

an analytical method which could be used for all of them, a typical wood rosin sample and a typical gum rosin sample were examined. It was found that wood rosin consisted of 96.1% of resin acid monomer, 1.2% resin acid dimer and about 3% of other components. Gum rosin consists of 91.0% of resin acid, 2.9% resin acid dimer and a very high concentration, 6.1% of other components. These preliminary studies indicate GPC to be a promising technique for resin acid analysis.

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## Gas Chromatographic Estimation of Individual Xylene Isomers in Straight-run Naphtha Cuts

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SEPARATION of the xylene isomers by gas chromatography using both capillary and packed columns has been the subject of numerous publications (1-9). Among the packed-column separations, the best results have been obtained with a modified Bentone-34 column (9) [bentonite clay of formula  $\text{Al}_2\text{O}_3(\text{SiO}_2)_4\text{H}_2\text{O}$ , reacted with dimethyldioctadecylammonium ion]. The Bentone column, though quite suitable for separation of  $\text{C}_8$  isomers in wholly aromatic mixtures, has limited selectivity for separating the aromatics from the corresponding saturates which have about the same boiling points, and therefore, it cannot be used for estimating the aromatics in petroleum fractions and other similar samples. Also, this column gives a poor separation of *o*-xylene from isopropyl benzene. The present study concerns the estimation of the individual xylene isomers in straight-run naphtha cuts boiling up to 150° C in the presence of all the usual saturates.

The separation is achieved by studying the behavior of several combinations of a Bentone column with various other columns to determine the conditions which are suitable for satisfactory resolution of the following three pairs of compounds:

***n*-Nonane and Ethyl Benzene.** *n*-Nonane (bp 150.8° C) has been assumed to be the typical paraffin in the xylene range, and its separation from the lowest boiling  $\text{C}_8$  aromatic, ethyl benzene (bp 136.2° C), was taken to represent the separation of the saturates from the aromatics. Because of nonavailability of branched and cycloparaffins of the xylene range, their actual separations from ethyl benzene could not be studied, but care was taken to ensure that the *n*-nonane-ethyl

benzene separation was sufficient to avoid interference with the ethyl benzene peak by any cycloparaffin, with a boiling point of about 150° C, whose retention time would be between that of *n*-nonane and ethyl benzene on the selective column combination used.

***p* and *m*-Xylene.** This is the most difficult pair to separate. A good separation of the *p*- and *m*-xylene pair normally implies a good separation of ethyl benzene from the next higher boiling isomer, *p*-xylene (bp 138.4° C), with the exception of the existence of very severe conditions when the boiling point elution order for the  $\text{C}_8$  aromatics is completely upset. The separation of *o*-xylene (bp 144.4° C) from the *p*- or *m*-isomer does not pose any problem on any of the stationary phases because of the large difference in boiling points.

***o*-Xylene and Isopropyl Benzene.** This pair is considered because of the tendency of the isopropyl benzene peak to interfere with that of the *o*-xylene on Bentone column and on most of the polar stationary phases. This difficulty may not arise for well fractionated cuts, because isopropyl benzene is well separated from *o*-xylene (bp 152.4° and 144.4° C, respectively). In actual practice, however, the presence of small amounts of  $\text{C}_9$  aromatics cannot be completely eliminated in xylene cuts from naphtha fractions. Other  $\text{C}_9$  aromatics are unlikely to interfere with any of the xylenes.

The separation of saturates from the aromatics with the same boiling point (first pair) can easily be achieved on a polar stationary phase, whereas for the 2nd pair, a modified Bentone column (9) is perhaps the most promising. Therefore, a suitable combination of the Bentone column with a polar one is likely to give the desired separation. But such a combination may not give any separation of the 3rd pair at all, because on many polar phases, the elution order of these two compounds is the reverse of that on Bentone. The behavior of the individual column combination, therefore, is studied and its selectivity properly adjusted to achieve a good separation of the 3rd pair without seriously impairing the other two separations.

#### EXPERIMENTAL

**Apparatus.** A Jobin-Yvon gas chromatograph equipped with a flame ionization detector system and a 2.5-mV Sefram

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Recorder was used for the present study. All columns were prepared from 1/8-inch copper tubing and joined together with suitable connectors in order to have very little dead space. The stationary phase shown as Bentone in Table I and in the discussion was in fact a mixture of 5% Bentone-34 and 5% dinonyl phthalate on 80/100 Chromosorb W, and was supplied by Wilkens Instruments and Research, Inc., U. S. A.

**Procedure.** The various stationary phases, whose concentrations were 10% in all cases, were prepared in the laboratory in the usual manner, using 60/80 Chromosorb P as the support. The method of packing the column, temperature, gas flow rate, etc., were kept as constant as possible. The study was first carried out with synthetic mixtures. Using the optimum conditions thereof, several typical cuts in the boiling range 45°–150° C were analyzed.

## RESULTS AND DISCUSSION

The relative separations of the three pairs on 4 typical polar phases  $\beta\beta'$ -oxydipropionitrile, 1,2,3-tris (2-cyanoethoxy) propane, Carbowax-1500, and UCON-Polar (50 HB-5100 supplied by Wilkens Instruments & Research, Inc.); one phase of intermediate polarity Tricresylphosphate; and two nonpolar phases, Apiezon "L" grease and Squalane, are shown in Figure 1. The relative retention times with respect to *p*-xylene for the 6 compounds are plotted on the various phases *vis-a-vis* those on Bentone, and the two points so obtained for one compound are joined by a straight line to get an idea as to how the different combinations of the two would behave. No intermediate points, however, were actually plotted.

As expected, no relative separation of the saturates from the aromatics occur on the two nonpolar phases, but separation is excellent on the two very polar phases,  $\beta\beta'$ -oxydipropionitrile and 1,2,3-tris(2-cyanoethoxy)propane, fairly good on Carbowax, and tolerable on UCON-polar and tricresyl phosphate.

The separation of ethyl benzene from *p*-xylene is of the same order in all cases, though it is somewhat better on the less polar phases. The *p*- and *m*-xylene pair fails to show any separation on any of the phases except Bentone.

The variation in the separation of the *o*-xylene from isopropyl benzene is rather great, and even the order is reversed. On Bentone and the two nonpolar phases, isopropyl benzene is eluted after *o*-xylene in accordance with its higher boiling point. The same order is maintained on tricresyl phosphate. On Carbowax and Uconpolar, the two peaks coincide. The elution order is reversed on 1,2,3-tris(2-cyanoethoxy)propane and  $\beta\beta'$ -oxydipropionitrile.

The behavior of the various polar phases is different for different separations, and one combination or another of the stationary phases will be preferable depending upon which pair-separation is desired. For a good overall separation of all three pairs, however, a combination of Bentone and tricresyl phosphate proved to be the best among the phases tried. From Figure 1, it follows that the proportion to which Bentone should be modified to achieve an overall good separation should be slight, particularly to maintain a reasonably good separation of the *p*- and *m*-xylene pair.

Actual combinations of 5-meter columns of Bentone and the 7 stationary phases (coating 10%, length 1 meter) were then tried under identical conditions, and the results obtained are summarized in Table I. The separation achieved in the various cases is expressed in terms of peak resolution,  $R_{12}$  and the peak spreading is expressed by the number of theoretical plates,  $N$ , defined as

**Table I. Separations Obtained on Various Column Combinations**

Column combination	Col length: Bentone-5m, others-1 m: quantity injected: 2 $\mu$ l; temp. 80° C: carrier gas: H <sub>2</sub> ; flow rate: 40 ml/min									
	<i>n</i> -Nonane-ethyl benzene				<i>p</i> and <i>m</i> -Xylene				<i>o</i> -Xylene-isopropyl benzene	
	Retention time, min		Retention time, min		Retention time, min		Retention time, min			
	<i>n</i> -Nonane ( <i>t</i> <sub>1</sub> )	Ethyl benzene ( <i>t</i> <sub>2</sub> )	<i>N</i> <sup>b</sup> <i>R</i> <sub>1,2</sub> <sup>a</sup> pair	<i>N</i> <sup>b</sup> ethyl benzene	<i>p</i> -Xylene ( <i>t</i> ' <sub>1</sub> )	<i>m</i> -Xylene ( <i>t</i> ' <sub>2</sub> )	<i>N</i> <sup>b</sup> <i>m</i> -xylene	<i>o</i> -Xylene ( <i>t</i> <sub>1</sub> '')	Isopropyl benzene ( <i>t</i> <sub>2</sub> '')	<i>N</i> <sup>b</sup> isopropyl benzene
Bentone	30.4	38.7	3.12	2927	42.9	47.9	1.52	55.4	58.3	<i>c</i>
Bentone-ββ'-oxydipropionitrile	28.7	41.7	5.17	3565	45.8	50.8	1.48	60.0	60.0	<i>c</i>
Bentone-1,2,3-tris(2-cyano-ethoxy)propane	26.7	39.2	5.66	3927	42.9	47.1	1.38	56.2	56.2	<i>c</i>
Bentone-Carbowax	37.9	53.3	5.00	4096	58.7	64.6	1.47	77.5	80.4	<i>c</i>
Bentone-UCON polar	36.7	52.1	5.40	3906	57.1	62.5	1.33	73.3	78.3	<i>c</i>
Bentone-tricresylphosphate	35.0	49.6	4.73	3856	54.2	59.6	1.36	70.0	75.4	1.24
Bentone-Apiezon L grease	53.3	55.8	<i>c</i>	<i>c</i>	62.9	67.5	<i>c</i>	79.6	85.8	1.29
Bentone-Squalane	46.7	46.7	<i>c</i>	<i>c</i>	51.2	55.0	<i>c</i>	63.3	70.0	1.64

$$^a R_{1,2} = (\text{Peak resolution for the pair}) = 2 \frac{t_2 - t_1}{w_2 + w_1}.$$

$bN = (\text{No. of theoretical plates for } t_2, t_2', \text{ and } t_2'')^2 \left( \frac{t_2}{w_2} \right)^2$  where  $w$  denotes the peak width at the base. See definitions under "Discussion".

\* Calculations not possible because of poor resolution of peaks.

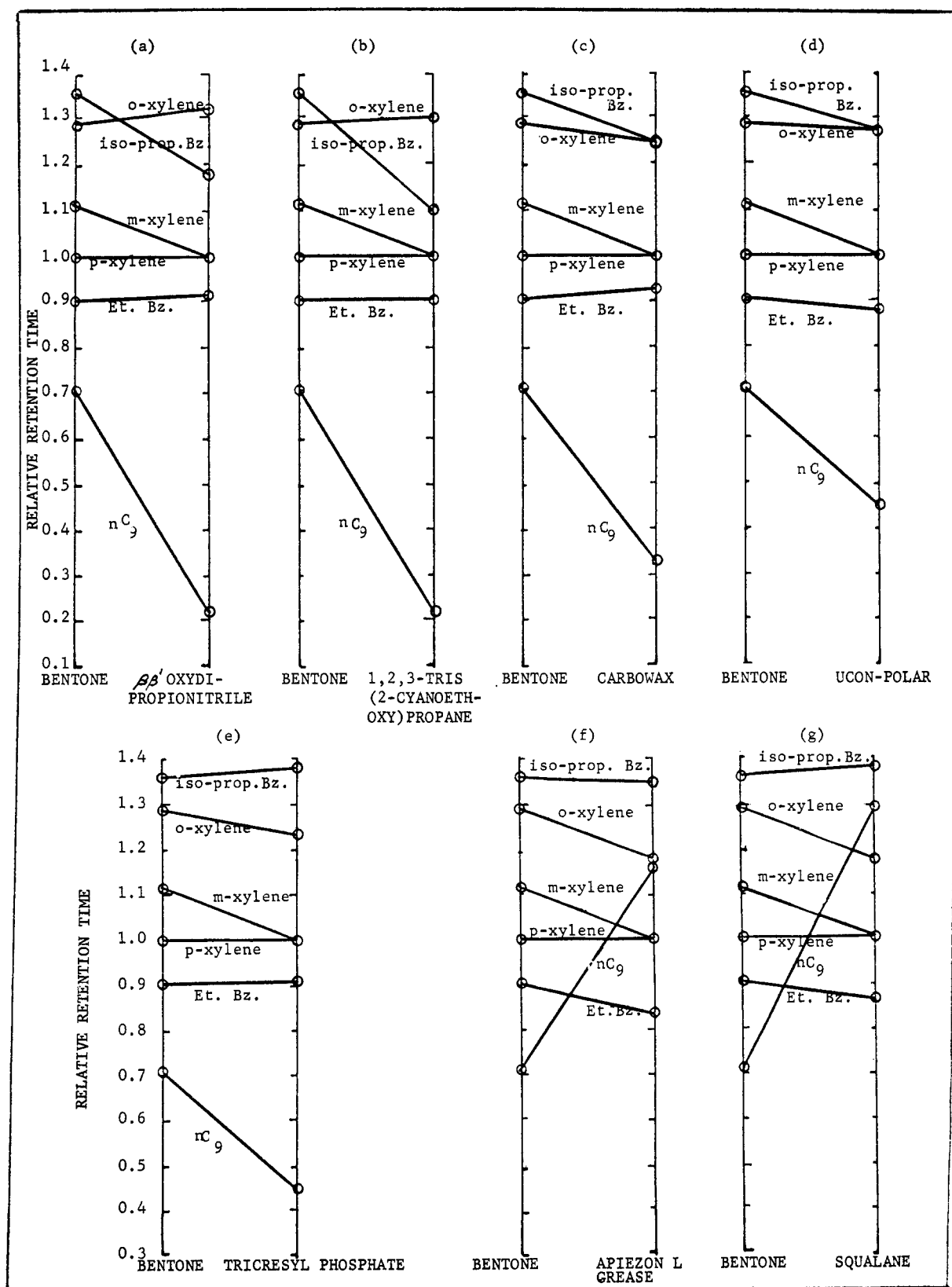


Figure 1. Relative retention times (relative to *p*-xylene) on various stationary phases at 80°C

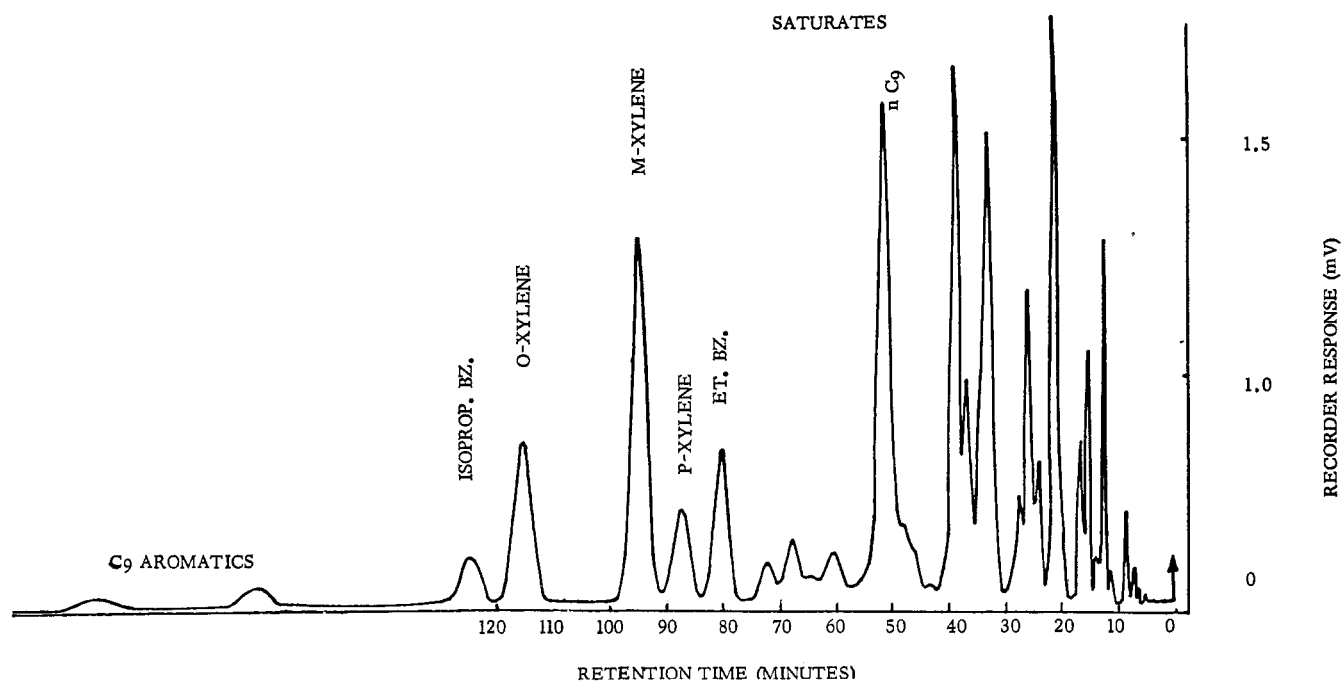


Figure 2. Typical chromatogram of a straight-run naphtha cut

Column: 5% bentone 34 + 5% dinonyl phthalate (5 meters) + 15% tricresylphosphate (1 meter); diameter  $\frac{1}{8}$  inch; col temp; 72° C; detector: F.I.D.; sample: 2  $\mu$ l Lakwa-naphtha cut (130°–150° C); carrier gas: H<sub>2</sub>; inlet pressure: 1.6 kg/cm<sup>2</sup>; flow rate: 40 ml/min

$$R_{12} = 2 \frac{t_2 - t_1}{w_1 + w_2} \quad (1)$$

and

$$N_1 = 16 \left( \frac{t_1}{w_1} \right)^2 \quad (2)$$

where  $t_1$  and  $t_2$  are the retention times of the first and second peak, respectively, and  $w_1$  and  $w_2$  are their widths at the base.

From the variation of the peak resolution values for the various column combinations, the conclusion drawn earlier regarding the suitability of the various stationary phases for separations of the three pairs, are corroborated generally. The change has been to the extent in which the proportions of the two phases are taken in the column combinations. Figures for theoretical plates show that the performance of the column combinations is of the same order although a small improvement is observed over the Bentone column alone. This was expected, considering that the columns added are truly partition columns while the Bentone column may not behave completely as a partition column.

To study whether further improvement was possible with the Bentone–tricresylphosphate combination, several concentrations between 10 to 30% of the latter phase were tried with the same column of Bentone. Also the experiments were repeated at three temperatures between 70° to 80° C, and the peak resolution and the *HETP* were calculated in each case. Slight improvement was found by increasing the tricresylphosphate concentration to around 15% and by reducing the temperature to about 72° C with a carrier gas flow of 40 ml/minute. Under these conditions, the

analysis time (based on the elution time of *o*-xylene) increased from about 80 to 120 minutes. A typical chromatogram of straight-run naphtha cut 130–150° C under these operating conditions is shown in Figure 2.

The quantitative results for the C<sub>8</sub> aromatic isomers were checked by ultraviolet spectrometry, as well as by estimation of the total aromatics on 1,2,3-tris(2-cyanoethoxy)propane column alone (ignoring the *p*-*m*-xylene separation), and by fluorescent indicator adsorption procedures (ASTM D 1319–65 T). The results were found to be in good agreement (within  $\pm 3\%$ ). This confirms that the various saturates with boiling points up to 150° C are eluted before ethyl benzene with the column combination and the operating conditions reported. The method can therefore be applied for quantitative estimation of individual C<sub>8</sub> aromatic isomers in usual naphtha cuts and other similar samples of appropriate boiling range. Obviously the initial boiling point of the cut is not significant if only the estimation of the C<sub>8</sub> aromatics is desired. The lower aromatics, toluene and benzene, if present, will emerge with the saturates. The final boiling point, nevertheless, should not be much higher than 150° C, because the higher saturates start interfering with the xylenes. To avoid gross errors, the absence of high-boiling hydrocarbons was ensured in all analyses by injecting the sample first into a simple boiling point separating column, squalane. The precision of the results will be governed mainly by the amount of higher-boiling saturates that may be present in an actual sample.

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