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IDENTIFICATION AND DETERMINATION OF LOW-BOILING  
PHENOLS IN LOW TEMPERATURE COAL TAR

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ABSTRACT

Low-boiling phenols in a low temperature bituminous coal tar distillate have been identified and quantitatively determined by gas-liquid partition chromatography. These phenols were also determined by the conventional technique of fractional distillation, followed by infrared analysis. Comparison of the two independent techniques of GLPC and IR was made. Phenol, cresols, xylenols and ethylphenols were included in the analyses.

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As part of an extensive program on separating and characterizing components in tar resulting from low temperature carbonization of bituminous coal, it was desired to identify and determine quantitatively the low-boiling phenols in a certain tar distillate. Examination of the literature published within the last ten years showed that information on identification of phenols in low temperature tar mostly represents work done outside of the United States (3,6,7,8,9,10). The best conventional quantitative procedure involves fractional distillation of the mixture of phenols, followed by infrared analysis. This technique has been recently described by Fair and Friedrich (2), who, however, do not give any actual examples of analysis of coal-tar distillates. An example, using essentially the same technique, is provided by Jones and Neuworth (4).

To complement as well as check the results obtained by distillation and infrared analysis, a completely independent method of separation and analysis was chosen. This was a gas-liquid partition chromatographic technique for phenols which had been previously described (5).

EXPERIMENTAL

Isolation of Mixture of Low-Boiling Phenols. A distillate was obtained from a sample of low temperature (500°C.) bituminous coal tar, furnished by the Pittsburgh Consolidation Coal Company, Library, Pa., under very mild temperature conditions, so as to reduce structural alterations of tar components to a minimum. For this purpose, a rotary vacuum stripper was constructed.

The stripper consisted of a 12-liter-capacity, stainless-steel, spherical flask, which was rotated at about 6 r.p.m. in a 20-gallon-capacity oil bath. A mechanical vacuum pump with a free-air flow rate of 375 liters per minute was used to reduce the pressure, and oxygen-free nitrogen was employed to maintain an inert atmosphere in the system. An ionization vacuum gauge with a range of 1000 mm. to 1 micron was used for continuous pressure indication. The main distillate was recovered with a cold-water Friedrichs condenser. A small portion of distillate, representing components distillable at room temperature and about 133 microns pressure (equivalent to very approximately 215°C. at 1 atmosphere), was recovered with a trap cooled with a mixture of trichloroethylene and solidified carbon dioxide. A similar trap was used to protect the sensing head of the ionization gauge. In operation, the bulk of the distillation takes place from the fresh film of hot tar, which is continually drawn up the wall at one side of the flask owing to the slow rotary motion. At about 125°C. and 133 microns about 21 weight-percent of the tar was distillable.

A Claisen alkali extraction was performed on the cold-trap portion of the distillate, following the procedure described by Woolfolk et al. (12). From this extraction the tar-acid content of the low-boiling distillate appeared to be about 20 volume-percent. This cold-trap material did not necessarily represent complete recovery of any of its components from the tar. It was, however, considered to be a good mixture for evaluation of a vapor-phase chromatographic technique because of its high volatility and relatively simple composition.

Distillation of Low-Boiling Phenols. A 37.25-g. portion of the low-boiling mixture of phenols isolated from the tar was fractionated in a Piro-Glover micro-spinning-band vacuum still. All air was flushed out of the still with oxygen-free dry nitrogen before the distillation was started. The still was operated at a head pressure of 50 mm. Hg, which very nearly represents the pot pressure, since the pressure drop in the spinning-band column is almost negligible. The boilup rate was approximately 30 to 40 ml. per hour, and the reflux ratio was 10 to 1. The speed of the band was fixed at 1800 r.p.m. Seven fractions were isolated, with a recovery of 96.2 weight-percent. All fractions were initially colorless, but fraction 7 developed a slight color on standing two days. The results of this distillation are shown in Table I and Figure 1. The temperature readings in Figure 1 are for an iron-constantan thermocouple in the still head as recorded on a 10-millivolt, 5-inch-span recorder, the cold junction being at room temperature, which was essentially constant. The weights of each component in each fraction were determined by conventional infrared spectrophotometry, using the following analytical wave lengths, in microns:

Compound	Fraction						
	1	2	3	4	5	6	7
Phenol	14.55	14.55					
o-Cresol	11.86	11.86	13.35				
2,6-Xylenol			11.02				
p-Cresol				12.24			
m-Cresol			14.57	14.57			
o-Ethylphenol				13.34	13.34	13.34	
2,4-Xylenol				12.47	10.27	12.27	
2,5-Xylenol					10.03	10.03	
2,3-Xylenol					11.11	14.17	
p-Ethylphenol						12.07	
m-Ethylphenol						11.04	
3,5-Xylenol						9.73	14.64, 10.56
3,4-Xylenol							12.33, 12.53

Gas-Liquid Partition Chromatography of Low-Boiling Phenols. The low-boiling mixture of phenols obtained from the tar was fractionated in a vapor phase chromatographic apparatus. A 12-foot column of  $\frac{1}{8}$ -inch tubing packed with Johns-Manville C-22 firebrick, 30-60 mesh, containing 31 weight-percent di-n-octyl phthalate was used at 160°C., with a carrier gas flow rate of 150 cc. helium per minute (15 psig. inlet, outlet at 1 atm.), and a 250 microliter sample. The efficiency of this column was determined using a charge of o-cresol and the equation given by Wiebe (11):

$$p \approx 2 \left( \frac{V_m}{V_m - V_e} \right)^2 \quad (1)$$

where  $p$  = number of theoretical plates.

$V_m$  = volume of effluent that has passed through the column when the zone maximum appears in the effluent.

$V_e$  = volume of effluent that has passed through the column when a point on the elution curve has been reached where the solute concentration is 1/eth of the maximum.

A value of 966 theoretical plates was obtained.

Table I

Fractionation of Low-Boiling Phenol Distillate in Spinning-Band Still

Fraction No.	Weight, Grams	Refractive Index, $n_D^{20}$	Components by Infrared Analysis		
			Major	Minor	Trace
1	8.00	1.5243	Phenol, 5.2 g.	o-Cresol, 2.8 g.	
2	7.84	1.5224	o-Cresol, 4.8 g.	Phenol, 3.0 g.	2,6-Xylenol, 0.8 g.*
3	7.88	1.5190	m-Cresol, 3.4 g.	p-Cresol, 2.3 g.	
4	3.39	1.5180	m-Cresol, 1.35 g.	o-Cresol, 1.4 g.	o-Ethylphenol, 0.15 g.
5	3.07	1.5173	2,4-Xylenol, 1.3 g.	p-Cresol, 0.6 g.	2,3-Xylenol, 0.12 g.
6	4.76	1.5150	2,4-Xylenol, 2.1 g.	2,5-Xylenol, 0.74 g.	o-Ethylphenol, 0.1 g.*
7	0.90	1.5152	2,4-Xylenol, 1.5 g.	3,5-Xylenol, 0.9 g.	2,3-Xylenol, 0.3 g.*
			3,4-Xylenol, 0.3 g.*	p-Ethylphenol, 0.8 g.	o-Ethylphenol, 0.1 g.*
			3,5-Xylenol, 0.3 g.*	m-Ethylphenol, 0.6 g.	c-Ethylphenol, 0.1 g.*
				2,5-Xylenol, 0.6 g.	
				m-Ethylphenol	
				2,3-Xylenol	
				2,3,5-Trimethylphenol	

\* Estimated quantities.

The results of fractionating the tar phenols are shown in Figure 2. As can be seen, there are eight obvious concentration maxima. Traps consisting of a short length of 12-mm. I. D. glass tubing fitted with a rubber serum bottle cap and syringe needle were filled with about 1 ml. of spectro-grade cyclohexane and used in an attempt to isolate the components producing the major peaks in the elution curve. Infrared analysis of the solutions corresponding to peaks 1 and 2 showed beyond any doubt that the compounds responsible for these peaks were phenol and o-cresol, respectively. However, contamination of subsequent solutions with residual phenol and o-cresol in the collection system made positive identification of the components responsible for other peaks impossible. Further identification was made possible by comparing the relative retention times of the various peaks with the relative retention times of individual pure low-boiling phenols under identical operating conditions. This comparison is presented in Table II; in addition, the retention times of the individual pure phenols are indicated in the lower portion of Figure 2.

Table II

Comparison of Experimental Relative Retention Times with Times for Individual Phenols

Peak No.	Relative Retention Time to Peak 2 (o-Cresol)	Compound	Relative Retention Time (Compared to o-Cresol)
1	0.75	Phenol	0.79
2	(1.00)	o-Cresol	(1.00)
3	1.13	2,6-Xylenol	1.12
4	1.31	m-Cresol	1.29
		p-Cresol	
5	1.53	o-Ethylphenol	1.53
6	1.67	2,5-Xylenol	1.66
		2,4-Xylenol	1.70
7	2.01	2,3-Xylenol	1.98
		p-Ethylphenol	2.02
8	2.16	3,5-Xylenol	2.08
9	2.42	3,4-Xylenol	2.47

The areas under each of the peaks in Figure 2 were obtained by means of a planimeter and the weight-percentages of phenols were calculated from these areas and the total area. For this calculation it is assumed that the thermal conductivities of the components are about the same, being homologs, and that therefore, areas under the recorded curves are directly proportional to the weight percent of the components (1). These values are given in Table III, which also includes the weight percents calculated from the infrared data given in Table I.

Table III

Comparison of Infrared and Vapor-Phase Chromatographic Analysis of Low-Boiling Mixture of Phenols

Compound	Weight-Percent by IR	Weight Percent by VPC
Phenol	22.5	21
o-Cresol	25	26
m-Cresol	13	} 26
p-Cresol	8	
2,4-Xylenol	13	} 13
2,5-Xylenol	3.5	
2,6-Xylenol	> 2	5
3,5-Xylenol	3	3
o-Ethylphenol	~1	2
m-Ethylphenol	1.5	} 3
p-Ethylphenol	2	
2,3-Xylenol	1	
3,4-Xylenol	~0.8	< 1
	~96	~99

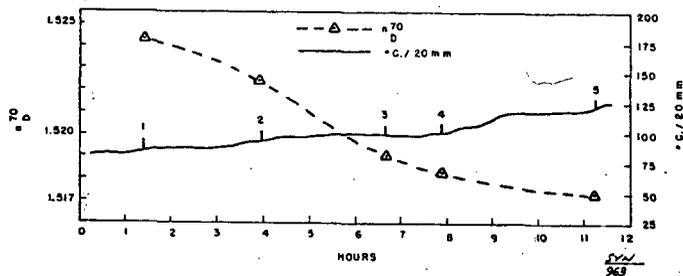


Figure 1. Fractionation of low-boiling phenol distillate in spinning band still.

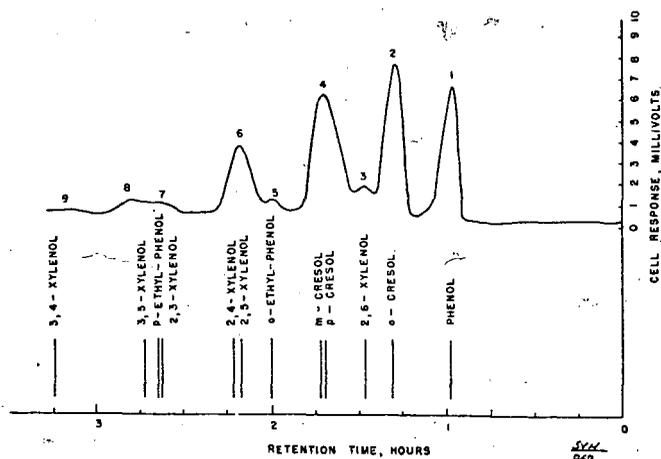


Figure 2. Vapor phase chromatography of low-boiling mixture of phenols and retention times of individual pure phenols.

## DISCUSSION

Figure 2 demonstrates that by means of gas-liquid partition chromatography alone a low-boiling mixture of phenols with as many as a dozen components can be fairly well characterized, both qualitatively and quantitatively. There can be no question about the identity of a component for those retention times for which calibrations have been made on all theoretically possible phenols and where the peaks for individual phenols are essentially isolated in time. Examples of this would be peaks 1, 2, 3, and 5. In addition, the quantitative analysis is always obtainable with acceptable accuracy from the areas under these peaks. In fact, the vapor-phase chromatographic analysis is undoubtedly much less subject to qualitative and quantitative errors, being such a simple and direct technique. However, it is limited in scope by the difficulty of resolving certain phenols which have very similar partition coefficients.

As can be seen in Table III the agreement between weight-percentages of phenols by infrared analysis and vapor-phase chromatographic analysis is fairly good. In the case of two compounds, 2,6-xyleneol and o-ethylphenol, only an estimate of the quantity could be made by IR analysis, whereas in the VPC analysis these two compounds gave two distinct peaks whose areas could be obtained with fair accuracy. The extent of fractionation of higher boiling phenols will be described in a future paper.

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