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Note

Quantitative analysis of mixtures of toluene and its side-chain-chlorinated derivatives by gas chromatography

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The side-chain chlorination of toluene involves the possibility of consecutive reactions, with the formation of benzyl chloride, benzal chloride and benzotrichloride. For the separation and quantitative analysis of these components in the product mixture, the most sensitive and selective technique is gas–liquid chromatography.

The chromatographic analysis of chlorinated derivatives of toluene has been described earlier[1–3]. Peak-area correction factors for the individual components of a seven-component mixture were reported by Freeman[1], and, using a thermistor detector, the peak area ratios were observed to be numerically equal to the mole ratios[2]. However, when platinum wire thermal conductivity cells were used instead of thermistors, the peak-area ratios differed distinctly from the mole ratios[3]. While calibration curves were used for the analysis of the binary mixtures, a nomographic method was used for the ternary ones.

Flame ionization detection has been employed by Yang *et al.*[4], and relative intensities based on peak area to mole fraction ratios were reported.

EXPERIMENTAL

The internal standard technique was employed for the routine analysis of toluene and its side-chain-chlorinated products, the standard being carbon tetrachloride (10%, w/w). A Perkin-Elmer Fractometer F-7 with a platinum wire thermal conductivity detector was used. The components were separated on a stainless-steel, hairpin-type column, packed with 15% silicone oil DC 200 on Celite 545; the carrier gas was helium (80 ml/min). The column temperature was increased at a programmed rate of 10°/min from 120 to 170°, a procedure which increased the analysis rate without any loss of resolution.

A typical recording is shown in Fig. 1. The observed relative retention times for the components toluene, benzyl chloride, benzal chloride and benzotrichloride are 1.86, 4.14, 5.84 and 7.60, respectively. The peak areas for the components in the synthetic mixtures were determined by coupling the detector response to a Perkin-Elmer electronic integrator Model D-4 which made baseline drift corrections and automatically attenuated the response to maximize the size of each peak on the chart paper. The molar response factor is determined by:

$$\text{molar response factor} = \frac{\text{moles of standard } (n_s)}{\text{moles of component} (n)} \cdot \frac{\text{area of component } (A)}{\text{area of standard } (A_s)}$$

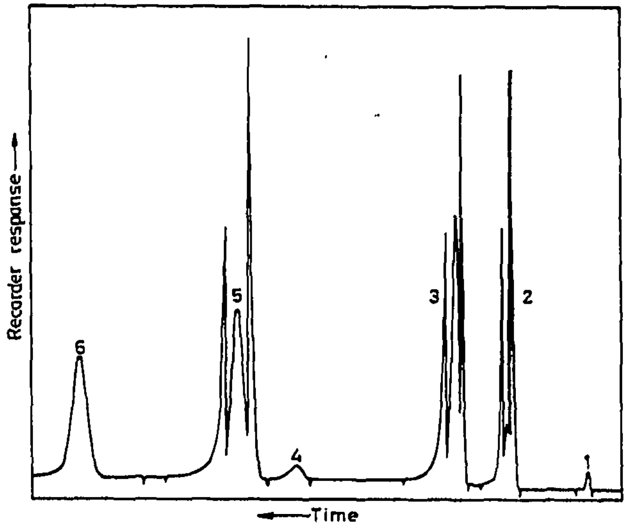


Fig. 1. Gas chromatogram. 1 = Air; 2 = internal standard; 3 = toluene; 4 = *o*-chlorotoluene; 5 = benzyl chloride; 6 = benzal chloride.

Linear plots of (A/A_s) *versus* (n/n_s) are shown in Figs. 2–5. The factors calculated from these plots are 0.8468 for toluene, 0.9350 for benzyl chloride, 1.0650 for benzal chloride and 1.1360 for benzotrichloride. Their linearity shows the absence of mutual interference by the components. Hence, the concentrations of the given components in the sample can be determined independently.

For comparison with the method of Haring and Knol[2], the mole fractions of the components in the mixture are also plotted against the corresponding peak-area

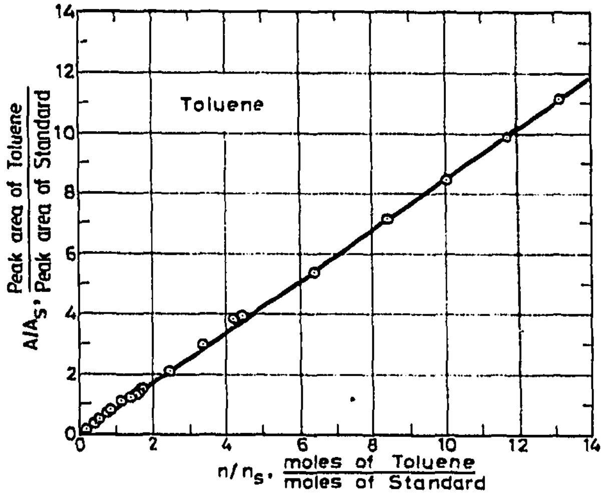
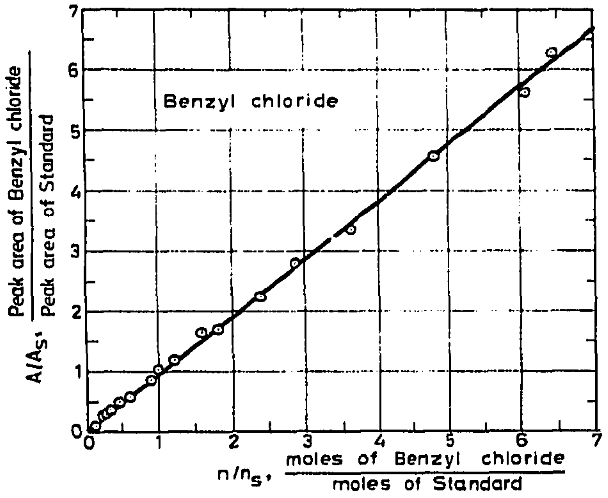


Fig. 2. Calibration graph for toluene.



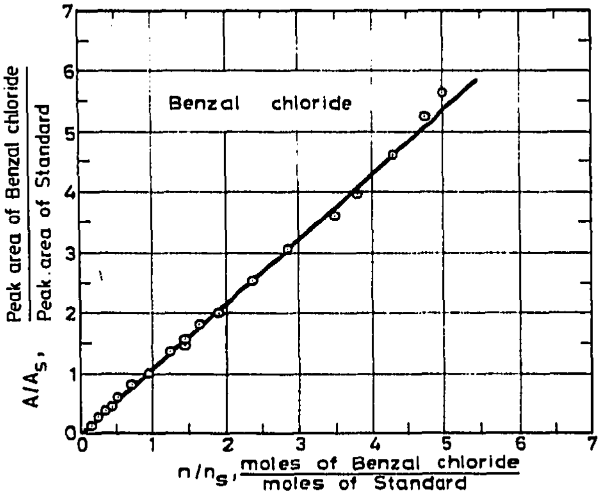
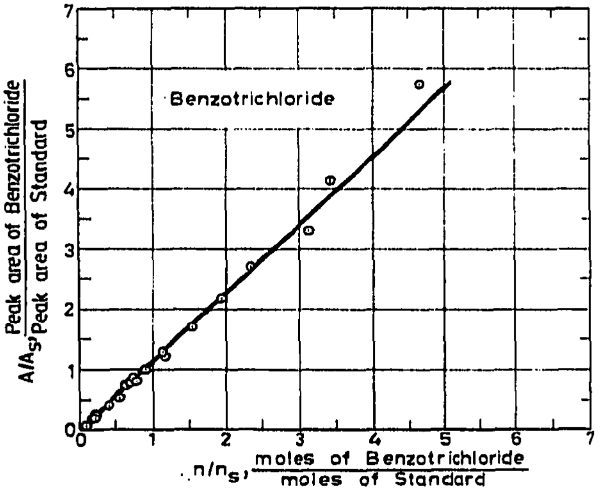


Fig. 3. Calibration graph for benzyl chloride.

Fig. 4. Calibration graph for benzal chloride.



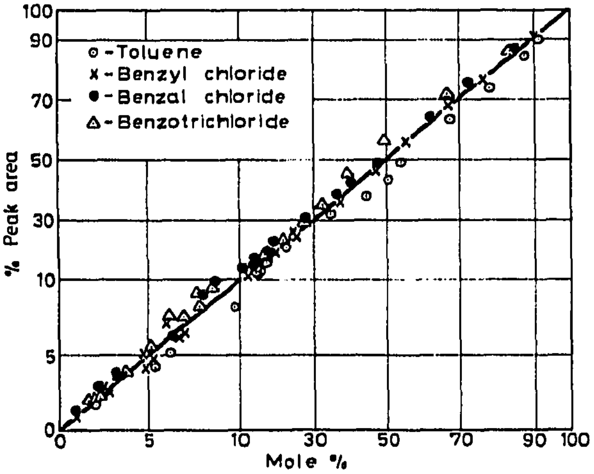


Fig. 5. Calibration graph for benzotrichloride.

Fig. 6. Plot of mole per cent of chlorinated products against per cent peak area.

fractions (Fig. 6). The large scatter of points indicates that such a simple calibration method is less suitable for the present data.

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