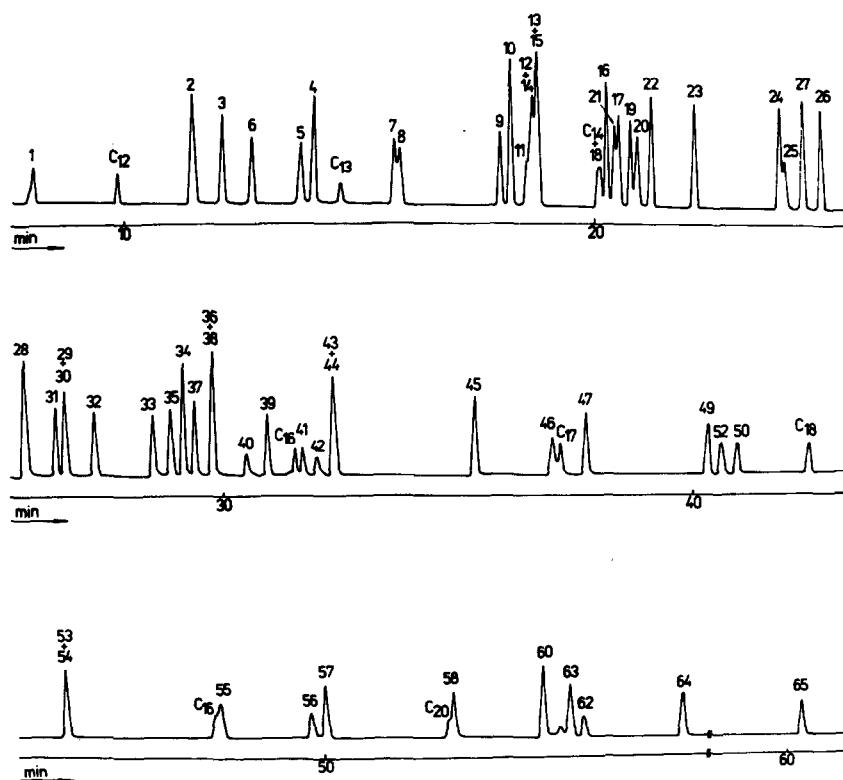Fig. 1. Chromatogram obtained by analysing the model phenol sample with addition of C_{12}–C_{20} n-alkanes by LTPGC in an OV-1701 glass capillary column (column No. 1/1) starting from 70°C with a temperature rise of 2°C/min. The peak numbers correspond to those in Table I.

TABLE II

RETENTION TEMPERATURES OF n-ALKANES FOUND EXPERIMENTALLY ON AN OV-1701 CAPILLARY COLUMN BY LTPGC STARTING AT DIFFERENT TEMPERATURES WITH A TEMPERATURE RISE OF 2°C/min

n-Alkane	Starting temperature (°C)					
	70	80	90	100	110	120
C_{12}	89.67	95.13	101.48	108.79	116.81	125.4
C_{13}	99.20	102.91	107.57	113.3	120.09	127.73
C_{14}	110.23	112.61	115.69	119.69	124.9	131.34
C_{15}	121.45	123.03	125.16	127.7	131.33	136.35
C_{16}	132.75	133.97	135.44	136.87	139.23	142.87
C_{17}	144.12	144.91	146.00	146.6	148.14	150.6
C_{18}	154.81	155.53	156.45	156.66	157.54	159.09
C_{19}	165.40	165.87	166.61	166.53	167.10	168.15
C_{20}	175.33	175.85	176.52	176.29	176.63	177.17

$$T_{RP} = \frac{(T_{RE,z+1} - T_{RE,z})[I(T_1) - T_1(dI/dT) - 100z] + 100T_{RE,z}}{100 - (dI/dT)(T_{RE,z+1} - T_{R,z})} \quad (4)$$

where T_{RE} is the retention temperature found under given LTPGC conditions, $I(T_1)$ the Kováts retention index at temperature T_1, (dI/dT) the temperature coefficient of the Kováts retention index and z the number of carbon atoms in the n-alkane chain.

Experimental retention temperatures of n-alkanes obtained under the various LTPGC conditions are given in Tables II and III. In Tables IV and V experimental retention temperatures (T_{RE}) are compared with retention temperatures predicted from eqn. 4 by applying the data given in Tables I–III. The reproducibility of the T_{RE} measurements can be obtained by comparing the corresponding data ($T_0 = 80°C$ and

TABLE III

RETENTION TEMPERATURES OF n-ALKANES FOUND EXPERIMENTALLY ON AN OV-1701 CAPILLARY COLUMN BY LTPGC STARTING AT 80°C WITH VARIOUS RATES OF TEMPERATURE INCREASE

n-Alkane	Temperature gradient (°C/min)			
	1	2	3	4
C_{12}	90.03	95.27	100.1	102.2
C_{13}	95.03	103.1	109.15	112.27
C_{14}	103.0	112.77	119.8	123.47
C_{15}	112.16	123.5	131.1	135.2
C_{16}	122.27	134.33	142.55	146.8
C_{17}	132.42	145.27	153.9	158.2
C_{18}	142.89	156.0	164.7	169.27
C_{19}	152.81	166.3	175.3	179.86
C_{20}	162.48	176.27	185.45	190.2

J. KRUPČÍK *et al*

TABLE IV

RETENTION TEMPERATURES OF PHENOL SAMPLE CONSTITUENTS PREDICTED (T_{RP}) AND FOUND EXPERIMENTALLY (T_{RE}) ON AN OV-1701 CAPILLARY COLUMN BY LTPGC STARTING AT DIFFERENT TEMPERATURES WITH A TEMPERATURE RISE OF 2°C/min

Peak No.	70°C		80°C		90°C		100°C		110°C		120°C	
	T_{RE}	T_{RP}	T_{RE}	T_{RP}	T_{RE}	T_{RP}	T_{RE}	T_{RP}	T_{RE}	T_{RP}	T_{RE}	T_{RP}
1	86.0	84.8	92.3	91.5	99.5	97.7	107.4	106.9	115.9	115.5	124.8	124.5
2	92.8	92.8	97.4	97.6	103.1	103.3	109.8	110.2	117.5	117.8	125.8	126.0
3	94.1	94.4	98.7	99.1	104.1	104.7	111.0	111.3	118.5	118.8	126.7	126.8
4	98.0	98.1	101.9	102.0	106.8	107.6	112.7	113.3	119.7	119.9	127.5	127.6
5	97.5	97.3	101.2	101.3	106.1	106.3	112.1	112.4	119.2	119.4	127.0	127.2
6	95.4	96.2	100.0	100.7	105.6	106.1	112.1	112.4	119.4	119.7	127.5	127.5
7	101.5	101.2	104.6	104.6	108.8	109.0	114.2	114.4	120.7	120.9	128.1	128.2
8	101.7	101.4	104.8	104.8	109.0	109.2	114.3	114.5	120.7	121.0	128.2	128.3
9	106.0	105.7	108.5	108.6	112.1	112.2	116.7	117.1	122.6	122.8	129.5	129.6
10	106.4	106.2	108.9	109.1	112.5	112.7	117.0	117.4	122.8	123.0	129.8	129.8
11	107.2	106.9	109.7	109.8	113.1	113.5	117.9	118.3	123.6	123.8	130.5	130.6
12	107.3	107.3	109.9	110.1	113.6	113.8	118.1	118.6	123.8	124.0	130.6	130.8
13	107.5	107.3	109.9	110.1	113.6	113.7	118.1	118.5	123.8	123.9	130.5	130.7
14	107.3	107.3	110.1	110.3	113.6	113.9	118.2	118.7	124.0	124.1	130.8	130.9
15	107.5	107.8	110.1	110.5	113.6	113.9	118.1	118.6	123.8	123.9	130.5	130.6
16	110.5	110.4	112.6	112.8	115.7	115.8	119.7	120.0	124.9	124.9	131.3	131.3
17	111.0	111.0	113.0	113.2	116.0	116.2	119.9	120.3	125.0	125.0	131.3	131.3
18	110.2	110.6	112.6	113.2	116.0	116.4	120.3	120.8	125.7	125.8	132.1	132.2
19	111.5	111.0	113.5	113.3	116.4	116.3	120.3	120.5	125.3	125.2	131.6	131.6
20	111.8	111.4	113.7	113.7	116.6	116.6	120.4	120.7	125.5	125.4	131.7	131.7
21	110.8	111.0	113.0	113.4	116.3	116.5	120.3	120.8	125.5	125.6	131.9	132.0
22	112.4	112.0	114.2	114.2	117.1	117.0	120.7	121.0	125.7	125.7	131.9	131.9
23	114.3	114.0	116.0	116.1	118.7	118.8	122.1	122.5	126.8	127.0	132.8	132.9
24	118.0	117.6	119.4	119.4	121.2	121.8	124.7	124.9	128.8	129.0	134.3	134.5
25	118.2	117.8	119.6	119.6	121.9	122.0	124.8	125.0	128.9	129.1	134.3	134.6
26	119.8	119.6	121.2	121.2	123.4	123.5	126.2	126.4	130.1	130.2	135.3	135.4
27	119.0	120.4	120.8	122.1	123.4	124.5	126.6	127.3	130.8	131.2	136.2	136.4

28	121.5	121.0	122.7	122.5	124.7	124.6	127.2	127.2	130.9	130.9	135.9	136.0
29	123.2	122.8	124.3	124.3	126.3	126.4	128.6	128.8	132.1	132.2	137.0	137.1
30	123.2	122.8	124.3	124.3	126.3	126.4	128.6	128.8	132.1	132.2	137.0	137.1
31	122.8	122.4	124.0	123.8	126.0	125.9	128.4	128.4	131.9	131.8	136.8	136.7
32	124.5	124.9	125.8	126.4	127.8	128.4	130.2	130.7	133.6	134.0	138.4	138.7
33	127.0	127.4	128.1	128.8	130.0	130.6	132.1	132.7	135.3	135.8	139.8	140.1
34	128.3	127.7	129.2	129.1	130.0	130.9	132.7	132.9	135.6	135.8	139.8	140.1
35	127.8	127.1	128.7	128.4	130.3	130.3	132.1	132.2	135.1	135.2	139.4	139.5
36	129.6	129.3	130.4	130.7	132.0	132.5	134.0	134.4	136.8	137.2	141.0	141.3
37	128.8	128.0	129.7	129.3	131.3	131.1	133.0	133.0	135.8	135.9	139.9	140.1
38	129.6	129.1	130.4	130.4	132.0	132.1	133.7	133.9	136.4	136.7	140.5	140.7
39	131.5	131.4	132.6	132.7	134.1	134.3	135.7	135.9	138.1	138.4	142.0	142.2
40	130.7	131.4	131.9	132.8	133.6	134.5	135.4	136.2	138.1	138.7	142.2	142.6
41	133.0	133.6	134.2	134.9	135.8	136.4	137.3	137.9	139.7	140.3	143.5	144.0
42	134.0	134.0	134.7	135.2	136.2	136.7	137.7	138.2	140.1	140.5	143.8	144.1
43	134.3	134.4	135.3	135.6	136.7	137.0	138.1	138.4	140.3	140.7	143.8	144.2
44	134.3	134.4	135.3	135.6	136.7	137.0	138.1	138.4	140.3	140.7	143.8	144.2
45	140.5	140.5	141.2	141.4	142.3	142.7	143.3	143.8	144.7	145.4	147.9	148.2
46	144.0	145.0	144.5	145.8	145.7	147.0	146.6	147.5	148.1	149.0	150.9	151.7
47	145.4	146.1	145.9	146.9	147.0	148.2	147.8	148.7	149.3	150.2	151.9	152.6
49	150.7	150.1	151.0	150.8	151.9	151.9	151.9	152.3	153.4	153.4	155.5	155.5
50	151.7	151.9	152.2	152.7	153.2	153.8	153.6	154.2	154.7	155.2	156.6	157.0
52	151.1	150.9	151.5	151.7	152.5	152.8	152.9	153.2	153.9	154.2	155.9	156.2
53	158.9	158.4	159.1	159.1	159.9	160.0	160.0	160.1	160.8	161.0	162.1	162.4
54	158.9	158.4	159.1	159.0	159.9	159.9	160.0	160.0	160.8	160.7	162.1	162.1
55	165.5	165.2	165.9	165.7	166.6	166.4	166.5	166.4	167.1	167.0	168.2	167.9
56	169.1	170.0	169.8	170.6	170.5	171.2	170.4	171.2	170.9	171.6	171.8	172.4
57	170.1	170.8	170.4	171.4	171.2	172.0	171.0	172.0	171.5	172.4	172.4	173.1
58	175.6	174.6	175.9	175.2	176.5	175.7	176.3	175.7	176.6	176.0	177.2	176.5
59		174.8		175.4		175.9		175.9		176.2		176.8
60*	179.4	180.1	179.8	180.8	180.4	181.2	180.2	181.2	180.5	181.3	181.0	181.7
61*		180.2		180.9		181.3		181.3		181.4		181.8
62*	181.2	181.8	181.5	182.4	182.1	182.8	181.9	182.8	182.2	182.9	182.7	183.3
63*	180.6	181.2	181.0	181.8	181.6	182.2	181.3	182.3	181.7	182.4	182.1	182.7
64*	185.5	185.4	185.7	186.0	186.4	186.4	186.0	186.4	186.3	186.5	186.6	186.6
65	194.6		194.8		195.4		195.0		194.9		195.4	

* Data were predicted using retention temperatures for C_{20} and C_{21} n-alkanes.

TABLE V

RETENTION TEMPERATURES OF PHENOL SAMPLE CONSTITUENTS PREDICTED (T_{RP}) AND FOUND EXPERIMENTALLY (T_{RE}) ON AN OV-1701 CAPILLARY COLUMN BY LTPGC STARTING AT 80°C WITH VARIOUS RATES OF TEMPERATURE INCREASE

Peak No.	1°C/min		2°C/min		3°C/min		4°C/min		
	T_{RE}	T_{RP}	T_{RE}	T_{RP}	T_{RE}	T_{RP}	R_{RE}	T_{RP}	T_{RP}
1	88.2	87.5	92.5	91.7	96.7	96.1	98.5	97.8	97.8
2	91.7	91.8	97.6	97.8	102.8	102.9	105.1	102.9	105.3
3	92.5	92.7	98.9	99.3	104.5	104.9	107.3	104.9	107.8
4	94.8	94.8	102.1	102.3	108.1	108.3	111.1	108.3	111.5
5	94.3	94.4	101.5	101.5	107.3	107.3	110.2	107.3	110.2
6	93.3	93.7	100.3	100.9	106.2	107.1	109.3	107.1	110.2
7	97.0	96.9	104.9	104.8	111.2	111.0	114.3	111.0	114.2
8	97.2	97.1	105.1	105.0	111.4	111.2	114.5	111.2	114.4
9	100.1	100.0	108.9	108.8	115.5	115.3	118.9	115.3	118.7
10	100.4	100.3	109.3	109.3	116.0	115.9	119.4	115.9	119.3
11	100.9	100.5	110.1	110.0	117.0	117.2	120.7	117.2	120.9
12	100.9	100.7	110.4	110.3	117.4	117.6	121.0	117.6	121.4
13	101.1	100.7	110.4	110.3	117.4	117.5	121.0	117.5	121.2
14	100.9	100.7	110.4	110.4	117.4	117.8	121.0	117.8	121.6
15	101.1	101.2	110.4	110.7	117.4	117.7	121.0	117.7	121.3
16	103.4	103.2	113.0	113.0	120.0	120.0	123.7	120.0	123.7
17	103.8	103.8	113.4	113.4	120.4	120.3	124.1	120.3	123.9
18	103.0	102.9	113.0	113.4	120.4	121.2	124.6	121.2	125.2
19	104.2	103.7	113.9	113.5	121.0	120.6	124.6	120.6	124.3
20	104.5	104.1	114.1	113.9	121.3	121.0	124.9	121.0	124.7
21	103.5	103.4	113.4	113.6	120.7	121.1	124.6	121.1	125.0
22	104.9	104.6	114.7	114.4	121.7	121.4	125.4	121.4	125.1
23	106.3	106.2	116.4	116.4	123.7	123.6	127.5	123.6	127.4
24	109.3	109.4	119.9	119.7	127.4	127.1	131.2	127.1	131.1
25	109.5	109.5	120.1	119.9	127.6	127.2	131.4	127.2	131.2
26	110.7	110.9	121.6	121.6	129.3	129.1	133.2	129.1	133.2
27	109.7	110.9	121.2	122.6	129.3	130.8	133.7	130.8	135.3
28	112.2	112.3	123.1	122.9	130.7	130.3	134.6	130.3	134.4
29	113.6	113.6	124.8	124.8	132.6	132.4	136.7	132.4	136.5

30	113.6	113.6	124.8	124.8	132.6	132.4	136.7	136.5
31	113.3	113.1	124.5	124.4	132.2	131.9	136.3	136.0
32	114.4	114.9	126.2	126.9	134.4	135.1	138.7	139.4
33	116.5	117.1	128.6	129.2	137.0	137.6	141.1	142.0
34	118.0	117.7	129.6	129.6	137.7	137.6	141.9	141.8
35	117.6	117.5	129.2	128.9	137.0	136.7	141.1	140.8
36	118.9	118.8	130.9	131.2	138.0	139.7	143.7	144.2
37	118.5	118.1	130.1	129.8	138.1	137.7	142.2	141.9
38	119.1	119.1	130.9	130.8	138.9	138.9	143.1	143.0
39	121.1	121.1	133.2	133.1	141.3	141.3	145.5	145.6
40	119.9	120.5	132.5	133.2	141.0	142.1	145.5	146.7
41	122.3	122.4	134.7	135.3	143.3	144.0	147.8	148.8
42	122.8	122.9	135.3	135.6	143.7	144.1	148.2	148.8
43	123.6	123.7	135.8	136.0	144.2	144.2	148.5	148.8
44	123.6	123.7	135.8	136.0	144.2	144.2	148.5	148.8
45	129.1	129.1	141.7	141.8	150.3	150.4	154.7	154.8
46	131.7	132.6	145.5	146.2	154.0	155.3	158.8	160.1
47	133.0	133.6	146.3	147.4	155.5	156.7	160.2	161.5
49	139.3	138.1	151.5	151.2	160.2	160.0	164.6	164.7
50	139.5	139.6	152.8	153.2	161.7	162.2	166.3	167.0
52	139.0	138.9	152.1	152.2	160.7	160.9	165.3	165.6
53	144.6	145.2	158.5	159.6	167.8	169.1	172.7	174.0
54	146.5	146.0	159.4	159.4	168.5	168.2	173.1	172.9
55	153.2	152.4	166.4	166.0	175.3	175.1	179.9	179.8
56	156.3	156.8	170.3	170.8	179.7	180.3	184.5	185.2
57	156.8	157.4	170.9	171.7	180.3	181.3	185.3	186.2
58	162.7	162.2	176.3	175.4	185.5	184.4	190.2	189.0
59		161.5		175.6		185.3		190.2
60*	165.9	166.6	180.2	181.0	189.8	190.9	194.8	196.0
61*		166.9		181.1		190.9		195.9
62*	167.6	168.3	181.9	182.7	191.5	192.6	196.5	197.7
63*	167.0	167.7	181.3	182.1	190.9	191.9	195.9	197.0
64*	172.2	172.3	186.2	186.2	195.5	195.9	200.3	200.8
65*	181.2		195.3		204.7		209.6	

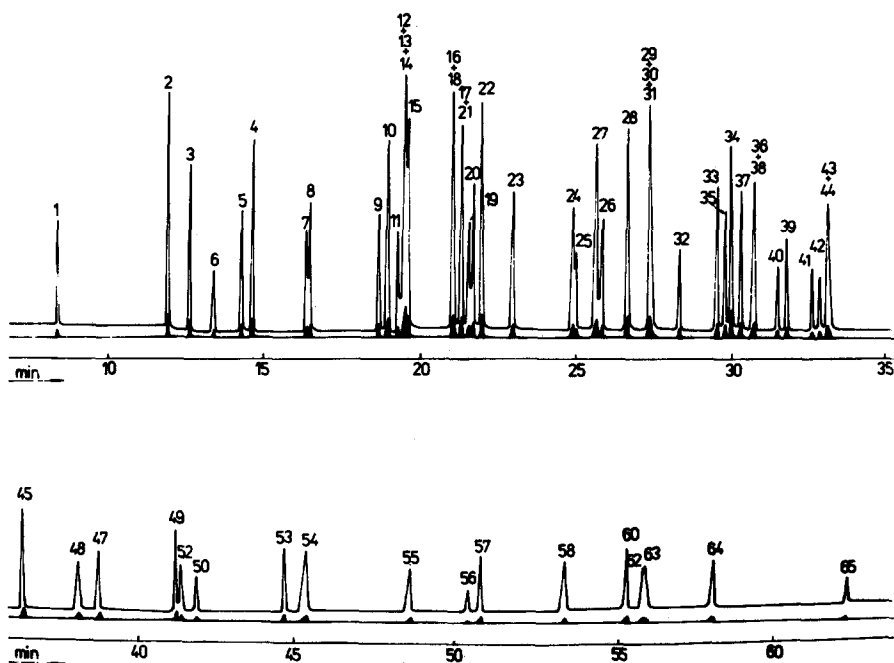* Data were predicted using retention temperatures for C_{20} and C_{21} n-alkanes.

Fig. 2. Chromatogram obtained by analysing a model phenol sample by LTPGC in an OV-1701 glass capillary column (column No. 1/1) placed in the GC–MS instrument (HP 5995) starting from 70°C with a temperature rise of 2°C/min. The chromatogram with shaded peaks was recorded using a 10-fold higher attenuation.

$r = 2$°C/min obtained on columns 1/1 and 1/2, respectively) in Tables IV and V. Deviations of the corresponding T_{RE} values are in the range 0–0.5°C. Most of the corresponding differences, $T_{RE} - T_{RP}$, are also in this range. However, these differences are much higher for peak 6 (1.2°C in Table IV) and peak 27 (1.4°C in Table IV). The relatively good agreement between T_{RE} and T_{RP} allows us to predict the LTPGC retention of the constituents of the phenol sample from the data given in Tables I–III (excluding peaks 6 and 27). The correctness of the prediction was checked by mass spectra obtained by GC–MS. Fig. 2 shows a chromatogram obtained by analysing the model sample by LTPGC in the OV-1701 glass capillary column No. 1/1 placed in the HP 5995 GC–MS instrument starting from 70°C with a temperature rise of 2°C/min.

The retention temperature can be predicted graphically from the combination of the dependences of the Kováts retention indices of phenol sample constituents on temperature and of the temperature-programmed retention indices of n-alkanes on retention temperature (Figs. 3–8). For the construction of Figs. 3–5 data from Tables I and II were used and for the construction of Figs. 6–8 data from Tables I and III were used.

The reprodicibility of measurements of retention temperatures and their agreement with the predicted values are used as a basis for the window in which the identification is performed. However, from the data in Tables IV and V it can be
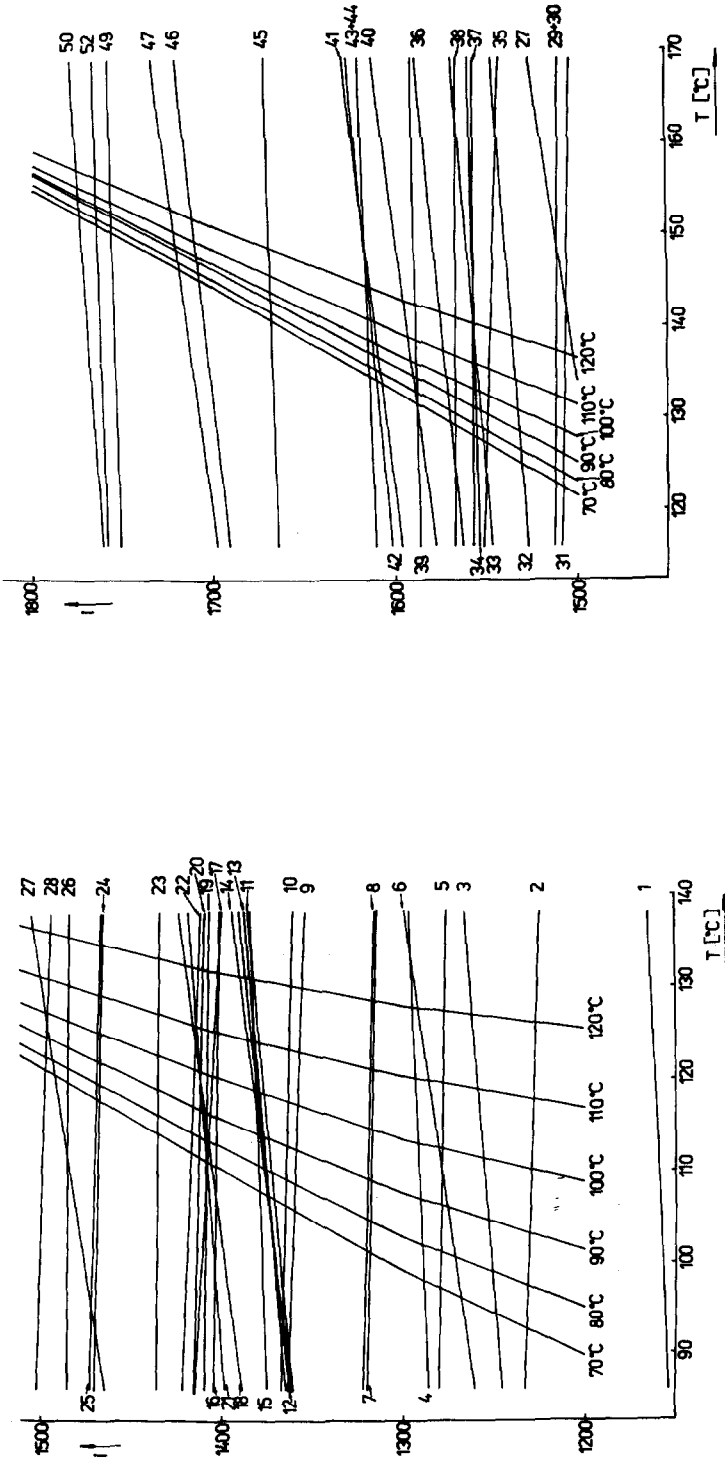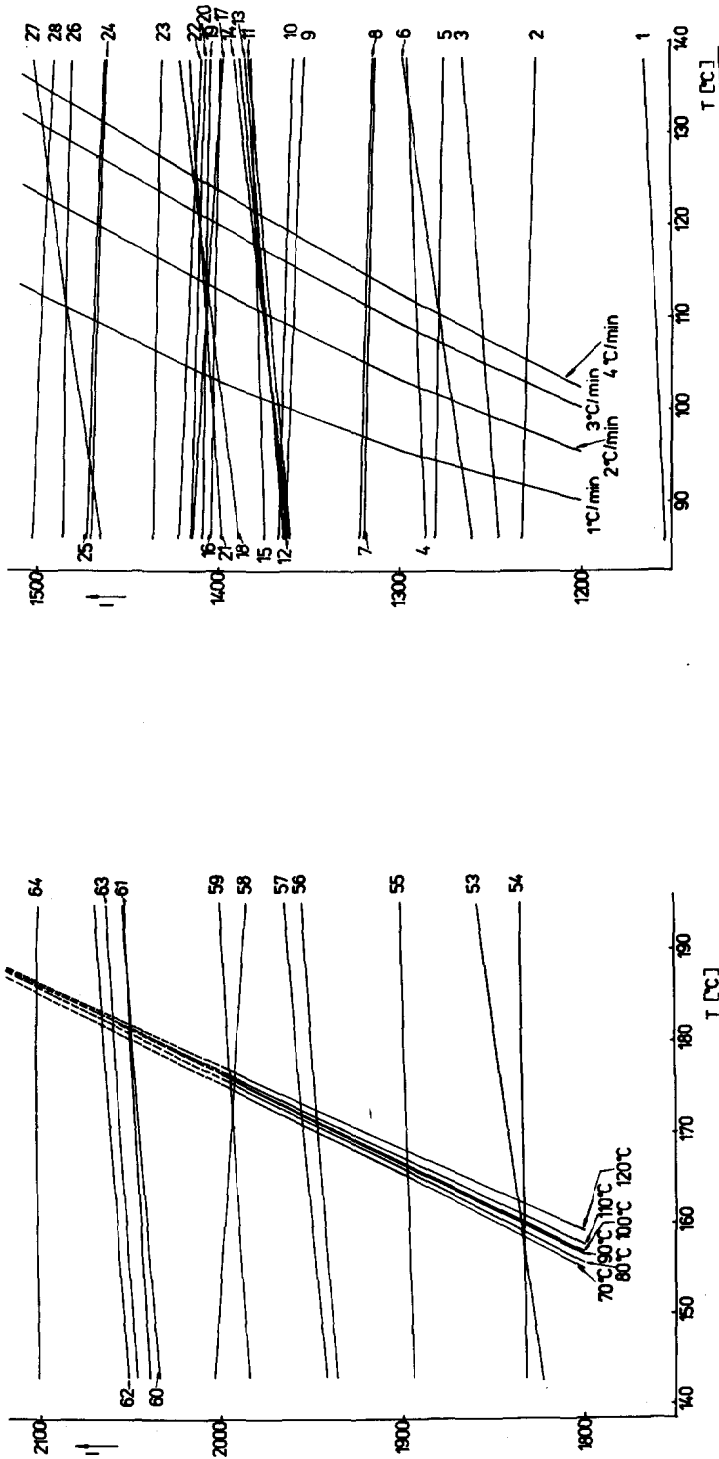
Fig. 3. Dependences of isothermal Kováts retention indices of phenol sample constituents eluted from OV-1701 between dodecane and pentadecane on temperature, combined with the dependences of the retention indices of n-alkanes on retention temperatures found under LTPGC conditions starting from different initial temperatures with a temperature rise of 2°C/min.
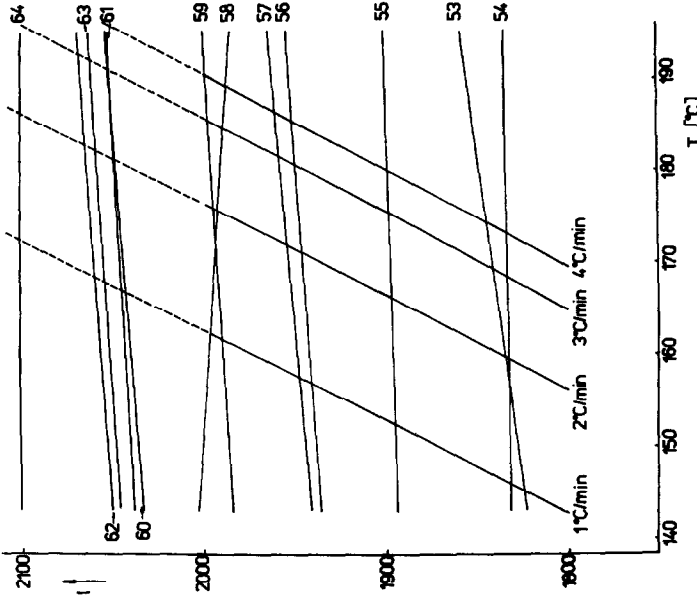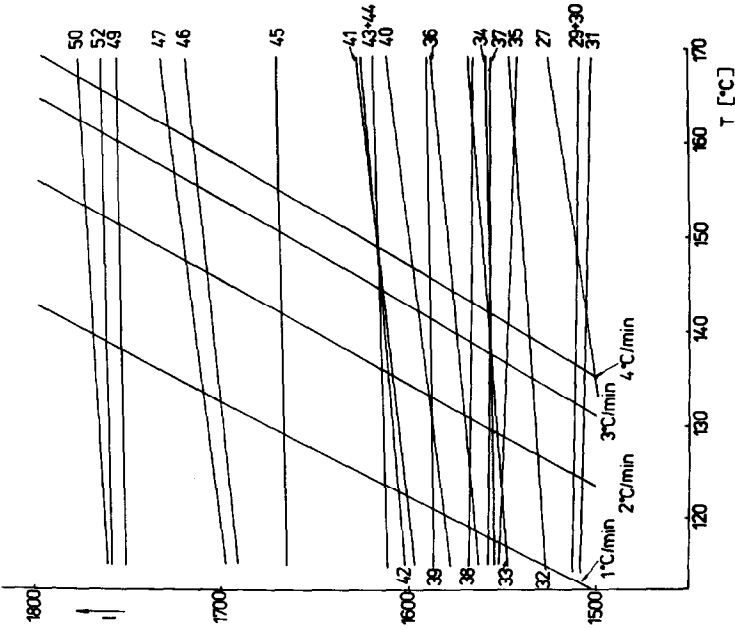
Fig. 4. Dependences of isothermal Kováts retention indices of phenol sample constituents eluted from OV-1701 between pentadecane and octadecane on temperature, combined with the dependences of the retention indices of n-alkanes on retention temperatures (details as in Fig. 3).

Fig. 5. Dependences of isothermal Kováts retention indices of phenol sample constituents eluted from OV-1701 between octadecane and heneicosane on temperature, combined with the dependences of the retention indices of n-alkanes on retention temperatures (details as in Fig. 3). Dashed lines represent extrapolation of dependences from nonadecane and eicosane.

Fig. 6. Dependences of isothermal Kováts retention indices of phenol sample constituents eluted from OV-1701 between dodecane and pentadecane on temperature, combined with the dependences of the retention indices of n-alkanes on retention temperatures found under LTPGC conditions starting from 80°C with various rates of temperature increase.

Fig. 7. Dependences of isothermal Kováts retention indices of phenol sample constituents eluted from OV-1701 between pentadecane and octadecane on temperature, combined with the dependences of the retention indices of n-alkanes on retention temperatures (details as in Fig. 6).

Fig. 8. Dependences of isothermal Kováts retention indices of phenol sample constituents eluted from OV-1701 between octadecane and heneicosane on temperature, combined with the dependences of the retention indices of n-alkanes on retention temperatures (details as in Fig. 6). Dashed lines represent extrapolation of dependences from nonadecane and eicosane.

concluded that in the window found in this work several peaks overlapped. The width of such a window is larger for phenols than for hydrocarbons, as the dI/dT values of phenols are much larger than those of hydrocarbons[3]. The correlation of retention data measurements of phenols with experimental conditions in both isothermal and LTPGC is currently being studied and will be published separately.

REFERENCES

1 H. Mayer, J. Nolte and B. Paschold, *Fresenius Z. Anal Chem.*, 315 (1983) 708.
2 J. Nolte, H. Mayer and B. Paschold, *Fresenius Z. Anal. Chem.*, 325 (1986) 20.
3 J. Krupčík, P. Čellár, D. Repka, J. Garaj and G. Guiochon, *J. Chromatogr.*, 351 (1986) 111.
4 J. Krupčík, D. Repka, T. Hevesi and J. Garaj, *J. Chromatogr.*, 406 (1987) 117.
5 J. Krupčík, D. Repka, T. Hevesi and G. Anders, *J. Chromatogr.*, 407 (1987) 65.
6 K. Grob, *Textbook for participants of Summer School in Preparation and Exploitation of Capillary Columns in Practice, Chemical Faculty, Slovak Technical University, Bratislava, May 21–25, 1985* (see also K. Grob, *Making and Manipulating Capillary Columns for Gas Chromatography*, Hüthig, Heidelberg, 1986).
7 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.