merisationsgrad $n = 8$ gut voneinander abtrennen. Höhere Homologe erleiden bei den angewendeten hohen Temperaturen Zersetzung.

Trägt man die Nettoretentionszeit (t_r) gegen die Zahl der $PNCl_2$-Glieder n auf, so erhält man bei dem oben angegebenen Temperatur-Programm eine Gerade bis $n = 7$. Der Wert für $n = 8$ liegt etwas zu hoch (Fig. 1). Bei isothermer Analyse ergibt sich für log t_r gegen n ebenfalls eine Gerade bis $n = 7$, für $n = 8$ war kein exakter Wert mehr zu messen (Fig. 2). Diese Messungen stellen neben den ^{31}P-NMR-Daten einen weiteren Beweis für die Ringstruktur der Glieder $n = 3$–7 dar.

Experimentelles

Die gas-chromatographischen Bedingungen waren: Glas-Säule, 1.2 m, Silikongummi SE-30, 10% auf Chromosorb W-HMDS, 60–80 mesh; Einspritzblock-Temperatur, 180° (Glaseinsatz); Säulentemperatur, programmiert 150–280°, 10°/Min.; Detektor, Wärmeleitfähigkeitszelle; Trägergas, 80 ml He/Min.

Es wurde ein Perkin-Elmer F 7 Gas-Chromatograph verwendet. Vergleichende ^{31}P-NMR-spektrometrische und gas-chromatographische Messungen erbrachten quantitativ übereinstimmende Resultate[1].

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Analysis of dihydric phenols by gas chromatography

The continuously increasing demand and use of new production methods of dihydric phenols has caused an increasing demand for analytical methods for these substances. In addition to a higher operative readiness of the analytical method, a higher degree of sensitivity and accuracy of the determinations has been claimed in some cases, though not all methods available comply with these requirements.

Paper chromatography[1–4], probably one of the most developed methods for the determination of phenols, is quantitatively not the most suitable. A decidedly unfavourable aspect of this method is that it is rather time-consuming. Similarly liquid–liquid chromatography is of little use[5,6]. The use of ionisation detectors for regis-

tering the retention time[7] improves the sensitivity, but does not change the total period of the analysis. Gas–liquid chromatography, which is comparatively quick, does not always offer satisfactory results. JANÁK AND KOMERS[8,9] obtained very good results when separating dihydric phenols by gas chromatography on mannitol as substrate. A disadvantage of this method is the low stability of the substrate. HENKEL[10], who first converted phenols to ethers, in the case of dihydric phenols obtained a mixture of mono- and di-ethers. NAUCKE AND TARKMANN[11] used Apiezon L on Celite. The peaks of the dihydric phenols were considerably elongated and unsymmetrical. We have ascertained that on the same phase as well as on non-polar and polar liquid phases the elution of dihydric phenols from the column is not quantitative (in the case of a kieselguhr support only 40 to 70 % and in all cases the results were not reproducible. It was thought that the use of an inert column packing might remove these unfavourable effects. Organic porous polymers of the styrene divinylbenzene type (Porapak, Chromosorb 102) have been used successfully.

Experimental and discussion

A gas chromatograph (Carlo Erba, Model D) with thermal conductivity cells was used for the study. The chromatographic column was of glass, length 1 m and diameter 1.5 mm. Porapak P (80/100 mesh) was used as support; 1 %, 3 % and 6 % Carbowax 20M was used as the stationary phase. The operating temperature was 230° and the flow rate of helium 22 ml/min. The oxygen content in the carrier gas was under 10 p.p.m. A model mixture prepared from standards of mono and dihydroxy phenols was analysed.

An experiment on Chromosorb 102 (Johns-Manville) confirmed our surmise. The quantitative analysis was reproducible although the peaks were still unsymmetrical. Owing to the asymmetry of the peaks an unsatisfactory separation of some of the dihydric phenols occurred. In the case of resorcinol and hydroquinone the elution of the two together was common. Coincident elution times also occurred between 2,3,6- and 2,3,5-trimethyl phenols and pyrocatechol as well as between 3,4,5-trimethyl-, 2,3,5,6-tetramethyl phenols and the methyl derivatives of pyrocatechol. A packing of the type styrene–divinylbenzene copolymer, for example Porapak Q, gave practically the same results, only the separation of the single components was worse. Porapak R hardly separated the dihydric phenols under the same operating conditions. Porapak P had the shortest absolute elution times for the given components.

It was therefore decided to test the separation effect of Porapak P coated with such a liquid phase as would increase the elution times of the dihydric phenols compared with other components present, and achieve a quantitative separation.

Fig. 1 shows the relation of relative elution times of mono- and dihydric phenols with respect to the percentage of Carbowax 20M on Porapak P. The elution times of the dihydric phenols, in general, increase with increasing volume of the liquid phase, and after the monohydric phenols. At the same time a decrease of the elution times of phenols with steric hindrance of the hydroxyl can be observed. This reduction is most conspicuous in the case of pentamethyl phenol, and to some extent in the case of tetra- and trimethyl phenols. It can be observed on a much smaller scale in the case of dihydric phenols with methyl groups in the vicinity of the hydroxyl group. With regard to the dihydric phenols the effect of the hydrogen bond of the hydroxyl groups evidently prevails. As a result of the values shown in Fig. 1 the kind of sep-

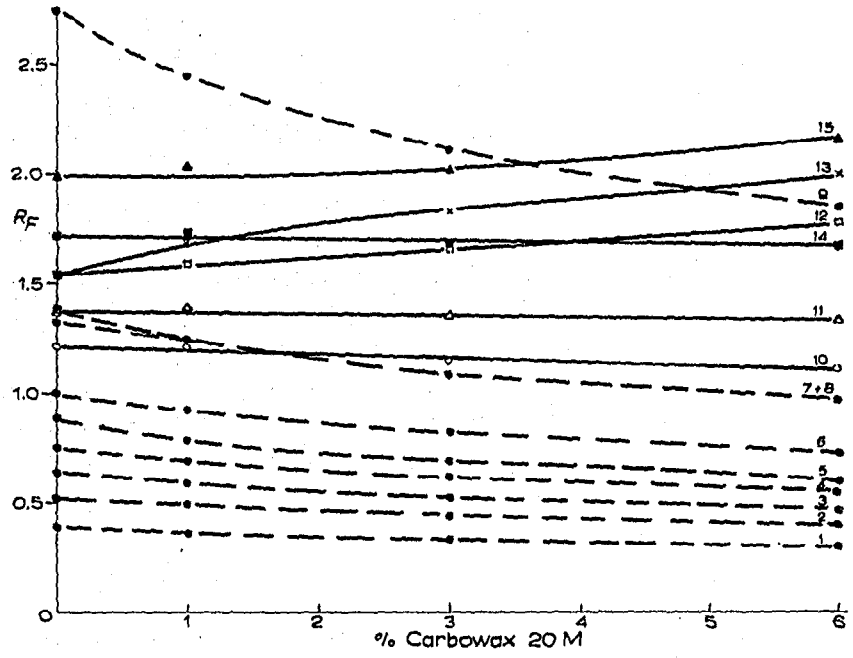

Fig. 1. Dependence of the relative elution times on the percentage of Carbowax 20M coated on Porapak P (pyrocatechol = 1.00). Temperature 230°. Monohydric phenols: 1 = Phenol; 2 = 3-methyl phenol; 3 = 2,4-dimethyl phenol; 4 = 2,3-dimethyl phenol; 5 = 2,3,6-trimethyl phenol; 6 = 2,3,5-trimethyl phenol; 7 = 3,4,5-trimethyl phenol; 8 = 2,3,5,6-tetramethyl phenol; 9 = pentamethyl phenol. Dihydric phenols: 10 = 3-Methyl pyrocatechol; 11 = 4-methyl pyrocatechol; 12 = hydroquinone; 13 = resorcinol; 14 = 2-methyl resorcinol; 15 = 4-methyl resorcinol.

TABLE I

RELATIVE ELUTION TIMES OF MONOHYDRIC AND DIHYDRIC PHENOLS ON PORAPAK P WITH 3% CARBOWAX 20M

Pyrocatechol = 1.00; temperature = 230°.

Component	*Relative elution time*
Phenol	0.33
3- and 4-Methyl phenol	0.44
2,4- and 2,5-Dimethyl phenol	0.52
2,3- and 3,5-Dimethyl phenol	0.62
2,3,6-Trimethyl phenol	0.69
2,3,5-Trimethyl phenol	0.82
3,4,5-Trimethyl phenol	1.08
2,3,5,6-Tetramethyl phenol	1.08
Pentamethyl phenol	2.11
Pyrocatechol	1.00
3-Methyl pyrocatechol	1.15
4-Methyl pyrocatechol	1.35
Hydroquinone	1.66
Resorcinol	1.83
2-Methyl resorcinol	1.68
4-Methyl resorcinol	2.02
4-Ethyl resorcinol	2.55
3-*tert.*-Butyl pyrocatechol	2.03
4-*tert.*-Butyl pyrocatechol	2.59
3,5-Di-*tert.*-butyl pyrocatechol	3.84

aration can be chosen in such a way as to reach an optimal quantitative separation.

In our case the most advantageous packing was Porapak P with 3 % Carbowax 20M, where for most purposes the best separation was obtained. 3,4,5-Trimethyl phenol and tetramethyl phenol elute on this packing after pyrocatechol but they can be read off. At a higher rate of separation they overlap with pyrocatechol. With a higher percentage of the polar phase a prolongation of the absolute elution times as well as an increase in the asymmetry of the elution curves takes place. The separation sharpness between pyrocatechol and 3-methylpyrocatechol becomes worse. Separations on Porapak P with a low percentage of stationary phase results in overlapping of pyrocatechol and 2,3,5-trimethylphenol, and the methyl derivatives of pyrocatechol also elute with 3,4,5-trimethyl and tetramethyl phenol. At the same time the separation of hydroquinone and resorcinol becomes worse.

The relative elution times of series of mono- and dihydric phenols were determined on Porapak with 3 % Carbowax 20M. Table I shows the measured values. The chromatogram of the model mixture is shown in Fig. 2. The quantitative determination was tested on mixtures prepared from standards of mono- and dihydric phenols. The results are listed in Table II. The areas of the single components were not corrected in the case of mixtures containing only dihydric phenols. In the case of mixtures of mono- and dihydric phenols the peak areas of dihydric phenols had to be corrected by a correction factor which was experimentally determined and is valid only for the conditions used.

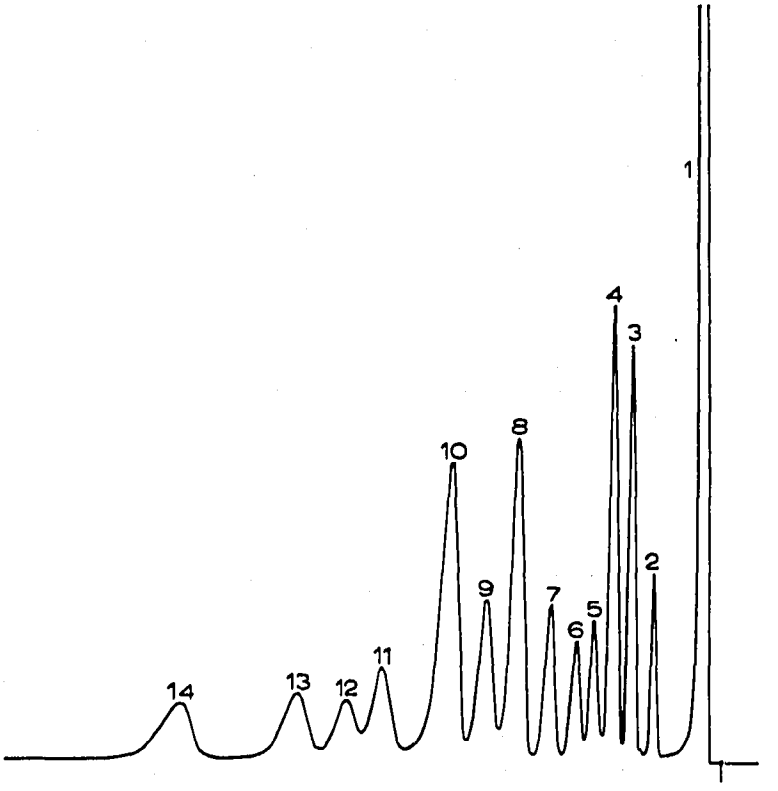

Fig. 2. Chromatogram of a model mixture of mono- and dihydric phenols on Porapak P coated with 3% Carbowax 20M at 230°. 1 = Solvent; 2 = phenol; 3 = 3-methyl phenol; 4 = 2,4-dimethyl phenol; 5 = 2,3-dimethyl phenol; 6 = 2,3,6-trimethyl phenol ; 7 = 2,3,5-trimethyl phenol; 8 = pyrocatechol; 9 = 3-methyl pyrocatechol; 10 = 4-methyl pyrocatechol; 11 = hydroquinone; 12 = resorcinol; 13 = 4-methyl resorcinol; 14 = 4-ethyl resorcinol.

TABLE II

QUANTITATIVE DETERMINATION OF MONOHYDRIC AND DIHYDRIC PHENOLS ON PORAPAK P COATED WITH 3% CARBOWAX 20M

Mixture	*Real value*		*Experimental value*		*Notes*
2,3,5-Trimethyl phenol	11.7		11.6		
Pyrocatechol	35.0		35.6		correction
4-Methyl pyrocatechol	53.3		52.8		factor
2,4-Dimethyl phenol	15.8		15.0		
2,3-Dimethyl phenol	18.3	56.2	19.6	56.4	
2,3,5-Trimethyl phenol	22.1		21.8		
Pyrocatechol	25.1		24.7		correction
4-Methyl pyrocatechol	18.7		18.9		factor
Pyrocatechol	10.8		11.3		without
3-*tert.*-Butyl pyrocatechol	22.7		22.0		correction
4-*tert.*-Butyl pyrocatechol	44.0		44.8		factor
3,5-Di-*tert.*-butyl pyrocatechol	22.5		21.9		

Conclusions

Qualitatively and quantitatively reproducible results for the determination of dihydric phenols by means of gas chromatography were obtained by using an inert column packing of the styrene–divinyl benzene copolymer type. A good resolution of dihydric phenols in a mixture with monohydric phenols was reached on Porapak P with 3 % Carbowax 20M at 230°. The analysis time was approx. 15 min which permits this method to be used for process analysis.

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