

Analysis of Aromatic Solvents by Gas Chromatography

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The utilization of stationary phases having a high degree of selectivity for different types of hydrocarbons has made possible the determination of saturated hydrocarbons in aromatic solvents over a wide range of boiling points. The application of various stationary phases to this analysis problem is discussed and examples are given of the separations obtained.

The determination of small amounts of saturated hydrocarbons in aromatic solvents such as "industrial pure benzol, toluol and xylol" has proved to be a difficult problem (*cf.* Ref.¹). A satisfactory solution, however, can be achieved by means of gas liquid partition chromatography using stationary phases specially chosen to satisfy the specific demands put on them in this connection.

"Industrial pure benzol" and "benzene crystallizable". The separation of the benzene and saturated constituents in these solvents can be effected by means of various stationary phases. The choice of stationary phase depends on the information required. If the total amount of saturates is of major interest, then *p*-nitroaniline picrate is suitable. This stationary phase is namely rather nonselective for saturates, these compounds being eluated mainly as one peak (*cf.* Fig. 1). In order to determine the individual saturated hydrocarbons, a combination with other columns is necessary. A full analysis of "industrial pure benzol" or "benzene crystallizable" can be achieved in the following way. The saturates, eluted from the *p*-nitroaniline picrate column, are condensed and re-run on a 6 m tetra-*n*-amylsilane column. Nine major components and three trace components were identified in "industrial pure benzol" * (*cf.* Fig. 2). The same components were present in "benzene crystallizable" although in smaller amounts and other proportions. A 6 m squalane column can also be used. The chromatogram obtained with this column is very similar to the one shown in Fig. 2. The silane column was chosen here because of its better separation of the pair, cyclohexane/3,3-dimethylpentane. In the actual sample, however, no 3,3-dimethylpentane was found. The pair, 2-methyl-

* The method used in the identification of the components will be described elsewhere.

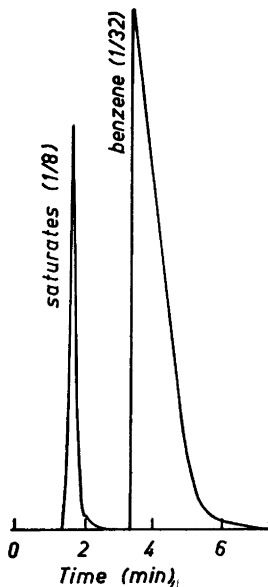


Fig. 1. "Industrial pure benzol." Column: *p*-nitroaniline picrate, 2 m. Temperature: 110°C. Flow of He: 20 ml/min. Recorder attenuation as denoted.

hexane/2,3-dimethylpentane, cannot be separated on either of these columns. If their proportions are wanted, then the peak has to be condensed and re-run on a 6 m di-*n*-octyl phthalate column.

"Industrial pure toluol". In addition to toluene and saturates, this solvent contains small amounts of benzene, ethylbenzene and xylenes. It is necessary to choose a stationary phase which can separate these constituents. *p*-Nitroaniline picrate has proved to be a satisfactory stationary phase. Separate peaks

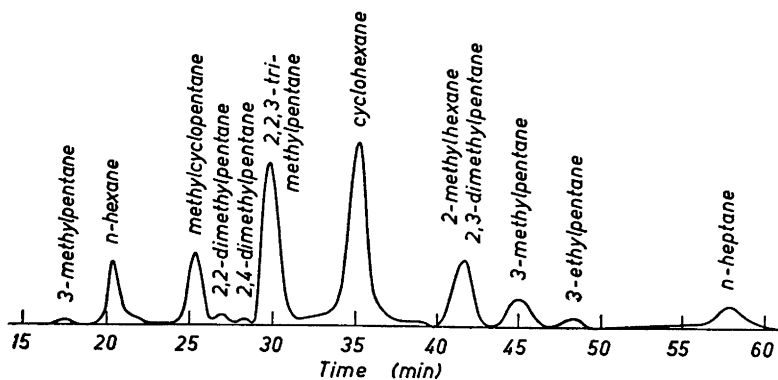
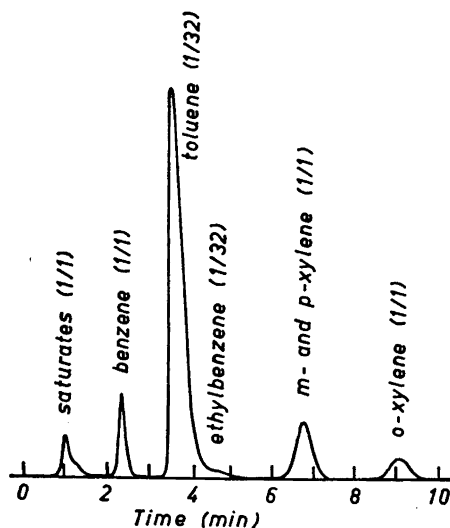


Fig. 2. Saturates in "industrial pure benzol." Column: tetra-*n*-amylsilane, 6 m. Temperature: 25°C. Flow of He: 80 ml/min.

Fig. 3. "Industrial pure toluol." Column: *p*-nitroaniline picrate, 2 m. Temperature: 110°C. Flow of He: 50 ml/min. Recorder attenuation as denoted.



were obtained for saturates, benzene, toluene, ethylbenzene, *m*-plus *p*-xylene and *o*-xylene. (cf. Fig. 3). A full separation of *m*- and *p*-xylene by gas liquid partition chromatography has not been achieved so far*. However, if the

* Golay² has obtained a partial separation of *m*- and *p*-xylene using a 150 ft capillary column coated with didecyl phthalate. A partial separation has also been reported on some packed columns utilizing Apiezon³, benzyldiphenyl⁴ or tetrahalophthalates⁵ as stationary phases.

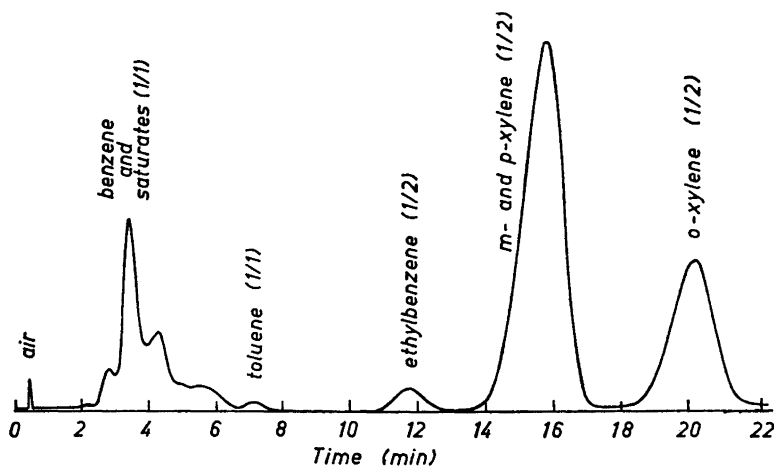


Fig. 4. "Industrial pure xylol." Column: fluorene picrate, 2 m. Temperature: 100°C. Flow of He: 80 ml/min. Recorder attenuation as denoted.

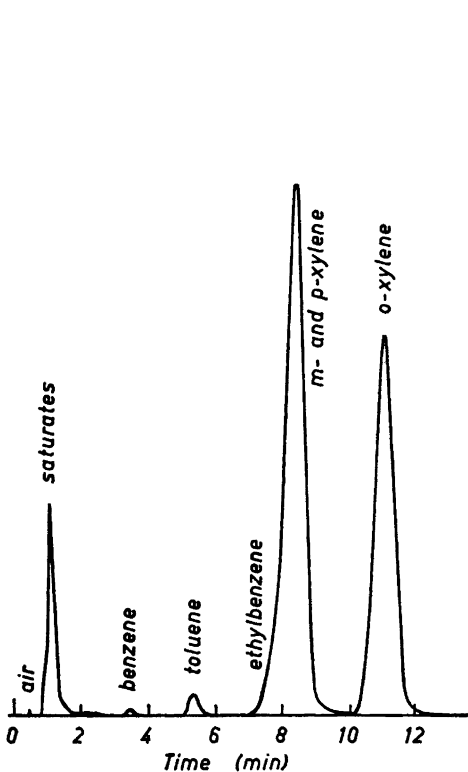


Fig. 5. "Industrial pure xylol." Column: β,β' -oxydipropionitrile, 2 m. Temperature: 100°C. Flow of He: 50 ml/min.

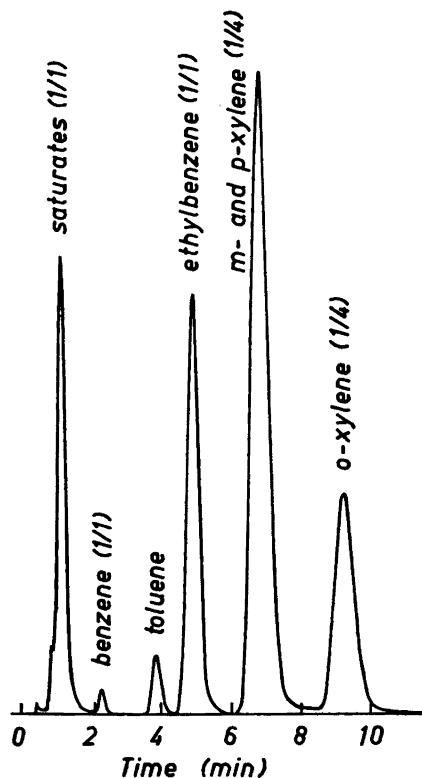


Fig. 6. "Industrial pure xylol." Column: *p*-nitroaniline picrate, 2 m. Temperature: 110°C. Flow of He: 50 ml/min. Recorder attenuation as denoted.

proportions of the two xylenes is wanted, it is possible to condense the mixture as it emerges from the column and analyze it using infrared spectrophotometry.

"Industrial pure xylol". The analysis of "industrial pure xylol" requires a stationary phase which is able to separate aromatic hydrocarbons and saturated hydrocarbons with an extremely high selectivity. To be useful it should release saturates boiling in the xylene range before releasing benzene. Fluorene picrate was reported by Keulemans, Kwantes and Zaal⁶ to release *n*-octane (b.p. 125°C) and isononane (b.p. 143°C) before benzene. It is obvious, however, that a 2 meter fluorene picrate column is not selective enough to separate the saturated hydrocarbons in "industrial pure xylol" from benzene (cf. Fig. 4). The best selectivity is shown by β,β' -oxydipropionitrile but the separation of *m*- plus *p*-xylene from ethylbenzene is rather bad (cf. Fig. 5). *p*-Nitroaniline picrate leaves only *m*- and *p*-xylene unseparated and is therefore the stationary phase best suited for this analysis (cf. Fig. 6).

Table 1. Analysis values for "industrial pure benzol, toluol and xylo".

Sample	Saturated hydrocarbons (wt %)	Benzene (wt %)	Toluene (wt %)	Ethylbenzene (wt %)	<i>m</i> - plus <i>p</i> -Xylene (wt %)	<i>o</i> -Xylene (wt %)
Swedish "industrial pure benzol"	3.3	96.7	—	—	—	—
Swedish "industrial pure toluol"	3.4	0.3	96.2	trace	0.1	trace
Imported "industrial pure toluol"	0.2	0.3	98.7	trace	0.6	0.2
Swedish "industrial pure xylo"	11.0	0.1	0.3	4.0	57.7	26.9
Imported "industrial" pure xylo"	4.8	0.2	0.8	7.1	62.3	24.8

Quantitative analysis. Experiments with synthetic mixtures indicated that the internal normalization method, in which the percentage area is put equal to the weight per cent, was accurate enough for the purpose. The analyses obtained for some solvents are summarized in Table 1. It is seen that relatively large variations in the contents of various components exist in the case of the Swedish and imported qualities of toluol and xylo.

In order to analyze "industrial pure benzol" and "benzene crystallizable" for their individual saturated components, the method previously described

Table 2. Analysis values for "industrial pure benzol".

Compound	wt %
Benzene	96.7
Cyclohexane	0.9
2,2,3-Trimethylbutane	0.8
Methylcyclopentane	0.3
2,3-Dimethylpentane	0.3
3-Methylhexane	0.2
2-Methylhexane	0.2
<i>n</i> -Hexane	0.2
<i>n</i> -Heptane	0.2
3-Ethylpentane	0.1
2,2-Dimethylpentane	0.02
2,4-Dimethylpentane	0.01
3-Methylpentane	0.01
Unknown compounds	0.05

was employed, *viz.* the saturated portion eluted from a *p*-nitroaniline picrate column was condensed and then analyzed on a 6 m tetra-*n*-amylsilane column or squalane column at 25°C. In both cases, the internal normalization method was used. More accurate values could be obtained by calibration using pure hydrocarbons but this was thought to be unnecessary in the present case. Typical values for "industrial pure benzol" are given in Table 2.

EXPERIMENTAL

The analyses were performed using a Perkin Elmer Vapour Fractometer Model 154.

Stationary phases

p-Nitroaniline picrate was prepared from *p*-nitroaniline and picric acid in chloroform solution according to Baril and Megrdichian⁷. β,β' -Oxydipropionitrile was prepared from acrylonitrile according to Bruson and Riener⁸. Squalane was obtained from May and Baker Ltd, Dagenham, England. Tetra-*n*-amylsilane was prepared from silicon tetrachloride and *n*-amylmagnesium bromide. Silicon tetrachloride (0.1 mole, 17.0 g) dissolved in abs. ether (25 ml) was added dropwise with stirring to a solution of *n*-amylmagnesium bromide prepared from *n*-amylbromide (1.0 mole, 151.0 g), magnesium (1.0 g.at., 24.3 g) and abs. ether (150 ml). After addition of the silicon tetrachloride, the reaction mixture was heated under reflux for 2 h and then most of the ether was distilled off. The residue was heated on a steam bath for another 2 h, cooled and hydrolyzed with dilute hydrochloric acid. The organic phase was taken up in ether, the ether solution washed with sodium carbonate solution and water and then dried. After distilling off the ether, the residue was fractionated in vacuum yielding 25.0 g (80 %) of crude tetra-*n*-amylsilane. The crude product was purified using conc. sulphuric acid and then heated over sodium and distilled. (Final product: b.p. 208–210° (17 mm), $n_D^{20} = 1.4494$, $d_4^{20} = 0.8058$, $MR_D = 104.1$ (found); 104.5 (calc.*). % Si 8.91 (found); 8.98 (calc.).

Columns

The columns were made from glass or aluminum tubing of 4 mm internal diameter. The stationary phase was applied in solution on to the carrier, using a suitable low-boiling solvent. The solvent was evaporated and the dry powder then evenly packed in the column. Data for the columns used were:

p-Nitroaniline picrate columns. Two 1 m glass columns were used in series. The stationary phase (20 %) was applied on Silocel C 22 (42–60 mesh).

Fluorene picrate column. A 2 m Perkin-Elmer stainless steel column G was used. The stationary phase (about 20 %) was applied on Celite 545.

β,β' -Oxydipropionitrile column. A 2 m aluminum column was used. The stationary phase (20 %) was applied on Chromosorb (30–60 mesh).

Squalane and tetra-*n*-amylsilane columns. In both cases, two 3 m aluminum columns were used in series. The stationary phase (3 %) was applied on Chromosorb (30–60 mesh).

Di-*n*-octyl phthalate columns. Two 3 m aluminum columns were used in series. The stationary phase (10 %) was applied on Chromosorb (30–60 mesh).

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