GAS–LIQUID CHROMATOGRAPHY OF MIXTURES CONTAINING PHENOL AND FIVE OF ITS *tert.*-BUTYL DERIVATIVES*

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(Received September 4th, 1962)

INTRODUCTION

The analysis of mixtures containing phenol and *tert.*-butylphenols is of interest in connection with the study of the acid catalyzed alkylation of phenol[1,2] with isobutylene. Substitution takes place almost exclusively in the *ortho* and *para* positions. Furthermore, even when the source of isobutylene is a hydrocarbon fraction containing other butenes, the reaction is selective and the major products are *tert.*-butylphenols.

Examination of the properties of these phenols, listed in Table I, shows that analysis by distillation will yield considerable information. However, the procedure is time consuming and not very accurate when compared with instrumental methods.

TABLE I

PHYSICAL PROPERTIES OF PHENOL AND SOME *tert.*-BUTYLPHENOLS

Compound	*M.p.* (°C)*	*B.p.* (°C)/760 mm*
Phenol	41	182
o-tert.-Butylphenol	—	221
p-tert.-Butylphenol	100	237
2,6-Di-*tert.*-butylphenol	39	253**
2,4-Di-*tert.*-butylphenol	57	263
2,4,6-Tri-*tert.*-butylphenol	131	278

* According to PARDEE AND WEINRICH[3], except as otherwise indicated.
** Estimated from the data of HART AND CASSIS[4].

Infrared spectra of the phenols are sufficiently selective to permit both qualitative and quantitative analysis[5,6] of the individual components. However, since impurities sometimes cause interference at the infrared analytical wavelengths, and since gas–liquid chromatography (G.L.C.) is usually more rapid, analysis by this procedure was investigated. This paper describes the results of the study.

* Paper read at the 8th National Analysis Instrumentation Symposium of the Instrument Society of America, April 30th–May 2nd 1962, in Charleston, W. Va., U.S.A.

SELECTION OF THE GAS–LIQUID COLUMN

The initial experiments with G.L.C. were encouraging but not entirely successful. When Silicone Oil 550 was used as the stationary liquid, the phenols (Table I) were separated in order of their increasing boiling points as shown by the chromatogram in Fig. 1. It was somewhat surprising that one pair of components, *o*- and *p-tert.*-butylphenol, was not resolved satisfactorily.

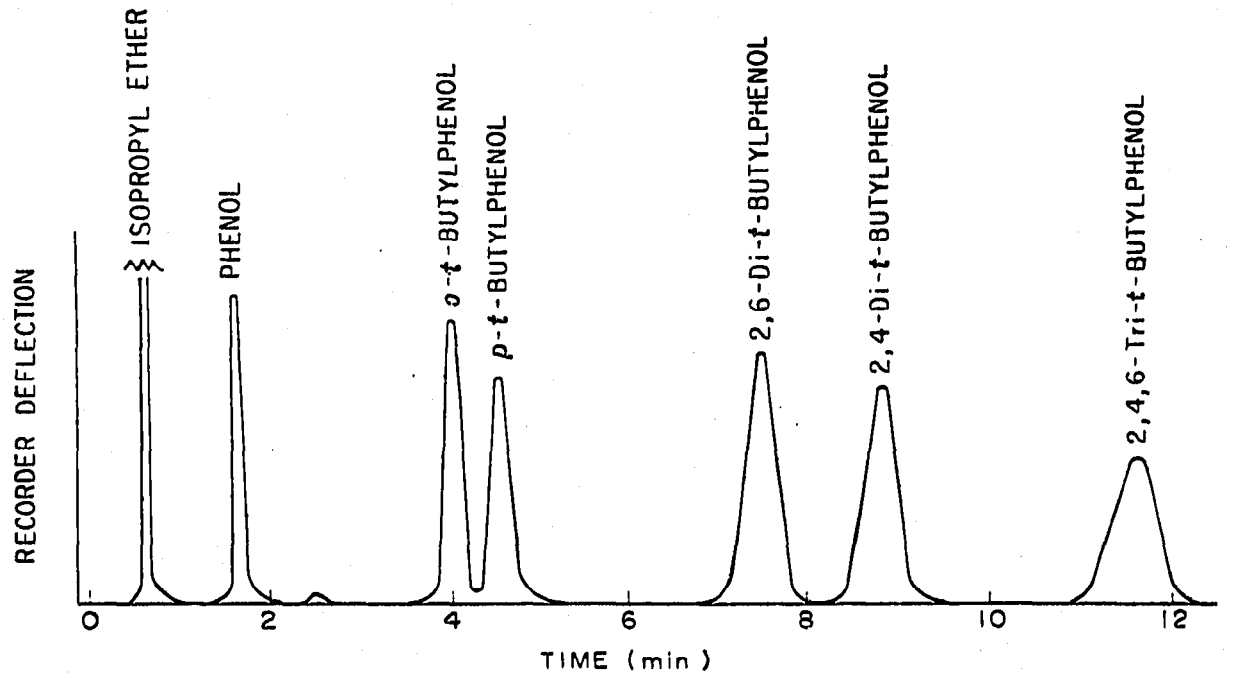

Fig. 1. Chromatogram of a synthetic blend of phenols on a 4 m Silicone Oil 550 column at 220°. Helium flow rate: 80 cm^3/min.

An attempt was made to increase the selectivity of the liquid phase by employing a more polar substance, Carbowax 4000. Again complete separation was not achieved, but unique properties were observed. Both of the completely hindered phenols, 2,6-di-*tert.*-butylphenol and 2,4,6-tri-*tert.*-butylphenol, emerged from the column simultaneously prior to phenol, even though its boiling point is much lower. Moreover, *o-tert.*-butylphenol was widely separated from *p-tert.*-butylphenol, although the latter was not completely resolved from 2,4-di-*tert.*-butylphenol.

These findings indicate the need for a two-stage column. McFADDEN[7] discussed the general case and demonstrated that the properties of a chromatographic column prepared from a mixture of two stationary liquid phases which do not interact chemically are equivalent to those of a two-stage column prepared in the same ratio. Therefore, in order to establish the ratio between Silicone and Carbowax to provide the optimum separation of *tert.*-butylphenols, columns prepared from several different mixtures of the two were examined. The total amount of liquid phase employed in each case was held constant.

Retention times for the *tert.*-butylphenols were measured relative to phenol for Silicone–Carbowax ratios between 5:1 and 1:2, that is between Carbowax concentrations in the liquid phase of 16.5 and 66.7 %, respectively. To facilitate the selection

of the particular stationary phase mixture, the data relative retention times *versus* Carbowax concentration in the stationary phase, were examined graphically as shown in Fig. 2. Unexpectedly, the data revealed not one but four mixtures that give maximum separation, each with a different order of emergence for the individual phenols. These stationary phases were located by determining the widest spacings between the lines representing retention times. The orders of emergence were

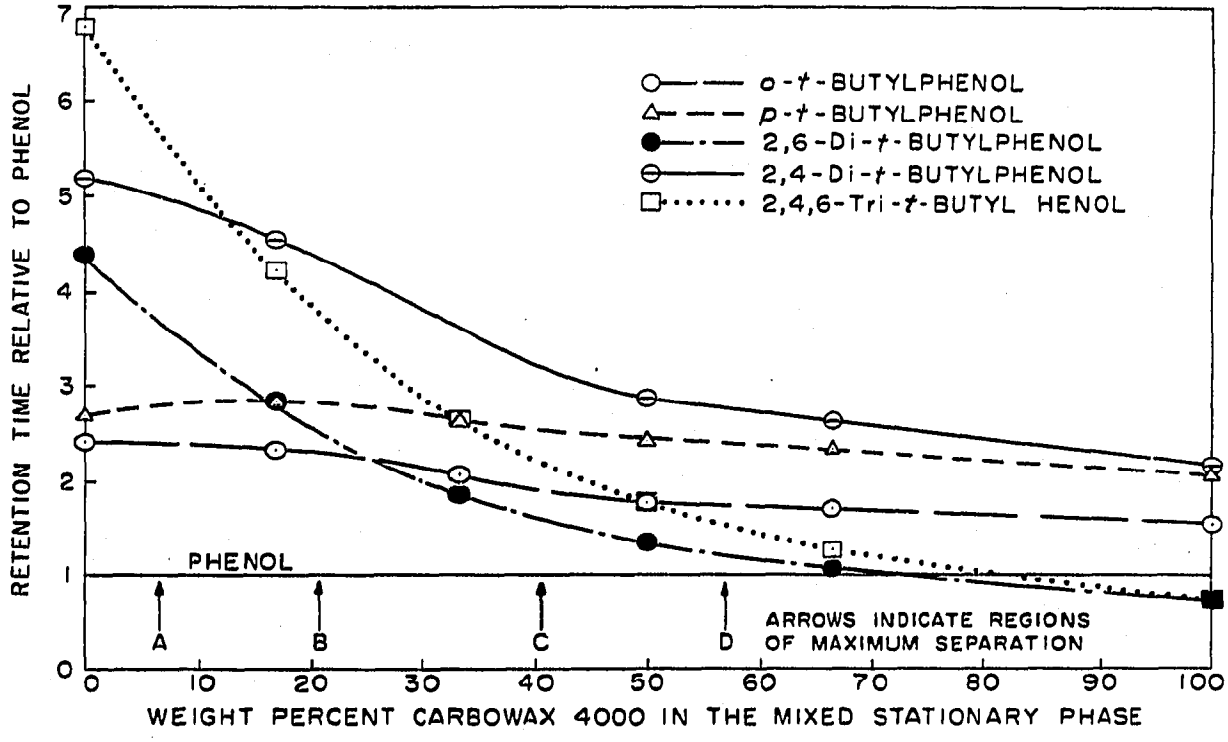

Fig. 2. Chromatography at 220° of phenol and *tert.*-butylphenols on 3 m mixed Silicone Oil 550 and Carbowax 4000 columns.

established by observing the order of the lines relative to that for phenol. The particular mixed liquid phases occur at Carbowax concentrations of 7.0, 21.5, 40.6 and 57.0 % and are indicated in Fig. 2 by the arrows labeled A, B, C, and D, respectively.

Columns were then prepared using these four selected ratios of liquid phases, and then tested in the same manner. The predicted different orders of emergence of the components were achieved as illustrated by the chromatograms shown in Fig. 3. Examination of these chromatograms shows that column C is clearly superior as regards separation ability so it was chosen as the analytical column.

ANALYSIS OF SYNTHETIC SAMPLES

The accuracy of the quantitative determination of the individual phenols by G.L.C. using column C was checked by analyzing two synthetic blends. One of the typical chromatograms appears as Fig. 4. The results, summarized in Table II, show a mean deviation of 0.4 % of the total and a maximum deviation of 1.0 %. It was necessary to employ relative area calibration factors with the blend having the high phenol content.

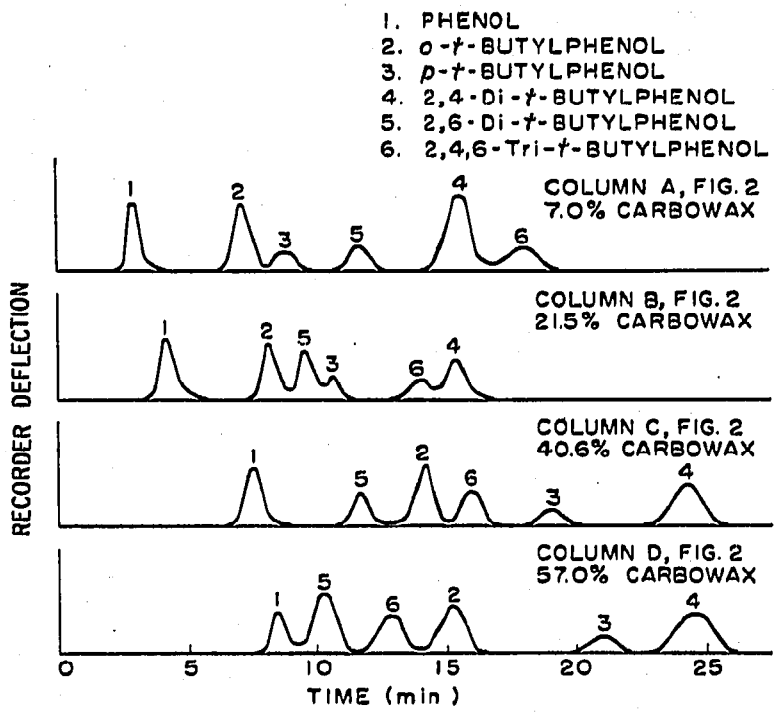

Fig. 3. Chromatography at 220° of *tert.*-butylphenols on selected 3 m columns containing Silicone Oil 550 and Carbowax 4000.

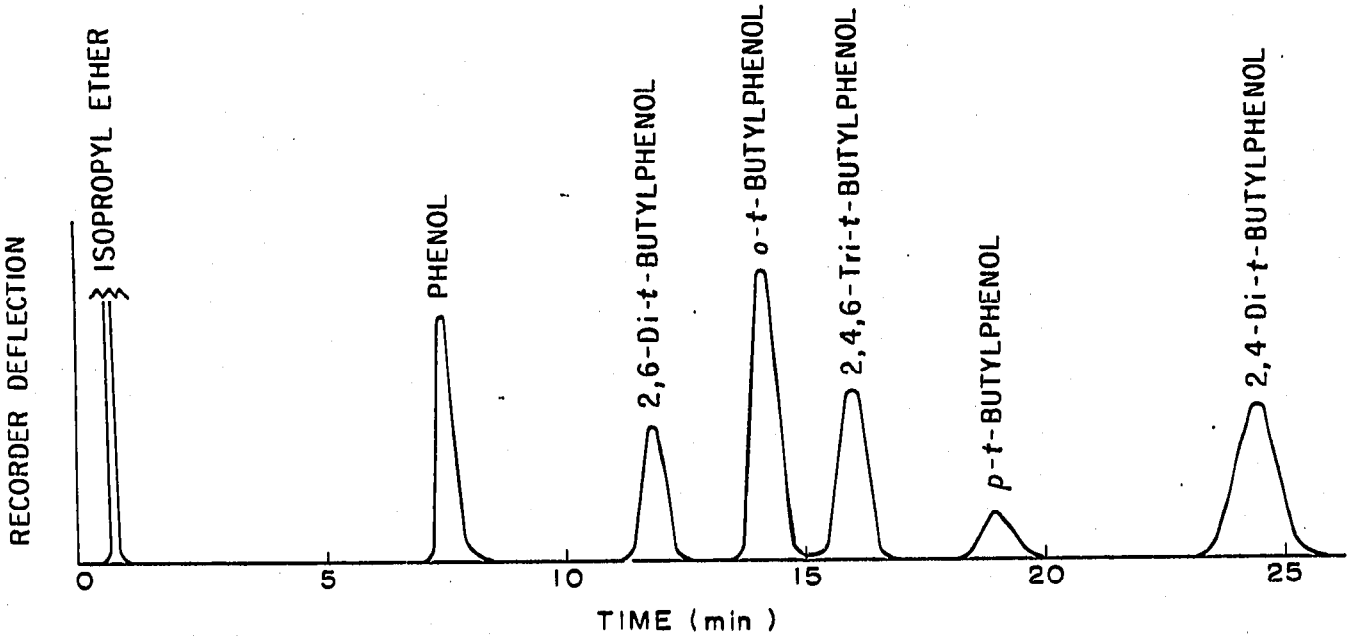

Fig. 4. Chromatogram of a synthetic blend of phenols on a 3 1/2 m column containing a 3:2 mixture of Silicone Oil 550 and Carbowax 4000 at 220°. Helium flow rate: 180 cm³/min.

TABLE II

DEVIATIONS IN ANALYSIS OF SYNTHETIC BLENDS OF PHENOL AND *tert.*-BUTYLPHENOLS

Compound	*Per cent by weight*									
	Weighed	Found*		Deviation		Weighed	Found**		Deviation	
		(1)	(2)	(1)	(2)		(1)	(2)	(1)	(2)
Phenol	4.8	5.6	5.8	+0.8	+1.0	43.2	43.0	43.4	—0.2	+0.2
o-tert.-Butylphenol	20.0	20.6	20.7	+0.6	+0.7	8.2	8.5	8.5	+0.3	+0.3
p-tert.-Butylphenol	2.4	2.4	2.4	0	0	39.3	39.8	39.5	+0.5	+0.2
2,4-Di-*tert.*-butylphenol	50.1	49.5	49.5	—0.6	—0.6	6.0	5.8	5.6	—0.2	—0.4
2,6-Di-*tert.*-butylphenol	8.6	8.2	8.5	—0.4	—0.1	1.9	1.6	1.7	—0.3	—0.2
2,4,6-Tri-*tert.*-butylphenol	14.1	13.7	13.1	—0.4	—1.0	1.4	1.3	1.3	—0.1	—0.1

* Equivalent to uncorrected area per cent.

** Corrected area %; factors employed: phenol 1.00; mono-*tert.*-butylphenols 1.20, di-*tert.*-butylphenols 1.29, tri-*tert.*-butylphenol 1.32; corrected area = measured peak area × factor.

APPLICATION OF THE PROCEDURE

On the basis of experience gained by application of the method to the analysis of process samples, an alternate procedure was devised. Isopropyl ether employed as a solvent as described in the experimental section was used as an internal standard. The accuracy obtained with this alternate procedure is somewhat poorer, but the amount of an individual phenol can be determined without regard to total area or the presence of uneluted higher boiling components in a sample.

Samples of individual phenols of 0.3 ml and 97–99% purity were isolated from a synthetic blend by using G.L.C. on a preparative scale. This experiment illustrates the feasibility of collecting chromatographic peaks from process samples. Infrared spectra of such isolated fractions would then reveal the presence of unexpected impurities being eluted along with a particular phenol.

During prolonged constant use of analytical column C, Silicone gradually bleeds away from the solid support. Finally, separation of the phenols is no longer satisfactory, and a fresh column must be prepared. Therefore, mixtures of Carbowax with various other stationary phases, for example, Silicone high vacuum grease or Apiezon wax, should be examined. Perhaps one of these will give a similar separation and at the same time a more stable column.

On the other hand, at temperatures below 200° column C is quite stable and has provided the means of analyzing many other complex mixtures. In addition, by employing matched columns to compensate for substrate bleeding, column C has been employed in temperature programmed operation up to 250°.

BEHAVIOR OF PHENOLS IN MIXED SILICONE–CARBOWAX GAS–LIQUID COLUMNS

It is interesting to speculate regarding the unique orders of emergence of the *tert.*-butylphenols from the mixed Silicone–Carbowax columns. When Carbowax alone is the stationary phase the order is remarkably different from that of the boiling point. This is in contrast to the behavior in Silicone where only simple solubility is involved. The difference can be explained on the basis that the strength of the interaction,

hydrogen bonding, between a phenol and Carbowax is greatly influenced by steric factors. Therefore, the retention time should depend primarily upon the number of substituents *ortho* to the phenolic hydroxyl group, rather than upon volatility. The behavior in mixed columns is more difficult to explain. For Carbowax concentrations greater than 50 % it is apparent that differences in the degree of hydrogen bonding is certainly the dominant factor. Below this concentration volatility gradually becomes of most importance. The completely hindered phenols exhibit the greatest change in retention time. These two compounds have high retention times in Silicone because of their low volatility (high boiling point) but low retention times in Carbowax due to the absence of hydrogen bonding. The mutual effect of these diverse properties in mixed columns causes their retention times to move between those of the other components. It is this phenomenon that results in different orders of emergence from mixed columns and provides the four mixtures giving different maximum separations.

EXPERIMENTAL

Apparatus and procedure

Analytical gas–liquid chromatography was performed using a Beckman Model GC-2 Gas Chromatograph operated at a temperature of 220°. The inlet pressure of the helium carrier gas was 55 p.s.i. and its rate of flow approximately 180 cm^3/min.

The column packings were prepared following the procedure described by JOHNS[8]. Seven parts of Chromosorb-W, 30 to 60 mesh, were coated with three parts of Silicone Oil 550, Carbowax 4000 or mixtures of the two. Stainless steel columns of 6 mm diameter and 3 m length were filled, then purged with carrier gas at 220° until a stable base line was achieved. Higher temperatures should be avoided with mixed packings, since the Silicone would be selectively eluted, changing column characteristics.

A phenol sample was dissolved in an equal quantity of isopropyl ether, then approximately 0.02 ml of the solution was introduced into the column with a hypodermic syringe. Ether was employed since it easily dissolves large quantities of solid phenols and aids in their vaporization. Therefore, it was also employed as an internal standard for determining relative calibration factors.

Preparative scale chromatography was accomplished using a revised Greenbrier Chroma-Lab instrument, Model 940. The injection block was rebuilt to provide for the rapid and complete vaporization of the larger sample. The column vent line between the detector and the fraction collection apparatus was equipped with a heater to prevent condensation of the materials being eluted from the column. Usually 300 g of packing were prepared as described above and filled into copper tubing of 13 mm inner diameter and 6 m length. A phenol sample was dissolved in ether then usually 2 ml of the solution was injected into the column. Fractions were trapped using ice water each time a peak indicated elution of a component from the column.

MATERIALS

The phenols employed in this study were purified by means of fractional distillation and recrystallization. Their purities were certified by comparison of melting points and infrared spectra with those of authentic samples.

Silicone 550 fluid is obtained from Dow Corning Corporation, Midland, Michigan (U.S.A.). Carbowax 4000 is a higher molecular weight polyethylene glycol available from Union Carbide Chemicals Company.

SUMMARY

Complete separation and quantitative analysis of mixtures of phenol and its five *ortho-* and *para-tert.*-butyl derivatives can be accomplished by gas–liquid chromatography. The column, three meters in length, contains a specially selected stationary phase that consists of three parts Silicone Oil 550 and two parts of Carbowax 4000. The particular amounts of Silicone and Carbowax are quite important, since changes in their ratio alter the retention times for the various phenols. This produces different orders of emergence for these phenols from particular mixed columns. Reasons for this occurrence are discussed. Analysis of synthetic samples shows the mean deviation of results to be 0.4% of the total with a maximum deviation of 1.0%.

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