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INVESTIGATION OF THE COMPOSITION OF COAL-TAR PHENOLS AND XYLENOLS BY CAPILLARY CHROMATOGRAPHY

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SUMMARY

Gas chromatographic analyses of technical coal-tar phenol products, dehydrated phenols, tricresol, dicresol and xylenols were carried out in an open-tubular column, 50 m long, containing tri-(2,4-xylenyl)phosphate at 130°. More than 40 phenol derivatives were identified in the dehydrated phenols and xylenols.

INTRODUCTION

One of the sources of phenol and its derivatives for the chemical industry is the coke industry, in which coal is processed on a large scale by the method of high-temperature coking process. The waste and coal tar resulting from this process serve as a source of coal-tar phenols; by rectification of phenols different phenolic products (phenol, cresols, fractions of dicresol, tricresol and xylenol) are obtained.

The increasing application of phenol derivatives has placed increased demands on the quality and quantitative composition of phenolic products, which may vary with the consumer,

The investigation of the composition of phenol mixtures resulting from coking is complicated by the presence of a considerable amount of components with similar boiling points, differing by only 1–2°. Coal-tar phenols contain about 50 components boiling within the range 200–260° [1]. The problems of the analysis of the composition of mixtures of phenolic products and of the pure constituents have been solved successfully by means of gas–liquid chromatography[2–8].

Comparative data show that packed columns, in spite of their wide use for the analysis of technical products, do not provide the complete separation of all of the isomers of methyl-, ethyl- and dimethylphenols. Thus, in the analysis of coal-tar phenols, even with the application of selective stationary phases such as tri(2,4-xylenyl) phosphate and dimethyl phthalate, some derivatives of phenol such as 2-ethylphenol and 2,3-dimethylphenol, 3-ethylphenol and 2,3-dimethylphenol, 3-ethylphenol and 3,5-dimethylphenol, and other pairs, remain unseparated [2,3,9–12]. Consequently, the data on the qualitative and quantitative compositions of phenol fractions obtained

using packed columns are not exhaustive and in most instances provide information only about the main components present in the fractions. Capillary columns do not suffer from most of the drawbacks mentioned above. The high efficiency of capillary columns permits the separation of all similar boiling homologues of phenol within a short period.

EXPERIMENTAL

As the stationary liquid phase, tri(2,4-xylenyl) phosphate (TXP), which shows a high selectivity with respect to phenols, was used[13–16]. The methods of preparation of the capillary column and the coating of the liquid phase have been described previously[17]. For the identification and quantitative determination of some phenol derivatives, the peaks of which overlap in the capillary column (I), the main fractions were also analysed in a packed column (II) containing Apiezon L. The column parameters and the conditions of analyses are given in Table I.

TABLE I

CONDITIONS OF ANALYSIS IN COLUMNS I AND II

Parameter	*Column I*	*Column II*
Apparatus	Chrom-41	Chrom-41
Column material	Stainless steel	Glass
Column length and diameter (m × mm)	50 × 0.25	4.4 × 3
Stationary phase	95% TXP + 5% H_3PO_4	20% Apiezon L + 0.5% Carbowax 6000
Solid support	—	Chromaton N (AW-HMDS), 0.1–0.125 mm
Detector	Flame ionization	Flame ionization
Carrier gas (nitrogen) pressure (kPa)	152	230
Column temperature (°C)	130	160, 180
Injection port temperature (°C)	260	—
Scale sensitivity (mV)	20	1000
Sample size (μl)	0.1–0.15	0.5

RESULTS AND DISCUSSION

The chromatograms of some industrial fractions of coal-tar phenols produced by a phenol plant are shown in Figs. 1–4. The identification has been carried out by using Kováts retention indices[17] and by the method of addition of pure standards.

A comparison of the chromatograms obtained in columns I and II made it possible to establish that, with the exception of C_6–C_8 phenols, the following derivatives of phenol are present in the dehydrated phenol fraction: 2,4,6-, 2,3,6-, 2,4,5-, 2,3,5-, 2,3,4- and 3,4,5-trimethylphenols, 6-ethyl-2-methylphenol, 2-,3- and 4- isopropylphenols, 2-isopropyl-6-methylphenol, 2-ethyl-4-methylphenol, 4-ethyl-2-methylphenol, 5-ethyl-3-methylphenol, 2-ethyl-5-methylphenol, 3-ethyl-6-methylphenol, 4-ethyl-3-methylphenol 2-, 3- and 4-*n*-propylphenols, 2-isobutylphenol, 2-*sec*.-butylphenol, 2-methyl-4-*n*-propylphenol, 3-methyl-6-*n*-propylphenol, 2,4-diethylphenol, 2,3,5,6- and 2,3,4,6-tetramethylphenols and 4-indanol. A comparison of the data

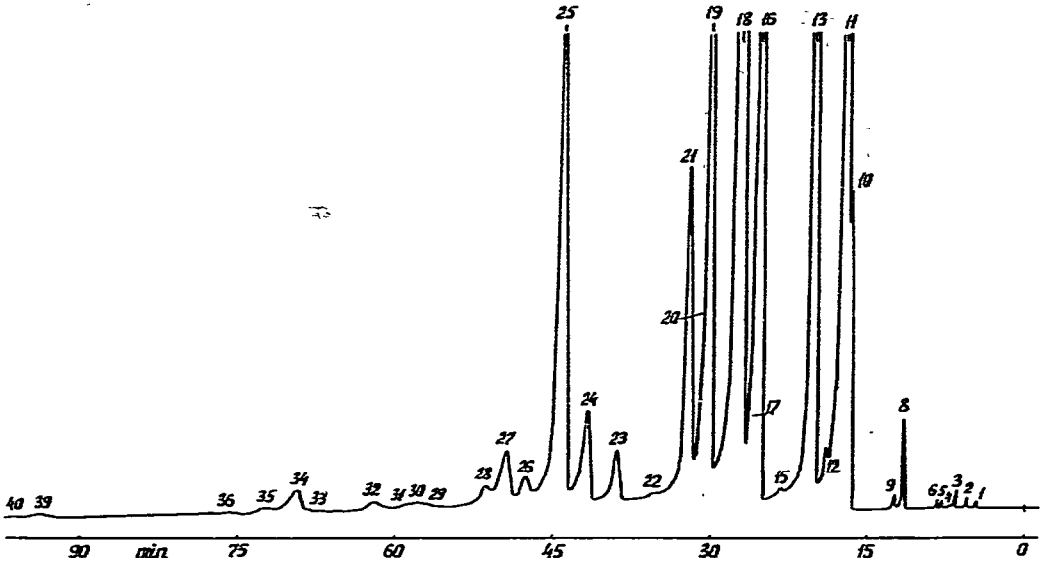

Fig. 1. Chromatogram of dehydrated phenol fraction; the interpretation of the peaks is given in Tables II and III.

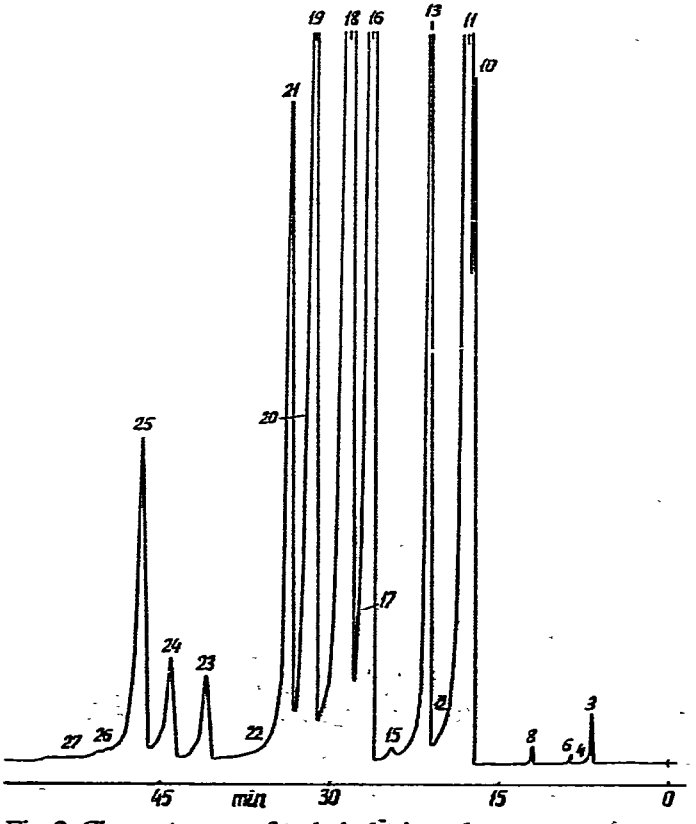

Fig. 2. Chromatogram of technical tricresol.

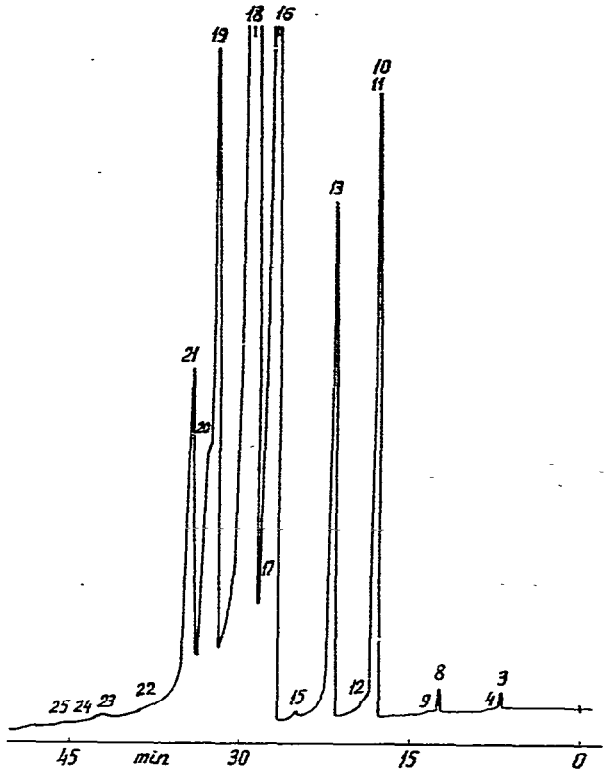

Fig. 3. Chromatogram of technical dicresol.

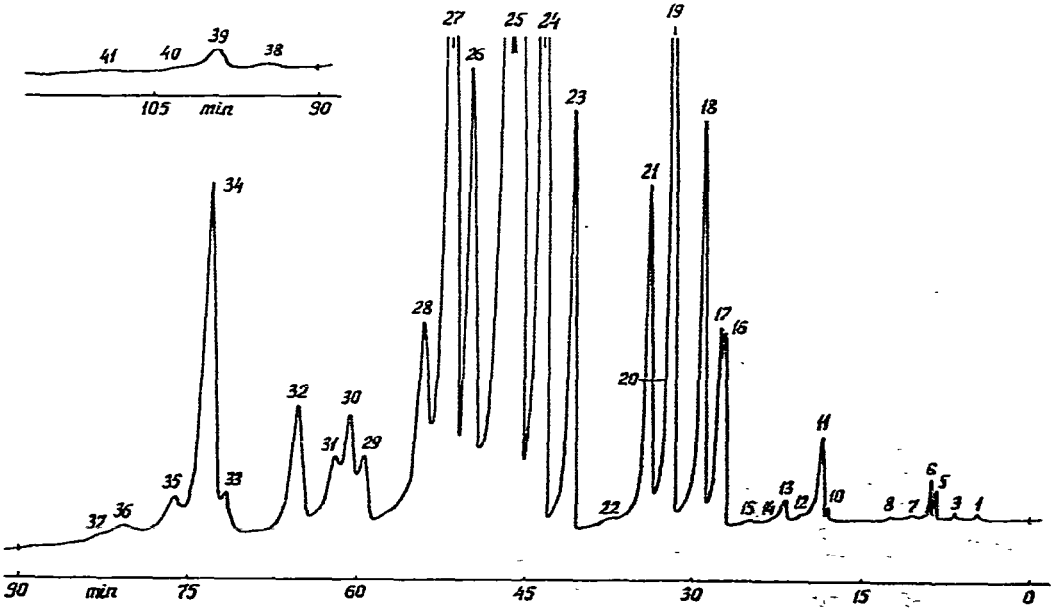

Fig. 4. Chromatogram of narrow xylenol fraction.

TABLE II

BOILING POINTS AND RELATIVE RETENTION TIMES OF PHENOL PRODUCTS IN COLUMN I

Number of peak on chromatograms	*Component*	*Boiling point (°C)*	*Relative retention time**
1–9	Unidentified	—	—
10	2,6-Dimethylphenol	200.6	0.96
11	Phenol	182.0	1.00
12	Unidentified	—	1.12
13	2-Methylphenol	191.0	1.21
14	Unidentified	—	1.25
15	6-Ethyl-2-methylphenol	213.0	1.41
16	4-Methylphenol	201.9	1.57
17	2,4,6-Trimethylphenol	220.6	1.61
18	3-Methylphenol	202.2	1.68
19	2-Isopropyl-6-methylphenol +	228–230	1.80
	2,4-dimethylphenol	211.3	1.87
20	2-Ethylphenol	204.5	1.91
21	2,5-Dimethylphenol	211.5	2.00
22	2,3,6-Trimethylphenol	234.0	2.08
23	2,3-Dimethylphenol	217.1	2.43
24	2-Isopropylphenol +	214.4	2.62
	4-ethylphenol	218.0	2.63
25	3,5-Dimethylphenol +	221.7	2.79
	2-ethyl-4-methylphenol +	222.3	2.79
	3-ethylphenol	217.0	2.82
26	4-Ethyl-2-methylphenol +	227.0	2.99
	2-*n*-propylphenol	221.0	3.02
27	2-Ethyl-5-methylphenol +	224.2	3.09
	3,4-dimethylphenol +	226.9	3.12
	3-ethyl-6-methylphenol	227.7	3.14
28	Unidentified	—	3.29
29	2,3,5,6-Tetramethylphenol +	248.0	3.56
	4-isopropylphenol	229.1	3.58
30	2,4,5-Trimethylphenol +	235.2	3.63
	2-isobutylphenol	228.3	3.63
31	2,3,4,6-Tetramethylphenol +	250.0	3.68
	3-isopropylphenol	228.0	3.68
32	2,3,5-Trimethylphenol +	235.3	3.94
	2-*sec.*-butylphenol	228.0	3.95
33	2,4-Diethylphenol	229.0	4.32
34	4-*n*-Propylphenol +	234.5	4.48
	5-ethyl-3-methylphenol	235.9	4.52
35	3-*n*-Propylphenol +	233.5–234.5	4.63
	2,3,4-trimethylphenol	234.5–237.0	4.74
36	2-Methyl-4-*n*-propylphenol +	240.0–242.6	4.80
	4-ethyl-3-methylphenol +	229.0	4.92
	3-methyl-6-*n*-propylphenol	235.0	4.92
37	2,5-Diethylphenol	242.5	5.13
38	5-Methyl-4-indanol +	250.0	5.71
	4-isobutylphenol +	243.9	5.79
	4-*sec.*-butylphenol	242.1	5.86
39	4-Indanol	247.0	6.07
40	3,4,5-Trimethylphenol	251.9	6.39
41	Unidentified	—	6.89

* Phenol = 1.00.

obtained with the results of analyses of analogous fractions published elsewhere[7,8,10,11,18–22] indicates that most of the above phenols have been identified here for the first time.

The high selectivity of TXP, the comparatively low temperature of the column 1 and also a low concentration did not permit some components to be identified, as their peaks showed too much tailing. This identification was achieved by increasing the size of the sample of the phenol fraction (4 μl) in the column at 180°, when several peaks were observed, including 5-indanol.

Peaks 1–9 and 12 (Figs. 1 and 4) remained unidentified, and are probably high-boiling hydrocarbons. Peak 28 also remained unidentified, and is probably 2-ethyl-3-methylphenol (according to the relationship between the logarithm of the relative retention times of phenols and the number of hydrocarbon atoms in the molecule).

During the analysis of xylenol fractions in column 1, in addition to the above compounds, 2,5-dimethylphenol, 5-methyl-4-indanol, 4-isobutylphenol and 4-*sec.*-butylphenol were identified. With an increase in the sample size to 4 μl in column II at 160°, the presence of 3-*n*-butylphenol, 3,4-diethylphenol, 2-ethyl-4,5-dimethylphenol and 6-methyl-4-indanol in xylenol fractions was established.

Quantitative calculations were carried out using the method of internal normalization without introducing the correction factor[7,23]. The areas of the peaks were determined with the aid of a 1-Tl digital proportional computer (Laboratorní přístroje, Prague, Czechoslovakia). The results of the analyses are given in Tables II and III.

Comparative calculations of the content of some components of fractions of dehydrated phenols obtained in both columns showed that the amounts of 2,4,6-trimethylphenol and 2-isopropyl-6-methylphenol giving overlapping peaks in column 1 with those of 4-methyl- and 2,4-dimethylphenol are small, not exceeding 0.25 and 0.20%, respectively. Approximately the same amount of ethylmethylphenols, the peaks of which overlap with the peaks of some dimethyl- and *n*-propylphenols, is contained in this fraction.

In column 1, the isomers of ethylphenol, except 3-ethylphenol, are separated from the corresponding dimethylphenols. However, the peak of 4-ethylphenol overlaps with that of 2-isopropylphenol. Calculations on the chromatograms obtained from column II showed that the total content of 3- and 4-ethylphenols in the phenol fraction does not exceed 1.5%. Hence, the total amount of isomers of ethylphenol in the dehydrated phenol fraction is 2.0–2.1%. Calculations on the chromatograms obtained

TABLE III

QUANTITATIVE RESULTS OF ANALYSES OF PHENOL PRODUCTS IN COLUMN I

Number of peak on chromatograms	*Component*	*Mean wt. (%)*				
		Dehydrated phenol	*Tricresol*	*Dicresol*	*Technical xylenol*	*Narrow xylenol fraction*
1–9	Unidentified	0.46	0.32	0.26	0.23	0.20
10	2,6-Dimethylphenol	0.83	1.30	2.70	0.10	0.05
11	Phenol	34.60	25.90		0.33	0.35
12	Unidentified	0.16	—	—	0.03	0.04

TABLE III *(continued)*

Number of peak on chromatograms	*Component*	*Mean wt. (%)*				
		Dehydrated phenol	*Tricresol*	*Dicresol*	*Technical xylenol*	*Narrow xylenol fraction*
13	2-Methylphenol	11.80	4.65	2.60	0.20	0.08
14	Unidentified	—	—	—	0.01	0.01
15	6-Ethyl-2-methylphenol	0.10	0.04	0.03	0.07	0.03
16	4-Methylphenol	11.95	18.98	26.34	3.25	0.72
17	2,4,6-Trimethylphenol				1.02	0.75
18	3-Methylphenol	22.52	31.35	55.25	7.41	1.95
19	2-Isopropyl-6-methylphenol + 2,4-dimethylphenol	5.45 —	7.86 —	6.80 —	— 10.50	— 4.21
20	2-Ethylphenol	0.61	1.07	1.50	—	—
21	2,5-Dimethylphenol	2.74	4.21	4.39	4.80	1.70
22	2,3,6-Trimethylphenol	0.17	0.09	—*	0.07	0.05
23	2,3-Dimethylphenol	0.48	0.74	0.13	3.10	2.70
24	2-Isopropylphenol + 4-ethylphenol	0.86	0.90	—	9.30	9.61
25	3,5-Dimethylphenol + 2-ethyl-4-methylphenol + 3-ethylphenol	5.70	2.42	—*	40.86	52.70
26	4-Ethyl-2-methylphenol + 2-*n*-propylphenol	0.20	0.17	—	3.01	3.75
27	2-Ethyl-5-methylphenol + 3,4-dimethylphenol + 3-ethyl-6-methylphenol	0.62	—*	—	8.30	11.22
28	Unidentified	0.15	—	—	1.75	1.89
29	2,3,5,6-Tetramethylphenol + 4-isopropylphenol	0.02	—	—	0.46	0.48
30	2,4,5-Trimethylphenol + 2-isobutylphenol	0.05	—	—	0.78	1.00
31	2,3,4,6-Tetramethylphenol + 3-isopropylphenol	0.04	—	—	0.48	0.49
32	2,3,5-Trimethylphenol + 2-*sec.*-butylphenol	0.07	—	—	0.87	1.02
33	2,4-Diethylphenol	—	—	—	0.17	0.21
34	4-*n*-Propylphenol + 5-ethyl-3-methylphenol	0.28	—	—	2.30	4.10
35	3-*n*-Propylphenol + 2,3,4-trimethylphenol	0.04	—	—	0.21	0.20
36	2-Methyl-4-*n*-propylphenol + 4-ethyl-3-methylphenol + 3-methyl-6-*n*-propylphenol	0.03	—	—	0.07	0.12
37	2,5-Diethylphenol	—	—	—	0.03	0.05
38	5-Methyl-4-indanol + 4-isobutylphenol + 4-*sec.*-butylphenol	—	—	—	0.01	0.02
39	4-Indanol	0.07	—	—	0.28	0.31
40	3,4,5-Trimethylphenol	—*	—	—	—*	—*
41	Unidentified	—	—	—	—	—*

* This component was not determined.

with an increased sample size permitted the determination of the approximate contents of 5-indanol and 3,4,5-trimethylphenol, the amount of which in phenol and xylenol fractions varies in the range 0.1–0.3%.

CONCLUSION

Qualitative and quantitative analyses of technical fractions of dehydrated phenols, tricresol, dicresol and xylenols in a capillary column 50 m long, containing tri(2,4-xylenol) phosphate as the stationary liquid phase, have been carried out. In this column, in the phenol and xylenol fractions, apart the main homologues of C_6–C_8 phenols, the isomers of trimethyl-, tetramethyl-, ethylmethyl-, diethyl- and propylphenols, 4- and 5-indanols and their homologues were identified.

The times required for the analysis of the dehydrated phenols and xylenols, tricresol and dicresol were 100–110, 50 and 40 min, respectively.

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