

QUANTITATIVE ESTIMATION OF BENZENE, TOLUENE, *o*-XYLENE AND *p*-XYLENE BY IR SPECTRA

AZHAR M. SYED

PCSIR Laboratories, Karachi 39

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Abstract. IR spectroscopic method for the quantitative estimation of mixture of benzene, toluene, *o*-xylene and *p*-xylene has been investigated by using base-line measuring technique to the unknown and standards. For an IR spectrometer used for routine type of analysis, certain limitations and errors have been proposed for such studies.

The project was undertaken to meet the immediate need for quantitative analysis of BTX mixture for a pilot-plant study by Engineering Research Division of these Laboratories. Therefore, only the existing facilities were examined for meeting this requirement. The only instrument available, has been a routine type of IR spectrometer having resolution not enough for such studies and some techniques have to be adopted. This method is very quick as only one-cell thickness has been used for the analysis of the quantities of all the four components in a wide range. The accuracy has been checked for about 20 samples and the average error lies between ± 2 to $\pm 4\%$. The applicability of this method may be extended to the petroleum distillates in an oil refinery or any other chemical engineering project where quick analysis of aromatics is required. Another aim of publishing this work has been the use of low cost IR spectrometer for these measurements, which a small department or factory may afford easily.

There are certain limitations in the use of IR spectrometers for quantitative analysis, which include reasonable compromise between resolution, scan time and signal to noise ratio. In order to perform highly precise measurements, more attention is to be given towards high resolution and sophisticated spectrometers.

For monochromatic radiation, the fundamental law governing absorption in solution is:

$$I = I_0 \exp(-KCl) \quad (1)$$

Where I is the intensity of radiation transmitted and I_0 is the intensity of incident radiation. K is known as 'absorption coefficient', C is the concentration and l is the cell thickness. Equation (1) may be written as

$$K = 1/Cl \log_e (I_0/I) \quad (2)$$

For practical purposes, it is convenient to use common logarithms and write as

$$\epsilon = 1/Cl \log_{10} (I_0/I) \quad (3)$$

Where ϵ is known as 'molecular extinction coefficient'. These relationships are commonly known as Beer's law and are used extensively in the quantitative estimation by spectroscopy.

Experimental

Spectra were recorded on a Perkin-Elmer 137 spectrometer which had a wavelength range of 2.5–15 μ with a limiting resolution of 0.04 μ at 10 μ . The ordinate was in linear transmittance with an accuracy of $\pm 1\%$ and reproducibility similar to accuracy.

Mixtures of known concentration were made by usual volumetric methods. Several attempts were made to select a suitable path length by recording spectra of mixtures in different cell thicknesses. Fixed path length liquid cells with NaCl windows were used.

Results and Discussion

Spectra of the four components were recorded separately and following spectral bands were selected; benzene (14.8 μ); toluene (13.8 and 14.4 μ); *o*-xylene (13.5 μ); *p*-xylene (12.6 μ).

Standard solutions of benzene, toluene and xylenes were prepared by the scheme given in Tables 1 and 2.

Cell thickness of 0.025 mm is found to be suitable for all the components of the standard solutions. Fig. 1 shows that in the presence of 34% toluene, the estimation of *o*-xylene is not possible below 1%. This

TABLE 1

Stand- ard solution	Volume (%)			
	Benzene	<i>o</i> -Xylene	<i>p</i> -Xylene	Toluene
A	2.0	34.0	34.0	30.0
B	5.0	37.5	37.5	20.0
C	10.0	40.0	40.0	10.0
D	20.0	37.5	37.5	5.0

TABLE 2

Stand- ard solution	Volume (%)			
	<i>o</i> -Xylene	Benzene	Toluene	<i>p</i> -Xylene
A-1	2.0	34.0	34.0	30.0
B-1	5.0	37.5	37.5	20.0
C-1	10.0	40.0	40.0	10.0
D-1	20.0	37.5	37.5	5.0

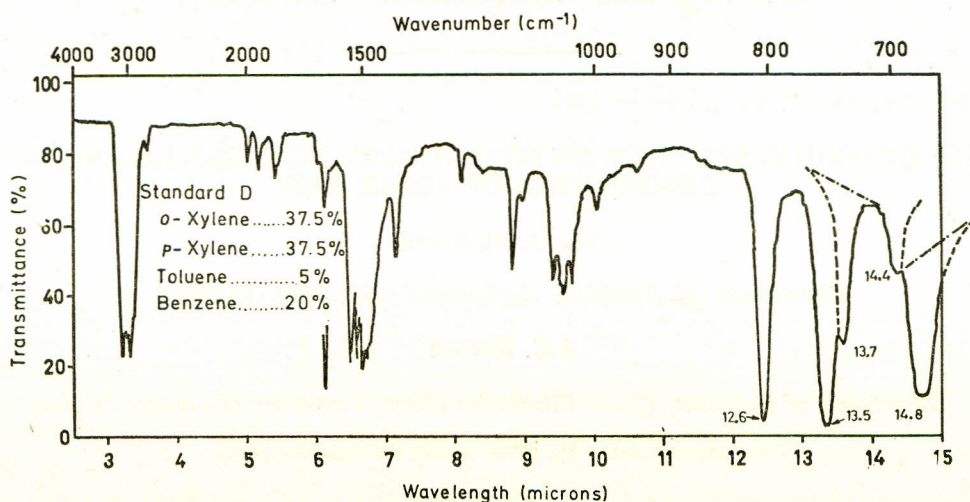


Fig. 1.

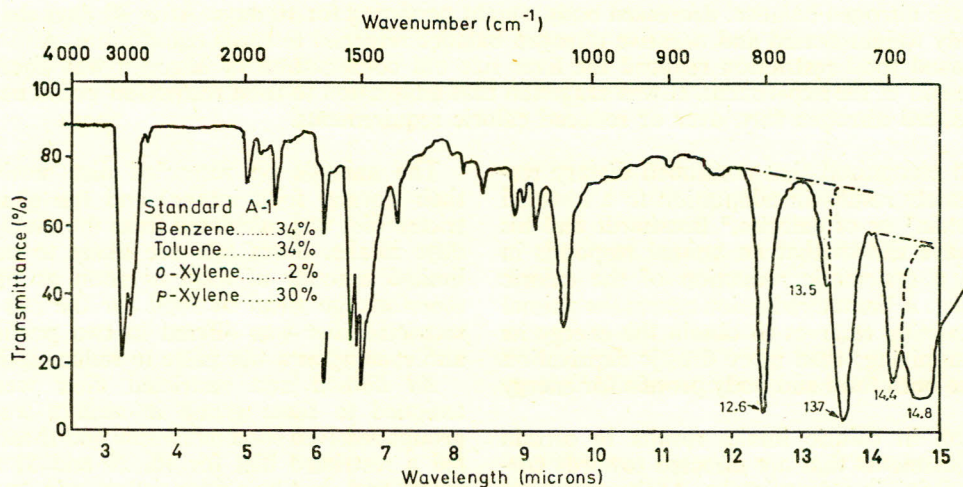


Fig. 2.

has been achieved after extrapolating the *o*-xylene band at 13.5 μ into Lorentzian shape.¹ A similar situation arises in the estimation of toluene in large quantity of benzene, where the toluene band at 14.4 μ has been extrapolated (Fig. 2).

The choice of drawing a base-line for a particular band is not critical, provided the same band of the standard and the unknown has the base-line drawn in a similar manner. The base-line has been drawn tangentially to all the bands in the present study and absorbances calculated accordingly.

Using the concentrations of the standards from Tables 1 and 2, Beer's law plots (absorbance \rightarrow concentration) were obtained separately for benzene, toluene, *o*-xylene and *p*-xylene. These working curves were used for determining the volume per cent composition of any unknown mixture directly, by calculating the absorbance and reading the corresponding concentration on the straight-line. Robinson² has shown that highest precision results, when the band being used is in the range 25–50% transmission (absorbance 0.3–0.6). Bands much weaker than this give little sensitivity, while bands stronger than this are too sensitive to noise level. For bands in the absorbance range 0.3–0.6 the analytical precision to be expected

is of the order of $\pm 3\%$. This is the approximate precision that will result with 'ordinary' spectrometers when the standard slit programme is used.

The sources of errors which may cause the deviations from Beer's law have been associated as due to: (1) variation of certain absorption band frequencies, shapes or intensities brought on by association effects between molecules which may vary with the change of concentration, and (2) false measurement by the spectrometers commercially available, where Beer's law is not obeyed unless the distribution of radiation passed by the spectrometer exit slit, is considerably narrower than the absorption band being measured. The overall errors involved in this method due to above-mentioned deviations have been checked and lie in the range of ± 2 to $\pm 4\%$.

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References

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2. D.Z. Robinson, Anal Chem., **23**, 273 (1951).