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COMPARISON OF GAS–LIQUID–SOLID CHROMATOGRAPHY WITH CAPILLARY-COLUMN GAS–LIQUID CHROMATOGRAPHY FOR THE ANALYSIS OF PHENOLS

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SUMMARY

A method for the qualitative and quantitative analysis of phenols by gas–liquid–solid chromatography has been developed and compared with analyses made by capillary-column gas–liquid chromatography. The new method yields a faster, more efficient separation of the isomeric cresols than has previously been reported, with quantitation equivalent to that of the capillary-column technique. Thus, a direct, quantitative analysis of phenols is possible without the need for derivatization of the sample.

INTRODUCTION

The quantitative analysis of mixtures of phenols by chromatographic techniques is difficult to achieve. These compounds are highly polar, and have low vapor pressures at ambient temperatures. Conventional packed columns do not adequately separate isomers with nearly identical polarities and vapor pressures, for example, *m*- and *p*-cresol, and 2,4- and 2,5-dimethylphenol[1–3]. Moreover, the commonly employed liquid phases are slowly destroyed at high temperatures by acidic phenols, and cannot be used above 125° (ref. 4); hence, long analysis times are unavoidable. The non-linear elution of the more polar phenols adversely affects the quantitative results of the analysis. Wall-coated and packed capillary columns offer an improvement in resolving power[5–8], but low operating temperatures are still required. Wall-coated capillary columns are widely used for the analysis of coal tar distillates.

Graphitized carbon black coated with small amounts of a suitable non-volatile acidic liquid phase has recently been introduced for the analysis of polar compounds[9–12]. Differential adsorption of sample molecules onto the surface of the carbon effects a separation based on differences in molecular geometry. The addition of a polar liquid phase modifies the adsorption of the solute by masking active sites on the carbon surface. This treatment reduces tailing and favors the elution of symmetrical peaks. The overall chromatographic separation combines gas–solid and gas–liquid partitioning, and is called gas–liquid–solid chromatography[13].

In this work, the optimal conditions for the quantitative analysis of phenols by capillary-column gas–liquid chromatography (CGLC) have been established.

Similar analyses were then performed by gas–liquid–solid chromatography (GLSC) in a conventional packed column, and the results were compared.

EXPERIMENTAL

A Perkin-Elmer Model 900 gas chromatograph (Perkin-Elmer, Norwalk, Conn., U.S.A.) was used with the injector and flame detector held at 250°. Retention times and peak areas were obtained from a Perkin-Elmer Model PEP-1 chromatographic data system. Chromatographic supplies were purchased from Supelco (Bellefonte, Pa., U.S.A.); chemicals were purchased from Aldrich (Milwaukee, Wisc., U.S.A.).

For gas–liquid chromatography, a stainless-steel capillary column (200 ft. × 0.5 mm I.D.) was coated at a flow-rate of 1 ml/min with a solution of 10% w/w diisodecylphthalate and 0.5% w/w phosphoric acid in acetone. Before use, the column was conditioned at 135° for 16 h. For analytical work, the column was kept at 135° with a helium carrier gas flow-rate of 2 ml/min, and an injector split ratio of 25:1. Useful life of this column exceeded 200 h.

GLSC was performed using a coiled glass column (6 ft. × 2 mm I.D.) packed with Carbopak A which was coated with 0.3% SP-1000 (a "modified" Carbowax 20M) and 0.3% phosphoric acid. This material is relatively soft, and care was taken that fines were not produced during packing by excessive vibration. The column was conditioned at 150° for 16 h before use. The column was held at 165° for 12 min, programmed at 6°/min, and held at 195° for the remainder of the analysis. The flow-rate of the helium carrier gas was 25 ml/min. An "Oxisorb" scrubber was used to remove water vapor and oxygen from the carrier gas, thus preventing rapid (6 h) deterioration of the column.

RESULTS AND DISCUSSION

The first column studied was a stainless-steel capillary coated with diisodecylphthalate and phosphoric acid. Anisole was used as an internal standard because of its high volatility, short retention time, and lack of a polar hydroxyl group, factors which favor quantitative elution. Ninety minutes were needed for an analysis at a column temperature of 135°.

A typical separation of sixteen phenols by CGLC is shown in Fig. 1. Response factors and relative retention times are given for these phenols and anisole in Table I. The separation obtained is a function of differences in polarity, and is proportional to molecular weight, lighter molecules generally appearing first. Exceptions are compounds with sterically blocked hydroxyl groups, which elute earlier than expected on the basis of molecular weight. Compounds having retention times as long as 80 min showed only slight tailing effects. From calculations based on the separation of *m*- and *p*-cresol, it can be shown that the resolution of these isomers is 0.96, and that the column has 12,400 theoretical plates, with a height equivalent to one theoretical plate (HETP) of 4.91 mm.

Preliminary work with a glass column filled with Carbopak A coated with SP-1000 and phosphoric acid gave erratic results. The resolving power of the column was rapidly lost, and after 6 h of use at 160°, *m*- and *p*-cresol were not resolved.

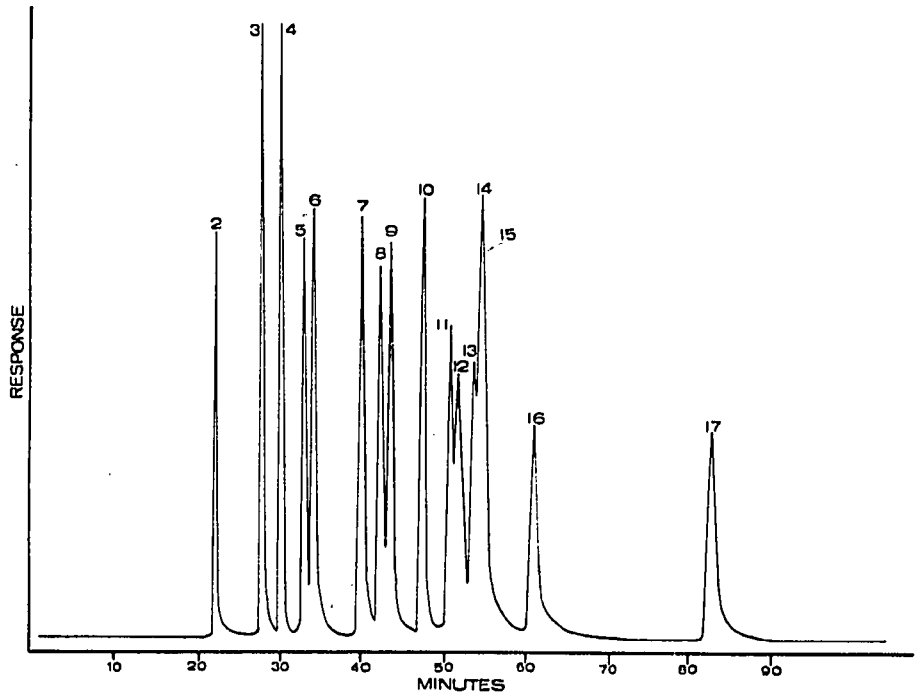

Fig. 1. Separation of sixteen phenols by CGLC on a wall-coated stainless-steel capillary column (200 ft. × 0.5 mm I.D.). The numbers refer to the compounds listed in Table I. Chart speed, 10 min/division; for other parameters, see Experimental.

TABLE I

RELATIVE RETENTION TIMES AND RESPONSE FACTORS OBTAINED IN THE ANALYSIS OF KNOWN MIXTURES OF PHENOLS BY CGLC

No.	*Compound*	*Relative retention time**	*Response factor (S.D.)**	
1	Anisole	1.00**	1.000	
2	Phenol	2.14	1.309	(0.045)
3	*o*-Cresol	2.65	1.103	(0.021)
4	2,6-Dimethylphenol	2.88	1.146	(0.013)
5	*p*-Cresol	3.16	1.471	(0.044)
6	*m*-Cresol	3.27	1.289	(0.057)
7	*o*-Ethylphenol	3.93	1.278	(0.029)
8	2,4-Dimethylphenol	4.07	1.283	(0.025)
9	2,5-Dimethylphenol	4.20	1.275	(0.012)
10	2,4,6-Trimethylphenol	4.57	1.380	(0.051)
11	*p*-Ethylphenol	4.97	1.535	(0.040)
12	2,3-Dimethylphenol	4.99	1.410	(0.028)
13	*m*-Ethylphenol	5.16	1.280	(0.041)
14	2,3,6-Trimethylphenol	5.22	1.183	(0.063)
15	3,5-Dimethylphenol	5.28	1.496	(0.063)
16	3,4-Dimethylphenol	6.01	1.507	(0.138)
17	2,3,5-Trimethylphenol	8.00	1.405	(0.082)

* Average of three determinations.
** Average retention time, 11.05 min.

Exclusion of water vapor and oxygen from the carrier gas gave reproducible results, and useful column life exceeded 100 h. Six inches of column nearest the injector were not packed, to ensure that the sample was volatilized before reaching the packing and to prevent irreversible absorption of the liquid sample onto the support.

A typical separation of sixteen phenols by GLSC is shown in Fig. 2. Response factors and relative retention times are given for these phenols and for anisole in Table II. The separation achieved here is a function of molecular weight and shape, and is less influenced by polarity; thus, the order of elution differes from that found with the capillary column. Although compounds having a long retention time, namely the three trimethylphenols, show some tailing, quantitation can easily be achieved. From calculations based on the separation of *m*- from *p*-cresol, it can be shown that the resolution of these isomers is 1.73, and that the column has 1626 theoretical plates, with a HETP of 1.12 mm. The GLSC column, having fewer theoretical plates than the CGLC column, is more useful for the separation of *m*- from *p*-cresol.

The CGLC column failed to separate 2,3-dimethylphenol from *p*-ethylphenol; it also failed to separate *m*-ethylphenol, 3,5-dimethylphenol, and 2,3,6-trimethylphenol from each other. In comparison, the GLSC column failed to separate 2,3- from 2,6-dimethylphenol, and 2,4- from 2,5-dimethylphenol. The clear separation of 2,3-dimethylphenol from other components is incomplete on both columns,

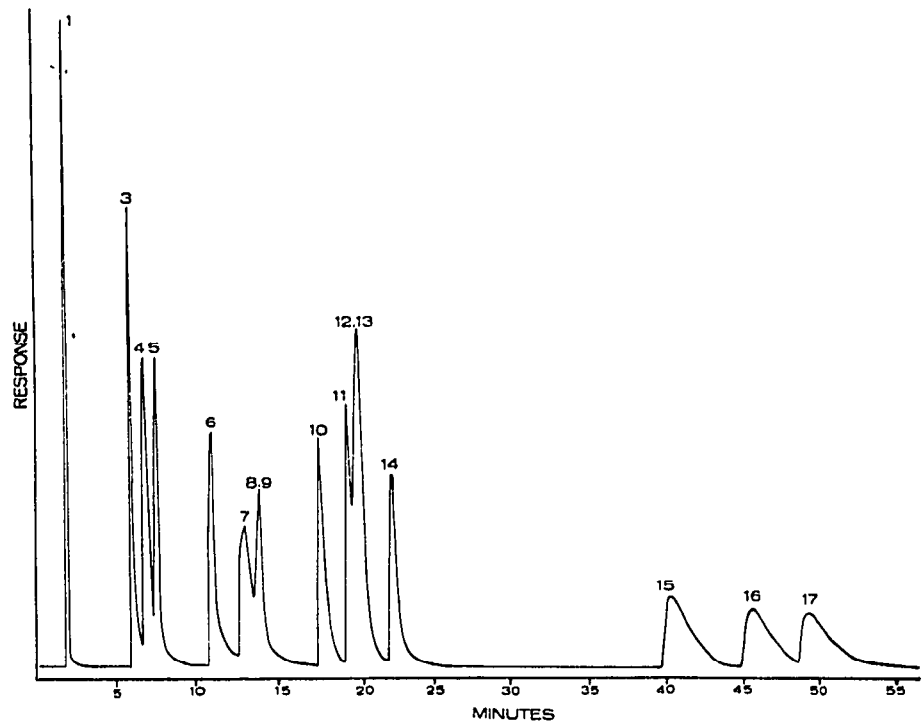

Fig. 2. Separation of sixteen phenols by GLSC on a glass column (6 ft. × 2 mm I.D.) containing Carbopak A coated with SP-1000 and phosphoric acid. The numbers refer to the compounds listed in Table II. Chart speed, 5 min/division; for other parameters, see Experimental.

TABLE II

RELATIVE RETENTION TIMES AND RESPONSE FACTORS OBTAINED IN THE ANALYSIS OF KNOWN MIXTURES OF PHENOLS BY GLSC ON CARBOPAK A

No.	*Compound*	*Relative retention time* *	*Response factor (S.D.)* *
1	Phenol	0.41	1.197 (0.023)
2	Anisole	1.00**	1.000
3	*o*-Cresol	1.40	1.121 (0.019)
4	*m*-Cresol	1.57	1.228 (0.050)
5	*p*-Cresol	1.73	1.377 (0.080)
6	*o*-Ethylphenol	2.58	1.343 (0.117)
7	*m*-Ethylphenol	2.96	1.209 (0.054)
8	2,4-Dimethylphenol	3.13	1.393 (0.153)
9	2,5-Dimethylphenol	3.15	1.392 (0.191)
10	*p*-Ethylphenol	3.76	1.858 (0.032)
11	3,5-Dimethylphenol	3.90	1.284 (0.041)
12	2,6-Dimethylphenol	4.58	0.830 (0.010)
13	2,3-Dimethylphenol	4.68	1.440 (0.109)
14	3,4-Dimethylphenol	5.14	1.440 (0.024)
15	2,4,6-Trimethylphenol	9.53	1.427 (0.081)
16	2,3,6-Trimethylphenol	10.69	1.430 (0.072)
17	2,3,5-Trimethylphenol	11.50	1.511 (0.196)

* Average of three determinations.
** Average retention time, 4.40 min.

but the interfering compound is different in each case. In the absence of *p*-ethylphenol or 2,6-dimethylphenol, proper choice of a column will permit a routine analysis of all the other phenols listed in Tables I or II.

The average response factor and standard deviation for three determinations of each compound are given in Table I for the CGLC column, and in Table II for the GLSC column. Response factors were determined using solutions containing equal weights of four test compounds and anisole by an area normalization calculation[14]. By this procedure, the concentration of a component in the sample is found by dividing its net peak area (raw peak area times response factor) by the total of all net peak areas. The average of all response factors is 1.334 for the CGLC column and 1.342 for the GLSC column. The close numerical correspondence of these values indicates no significant difference in the accuracy of the two methods. The range in values of the individual response factors is due in part to the relative purities of the standards and to the performance of the particular chromatographic system used. Each laboratory must determine response factors for its particular system.

The standard deviation of the response factor may be taken as a measure of the precision of analysis for each compound. The sixteen phenols studied may be divided into two groups: four compounds of primary interest, namely phenol and the three isomeric cresols, and twelve compounds of secondary interest, namely, the six dimethylphenols, three trimethylphenols, and three ethylphenols. For phenol and the three cresols, the pooled standard deviation of the analysis for these four

compounds is 0.035 on the GLSC column, and 0.031 on the CGLC column. No significance can be attributed to the difference between these two values. The dimethylphenols, trimethylphenols, and ethylphenols show less precision on the GLSC column (pooled standard deviation 0.114) than on the CGLC column (pooled standard deviation 0.062).

CONCLUSIONS

The advantages of GLSC over CGLC for the analysis for phenol and the three isomeric cresols are summarized in Table III, where it can be seen that an analysis can be accomplished by GLSC in one-fourth the time needed for CGLC, with better results. The HETP of the GLSC column is significantly less than that of the CGLC column, but owing to its shorter length, the GLSC column has fewer total plates. Despite this, a more efficient separation and superior resolution of *m*- from *p*-cresol are obtained. Finally, compounds not separated by either column are listed in Table III.

TABLE III

COMPARISON OF CHROMATOGRAPHIC METHODS FOR THE ANALYSIS OF COAL TAR DISTILLATES

Property	*Column type*	
	GLSC	*CGLC*
Time for separation of *o*-, *m*-, and *p*-cresol, min	8	37
Standard deviation of triplicate analyses for phenol and isomeric cresols	0.035	0.031
Resolution ratio of *m*- and *p*-cresol	1.73	0.96
Average response factor for sixteen phenols	1.342	1.334
HETP, mm	1.12	4.90
Compounds not separated	2,3- and 3,6-dimethylphenol 2,4- and 2,5-dimethylphenol	2,3-dimethylphenol and *p*-ethylphenol 3,5-dimethylphenol, *m*-ethylphenol, and 2,3,6-trimethylphenol

GLSC employing Carbopak A coated with SP-1000 and phosphoric acid is shown to be suitable for accurate, precise, and rapid analysis of mixtures of phenols. This method gives a superior resolution of *o*-, *m*-, and *p*-cresol with no sacrifice in quantitation as compared to analysis by CGLC. The easy elution of phenol and the cresols from the GLSC column makes possible a rapid quantitative analysis without the need for derivatization of the sample.

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