

CHROM. 10,057

GAS CHROMATOGRAPHIC SEPARATION OF PHENOLS ON A POLYPHENYL ETHER WITH SIX RINGS. I

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(Received March 4th, 1977)

SUMMARY

The separation of C_7 - C_{15} monohydric alkylphenols, C_9 and C_{10} indanols, C_{10} and C_{11} naphthols, and 5,6,7,8-tetrahydro-1-naphthol on a column packed with 5% (w/w) of a polyphenyl ether with six rings on Chromaton N AW HMDS has been studied. The retention indices for the column temperatures used (140 and 160°) were determined. It was found, that a relationship between retention index and number of C atoms can find only limited use in the identification of individual phenols.

INTRODUCTION

Gas chromatography (GC) is a very sensitive method for the analysis of rich mixtures of monohydric and polyhydric phenols. The structure of phenols permits a number of properties resulting largely from the presence of the hydroxyl group bound to the aromatic nucleus to be employed for their separation. By comparing non-polar and polar stationary phases, the effect of Van der Waals forces¹ causing changes in the vapour pressure of the material above the packing in a separation column can be studied.

The dipoles of the molecules of a phenol being chromatographed and of those of the stationary phase cause mutual association. The energy of this association is a normal fractional bond energy and is influenced by the temperature and structure of the molecules (the magnitude of the dipole moment, the steric conditions of association). This influence can be seen from the effect of polar selective stationary phases of the sulphone type¹. With increasing polarity of the stationary phase a certain selectivity occurs which gives rise to a relative increase in the sorption of highly polar phenols. With some phenols, however, a decrease in the formation of intermolecular hydrogen bonds due to steric hindrance, together with a decrease in the dipole moment, is observed. In agreement with this concept, an increase in the size of the molecules of the stationary phase results in a decrease in its dipole moment and, consequently, in the selectivity of separation¹.

With fractional bonds, which involve dipole associations of whole molecules, the vapour pressure will be the main factor in the determination of the order of elution of phenols. If the functional groups conferring the electrical asymmetry of the mole-

cules are more favourable towards a closer approach of the molecules, the result will be a dipole association of much higher energy. This type of bond is represented by hydrogen bridges in the GC of phenols.

The formation and particularly the strength of the hydrogen bonds between the hydrogen atom of the hydroxyl group of a phenol and the electronegative centres of a stationary phase are determined by the dipole moment and the steric screening of the functional groups.

A possible means of influencing the formation of hydrogen bridges is the conversion of phenols into ethers^{2,3}. In analytical practice this operation has the following significance:

(1) By preventing the formation of hydrogen bridges between the individual molecules, the boiling points of the substances being analysed are lowered, which permits a decrease in the temperature of the separation process. In a number of instances the separation of isomers with low boiling points can be carried out or improved in this way.

(2) The etherification of the hydroxyl groups of phenols decreases their polar character. As a result, the influence of the vapour pressure of the individual substances in the separation process and of their boiling points is increased. The differences in the boiling points of ethers are different from those of the phenols and, consequently, the GC separation of ethers is also different.

(3) As ethers are less polar than phenols, in many separation systems their gas chromatographic profiles are more symmetrical. The same purpose as is achieved by etherification, *i.e.*, influencing the formation of hydrogen bridges, is accomplished by the conversion of phenols into esters^{4,5}.

The use of the functional derivatives has certain restrictions. The sterically hindered hydroxyl groups of phenols can react with the reagent slowly and incompletely, and reverse hydrolysis must also be considered^{6,7}.

In the separation of methoxy derivatives of phenols, polar stationary phases are affected not only by the intermolecular hydrogen bridges, but also by the intramolecular hydrogen bonds^{8,9}. The stationary phases and the operating conditions used for the GC separation of phenols up to 1966 were summarized by Dietzsch¹⁰, and we subsequently extended this survey up to the end of 1974¹¹ and included earlier work not covered by Dietzsch.

One of the most selective stationary phases for the GC separation of phenol mixtures is tri(2,4-xylenyl) phosphate^{12,13}. Its disadvantages, however, include its limited thermal stability and its unsuitability for separating phenol mixtures containing dihydric phenols. As we required a stationary phase that would permit the separation of both monohydric and dihydric phenols, we tested several stationary phases recommended in the literature^{14,15}.

The best results were achieved with a stationary phase consisting of a polyphenyl ether with 6 rings. For reasons of simplicity, a set of monohydric phenols is considered in this paper.

EXPERIMENTAL AND RESULTS

A Chrom IV gas chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia) with a flame-ionization detector was used. The glass column was 2.4 m ×

2 mm I.D. A polyphenyl ether (6 rings) was used as the stationary phase, its concentration on the support Chromaton N AW HMDS (0.16–0.20 mm) being 5% (w/w). The temperature of the feed chamber was 250–350°, the amount of sample used was 0.2–0.6 μ l and the pressure of the carrier gas (nitrogen) was 133.9 kPa.

The separation of 102 phenols was studied isothermally at 140° and 160°, these temperatures being selected from optimization experiments. The phenols available were divided into several mixtures, which were repeatedly analysed in a mixture with *n*-alkanes. From the elution data measured the retention indices were calculated using a Hewlett-Packard H-9300 desk-top calculator according to the relationship valid for the isothermal process. The retention indices obtained are given in Table I.

At 160° the retention indices (*I*) were determined for the whole set of standards. At 140° the Kováts retention indices were measured mostly with phenols that required for their separation a temperature lower than 160°.

DISCUSSION

The retention indices were in the range 1200–2300 *I* units, with most of the phenols having values in the range 1400–1800 *I* units. Of the C₆–C₁₀ monohydric phenols, which are most frequently involved in the analyses of phenol mixtures, the retention indices at 160° were in the range 1281 (phenol)–1782 (2,3,4,5-tetramethylphenol). None of the standards gave a constant retention index in the range 140–180°, an increase in temperature resulting in an increase in the *I* values. The value most frequently determined was $\Delta I/20^\circ = 8\text{--}14$ *I* units.

A graphical representation of the relationship $I = f(\text{number of C atoms})$ in the homologous series of *n*-alkylphenols (Fig. 1) shows that there is an anomaly in the elution data in that there is a sudden change in the slope with all three derivatives that have an *n*-alkyl substituent longer than C₃ on the aromatic nucleus.

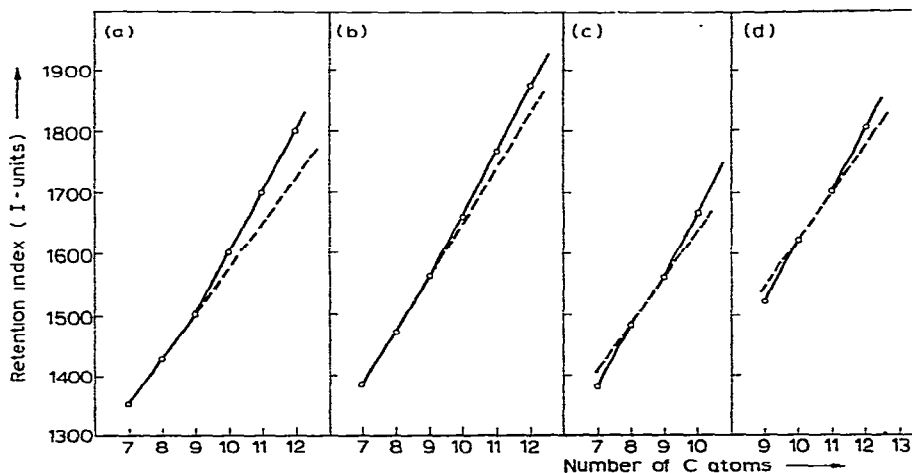


Fig. 1. $I = f(\text{number of carbon atoms})$ for homologous series of monohydric phenols on a column packed with 5% polyphenyl ether (6 rings) on Chromaton N AW HMDS at 160°. (a), 2-*n*-Alkylphenols; (b), 4-*n*-alkylphenols; (c), 3-*n*-alkylphenols; (d), 2-ethyl-5-*n*-alkylphenols.

TABLE I

RETENTION INDICES OF PHENOLS ON A COLUMN PACKED WITH 5% POLYPHENYL ETHER (6 RINGS) ON CHROMATON N AW HMDS

No.	Substance	Retention index		ΔI
		140°	160°	
1	Phenol	1272	1281	9
2	2-Methylphenol	1346	1354	8
3	3-Methylphenol	1378	1386	8
4	4-Methylphenol	1377	1385	8
5	2-Ethylphenol	1423	1430	7
6	3-Ethylphenol	1475	1483	8
7	4-Ethylphenol	1465	1473	8
8	2,3-Dimethylphenol	1486	1495	9
9	2,4-Dimethylphenol	1445	1456	11
10	2,5-Dimethylphenol	1443	1453	10
11	2,6-Dimethylphenol	1403	1416	13
12	3,4-Dimethylphenol	1519	1530	11
13	3,5-Dimethylphenol	1479	1489	10
14	2- <i>n</i> -Propylphenol	1496	1502	6
15	3- <i>n</i> -Propylphenol	1558	1565	7
16	4- <i>n</i> -Propylphenol	1555	1563	8
17	2-Isopropylphenol	1470	1478	8
18	3-Isopropylphenol	1523	1531	8
19	4-Isopropylphenol	1519	1527	8
20	2-Ethyl-4-methylphenol	1513	1523	10
21	2-Ethyl-5-methylphenol	1519	1529	10
22	2-Ethyl-6-methylphenol	1472	1485	13
23	3-Ethyl-5-methylphenol	1571	1581	10
24	3-Ethyl-6-methylphenol	1518	1528	10
25	4-Ethyl-2-methylphenol	1533	1539	6
26	4-Ethyl-3-methylphenol	1596	1608	12
27	2,3,4-Trimethylphenol	1624	1638	14
28	2,3,5-Trimethylphenol	1583	1593	10
29	2,3,6-Trimethylphenol	1542	1551	9
30	2,4,5-Trimethylphenol	1579	1593	14
31	2,4,6-Trimethylphenol	1508	1516	8
32	3,4,5-Trimethylphenol	1656	1667	9
33	2- <i>n</i> -Butylphenol	1594	1600	6
34	3- <i>n</i> -Butylphenol	1659	1668	9
35	4- <i>n</i> -Butylphenol	1654	1661	6
36	2-Isobutylphenol	1524	1532	8
37	4-Isobutylphenol	1594	1599	5
38	2- <i>sec.</i> -Butylphenol	1542	1550	8
39	4- <i>sec.</i> -Butylphenol	1604	1612	8
40	2- <i>tert.</i> -Butylphenol	1532	1538	6
41	3- <i>tert.</i> -Butylphenol	1592	1598	7
42	4- <i>tert.</i> -Butylphenol	1584	1593	9
43	2-Methyl-4- <i>n</i> -propylphenol	1615	1623	8
44	2-Methyl-6- <i>n</i> -propylphenol	1545	1553	8
45	3-Methyl-6- <i>n</i> -propylphenol	1592	1602	10
46	4-Methyl-2- <i>n</i> -propylphenol	1584	1593	9
47	2-Methyl-6-isopropylphenol	1519	1529	10
48	3-Methyl-6-isopropylphenol	1567	1575	8
49	2,4-Diethylphenol	1595	1602	7
50	2,5-Diethylphenol	1613	1624	9

TABLE I (continued)

No.	Substance	Retention index		ΔI
		140°	160°	
51	2,6-Diethylphenol	1537	1549	12
52	3,4-Diethylphenol	1671	1682	11
53	2,3,4,5-Tetramethylphenol		1782	
54	2,3,4,6-Tetramethylphenol	1674	1690	16
55	2,3,5,6-Tetramethylphenol	1667	1683	16
56	2-Ethyl-4,5-dimethylphenol	1648	1656	8
57	2- <i>n</i> -Pentylphenol		1700	
58	4- <i>n</i> -Pentylphenol		1765	
59	4- <i>tert.</i> -Pentylphenol	1691	1703	12
60	2-Ethyl-5- <i>n</i> -propylphenol	1692	1706	14
61	2- <i>tert.</i> -Butyl-4-methylphenol	1603	1608	5
62	2- <i>tert.</i> -Butyl-5-methylphenol	1624	1633	9
63	2- <i>tert.</i> -Butyl-6-methylphenol	1564	1578	14
64	4- <i>tert.</i> -Butyl-2-methylphenol	1591	1601	10
65	4- <i>tert.</i> -Butyl-3-methylphenol		1764	
66	Pentamethylphenol		1874	
67	2- <i>n</i> -Hexylphenol		1800	
68	4- <i>n</i> -Hexylphenol		1871	
69	3- <i>n</i> -Butyl-6-ethylphenol		1807	
70	2,6-Diisopropylphenol	1608	1616	8
71	2-Cyclohexylphenol		1926	
72	4-Cyclohexylphenol		1996	
73	2-Phenylphenol		1912	
74	3-Phenylphenol		2165	
75	4-Phenylphenol		2177	
76	2-Benzylphenol		2100	
77	4-Benzylphenol		2200	
78	4-Isooctylphenol		1891	
79	2- <i>tert.</i> -Octylphenol		1804	
80	4- <i>tert.</i> -Octylphenol		1892	
81	2,4-Di- <i>tert.</i> -butylphenol	1722	1728	6
82	2,5-Di- <i>tert.</i> -butylphenol		1841	
83	2,6-Di- <i>tert.</i> -butylphenol	1643	1651	8
84	3,5-Di- <i>tert.</i> -butylphenol		1800	
85	2-Benzyl-4-methylphenol		2189	
86	4-Methyl-2- <i>tert.</i> -octylphenol		1842	
87	2-Methyl-4- <i>tert.</i> -octylphenol		1904	
88	2-Methyl-6- <i>tert.</i> -octylphenol		1804	
89	2,6-Di- <i>tert.</i> -butyl-4-methylphenol	1695	1701	6
90	4-(2-Phenylisopropyl)phenol		2271	
91	2,4,6-Tri- <i>tert.</i> -butylphenol		1722	
92	4-Indanol	1668	1689	21
93	5-Indanol	1697	1712	15
94	5-Methyl-4-indanol	1719	1741	22
95	6-Methyl-4-indanol	1764	1784	20
96	7-Methyl-4-indanol	1782	1802	20
97	1-Naphthol		1944	
98	2-Naphthol		1969	
99	7-Methyl-2-naphthol		2062	
100	5,6,7,8-Tetrahydro-1-naphthol		1835	
101	2-Allylphenol	1488	1498	10
102	2-Allyl-6-methylphenol	1535	1542	

In the relationship valid for 2-*n*-alkyl phenols a change in slope occurred at 2-*n*-propylphenol. With 4-*n*-alkylphenols this change occurred between 4-*n*-propyl- and 4-*n*-butylphenol.

The relationships $I = f(\text{number of C atoms})$ valid for *n*-alkylphenols with increasing size of the alkyl group in position 3 do not correspond to the relationship valid for 2- or 4-*n*-alkylphenols. With 3-*n*-alkylphenols and 2-ethyl-5-*n*-alkylphenols (increasing length of *n*-alkyl group in position 3 towards phenolic hydroxyl) the connecting lines between the alkyl groups studied containing 1-2 and 3-4 carbons are sufficiently, parallel however, not for the connecting line between *n*-alkyl groups with 2 and 3 carbon atoms.

The variation of the ΔI values with the length of the *n*-alkyl groups shows that for mono-*n*-alkylphenols ΔI is highest with *n*-alkyl groups in the *meta*-position and lowest for those in the *ortho*-position. With the C_7-C_9 alkyl phenols, when the molecule is increased by a $-CH_2-$ group in position 2 $\Delta I = 70$, in position 4 $\Delta I \approx 80-90$ and in position 3 $\Delta I = 90-100$. The highest value of ΔI (CH_2) was found for 4-*tert.*-butyl- and 4-*tert.*-pentylphenol.

The anomalous course of the relationship $I = f(\text{number of C atoms})$, like the changes in slope of the relationships $\log R_{i, rel} = f(\text{number of C atoms})$ for *n*-alkylphenols during elution on a stationary phase consisting of 95% tri(2,4-xylene) phosphate + 5% H_3PO_4 ¹¹, cannot be explained satisfactorily. The study of this interesting GC behaviour of phenols, however, is being continued.

CONCLUSIONS

From the results, the following conclusions can be drawn:

(1) The possibility of identifying phenols eluted from the GC column by means of a graph of $I = f(\text{number of C atoms})$ with the stationary phase used here is very limited.

(2) For C_7-C_9 2- and 4-*n*-alkylphenols, for which necessary standards are usually available, the course of the relationship $I = f(\text{number of C atoms})$ can be extrapolated or interpolated.

(3) For substances with an *n*-alkyl group longer than C_3 it is necessary to know where changes in the course of the relationship $I = f(\text{number of C atoms})$ occur.

(4) With the homologous series of phenols with an alkyl group in the *meta*-position no interpolation or extrapolation in the range C_7-C_9 is possible.

Identifications made on the basis of the relationship $I = f(\text{number of C atoms})$ without considering the above factors will lead to faulty conclusions.

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