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## Note

### Separation and identification of phenols in kerosene using silylation and gas chromatography

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The separation of phenols by gas chromatography is made difficult by their high polarity and special care has to be taken in the choice of the stationary phase. Isomers with nearly identical polarities and vapour pressures, such as 3- and 4-methylphenol and 2,4- and 2,5-dimethylphenol, are difficult to separate. These problems have been discussed in previous papers<sup>1-9</sup>.

Derivatization of a phenol into an ester or an ether reduces its high polarity and increases the number of useful stationary phases. Methyl ethers<sup>10,11</sup>, acetates and trifluoroacetates<sup>10,12</sup> and O-isobutyloxycarbonyl derivatives<sup>13</sup> have been used to improve the separation of alkylphenol isomers.

Another and often more successful method is to prepare the trimethylsilyl (TMS) ethers of the phenols<sup>14-18</sup>. The conversion of phenols into their TMS derivatives is rapid and, for the most of the procedures, quantitative.

Souter and Bishara<sup>15</sup> used a SCOT column coated with OV-17 to separate the three isomeric ethylphenols for quantitative analysis. In this investigation, we tried to use SCOT columns to separate and quantify other alkylphenol isomers. We examined an Arabian kerosene and a caustic extract of kerosene fractions from an industrial refining process, for which it was of interest to use the same gas chromatographic equipment which is used in the routine analysis of crude oil fractions (*i.e.*, a non-polar stationary phase such as SE-30).

Silylation of the phenols was used to decrease their high polarity.

## EXPERIMENTAL

### TMS reagent

Bis(trimethylsilyl)trifluoroacetamide was obtained from E. Merck (Darmstadt, G.F.R.).

### Gas chromatography

The gas chromatograph used was a Hewlett-Packard Model 5720A equipped with a hydrogen flame-ionization detector (FID). The column was a 30 m × 0.5 mm I.D. commercial SCOT column coated with SE-30 (from SGE, North Melbourne, Australia). The gas flow-rates were as follows: carrier gas (helium) 2, hydrogen 15 and air 215 ml/min. The injector temperature was 250° and the detector temperature 300°.

*Recovery of the naphthenic acids and phenols from the caustic kerosene extract*

A 100-ml volume of the caustic solution was extracted once with 10 ml of pentane to remove hydrocarbons. After addition of concentrated hydrochloric acid to adjust the pH to 6, a 5% solution of sodium hydrogen carbonate was added until the solution was alkaline (to litmus paper) and any precipitate completely had redissolved. The clear solution was extracted three times with diethyl ether and the ethereal layer containing the phenols was washed with distilled water and dried overnight with sodium sulphate. The aqueous layer was acidified until the effervescence of carbon dioxide ceased and the acids released were extracted three times with diethyl ether, washed with distilled water and dried overnight with sodium sulphate.

After removal of the sodium sulphate and diethyl ether, the fractions were treated on a water-bath (90–100°) for about 30 min.

*Recovery of the phenols from kerosene*

A 600-ml volume of the sample were extracted four times with 150 ml of a 2.5% solution of sodium hydroxide previously heated to about 70°. The caustic extract was further treated as previously described.

*TMS ethers*

Two or three drops of bis(trimethylsilyl)trifluoroacetamide were added to one drop of the phenol extract and the mixture was heated on a water-bath at 70° for 30 min. After cooling, the TMS ethers were extracted with 1 ml of diethyl ether and washed with 0.5 ml of distilled water.

RESULTS AND DISCUSSION

Fifteen alkylphenols were chromatographed to investigate their separation and to determine their retention times relative to that of phenol. Table I shows the

TABLE I

ADJUSTED RETENTION TIMES OF ALKYLPHENOLS AND THEIR TMS DERIVATIVES ON A 30 m × 0.5 mm I.D. SCOT COLUMN COATED WITH SE-30

Phenol	Untreated, 150°	TMS ether	
		150°	130°
Phenol	1.00	1.00	1.00
2-Methyl-	1.55	1.54	1.64
3-Methyl-	1.78	1.62	1.73
4-Methyl-	1.78	1.75	1.85
2-Ethyl-	2.31	2.29	2.51
2,5-Dimethyl-	2.55	2.44	2.67
3,5-Dimethyl-	3.05	2.52	2.87
3-Ethyl-	2.85	2.53	2.89
2,4-Dimethyl-	2.55	2.58	2.93
4-Ethyl-	—	2.69	3.03
2,6-Dimethyl-	2.05	2.78	3.11
2,3-Dimethyl-	3.29	2.98	3.34
2,4,6-Trimethyl-	3.50	4.55	5.40
2,3,6-Trimethyl-	4.10	—	—
2,3,5-Trimethyl-	4.98	—	—

retention times for both the untreated alkylphenols and their TMS derivatives, indicating that each of the isomeric pairs 3- and 4-methylphenol and 2,4- and 2,5-dimethylphenol is eluted as a single component when untreated, but their TMS ethers are well separated. The three monomethylphenols are baseline separated at a column temperature of 130° (Fig. 1). 3,5-Dimethyl- and 3-ethylphenol however, are well separated when untreated, but their TMS derivatives are poorly or not separated.

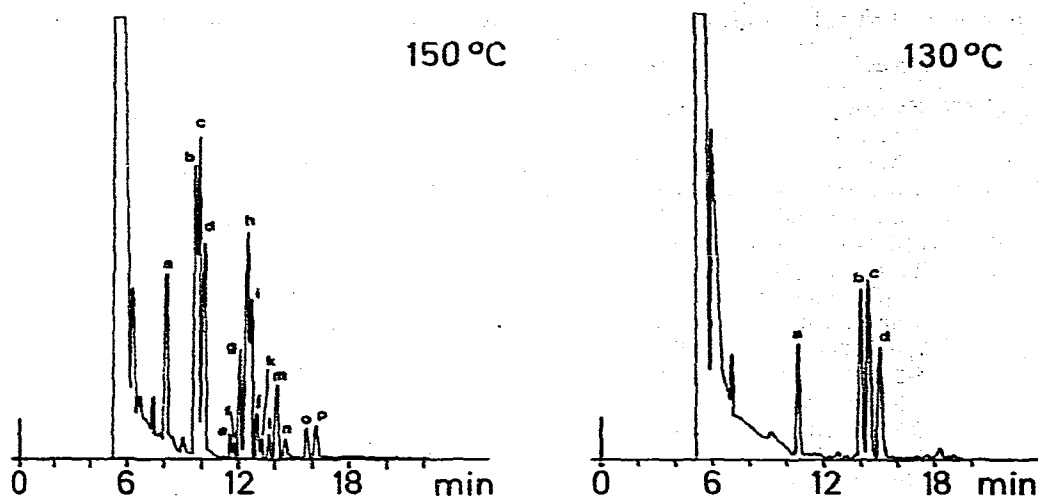


Fig. 1. Gas chromatogram of TMS ethers of alkylphenols found in a kerosene refining process extract. The chromatogram at 130° shows the baseline separation of (b) 2-methylphenol, (c) 3-methylphenol and (d) 4-methylphenol. The other identified components are listed in Table III.

An experimental mixture of five alkylphenols of known composition was prepared and added to a kerosene sample from which the phenols had previously been removed. The added phenols were extracted with sodium hydroxide solution, converted into their TMS derivatives and chromatographed. The results are given in Table II.

The phenols were also extracted from two portions of an Arabian kerosene,

TABLE II

RELATIVE AMOUNTS OF ADDED PHENOLS (GIVEN AS % BY WEIGHT) EXTRACTED FROM A KEROSENE SAMPLE FROM WHICH THE PHENOLS HAD PREVIOUSLY BEEN REMOVED

Phenol	Added	Recovered
Phenol	21.6	22.0
2-Methyl-	9.2	10.0
3,5-Dimethyl-	34.4	33.1
2,4-Dimethyl-	18.9	18.9
2,4,6-Trimethyl-	15.9	16.0

to one of which 2,4,6-trimethylphenol was added as an internal standard. The total amount of phenols was determined to be 0.03% (w/w), and their relative amounts are given in Table III together with those of the phenols from the refining process extract. Area correction factors for the FID were ignored.

TABLE III

## RELATIVE AMOUNTS (% BY WEIGHT) OF ALKYLPHENOLS FOUND IN AN ARABIAN KEROSENE AND A KEROSENE REFINING EXTRACT

The letters in the first column indicate the components in the gas chromatogram (Fig. 1).

<i>Component</i>	<i>Phenol</i>	<i>Refining extract</i>	<i>Arabian kerosene</i>
a	Phenol	9.2	12.5
b	2-Methyl-	16.6	2.3
c	3-Methyl-	17.9	2.0
d	4-Methyl-	11.1	1.6
e	Unidentified-	1.2	3.5
f	2-Ethyl-	0.6	2.3
g	2,5-Dimethyl-	6.4	8.2
h	3,5-Dimethyl- and 3-ethyl-	13.0	23.0
i	2,4-Dimethyl-	9.0	8.2
j	4-Ethyl-	2.6	1.2
k	2,6-Dimethyl-	1.1	11.3
l	2,3-Dimethyl-	1.8	3.1
m	Unidentified	4.6	2.3
n	Unidentified	1.2	1.2
o	Unidentified	1.9	1.2
p	Unidentified	1.8	3.9
—	Unidentified	—	2.7
—	Unidentified	—	5.8
—	2,4,6-Trimethyl-	—	3.7

None of the trimethylphenols was found in the refining process extract and only 2,4,6-trimethylphenol was detected in the Arabian kerosene.

For 3,4-dimethylphenol the retention time is not known, but it seems reasonable to expect this phenol to be eluted between 2,3-dimethyl- and 2,4,6-trimethylphenol<sup>17</sup>, and it may be one of the unidentified components indicated in Table III. The unidentified components in the gas chromatogram may be naphthenic acids or unreacted phenols.

TABLE IV

## NAPHTHENIC ACIDS AND PHENOLS RECOVERED FROM THE REFINING PROCESS EXTRACT OF KEROSENE (% v/v)

<i>No.</i>	<i>Phenols</i>	<i>Acids</i>
1	18.0	10.5
2	17.0	11.0
3	18.0	10.5
Average	17.6	10.6

Amounts of naphthenic acids and phenols recovered from the refining process extract of kerosene are given in Table IV. The ratio of phenols to acids is about 1.7 (v/v).

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