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Note

Determination of free monomeric toluene diisocyanate (TDI) and 4,4'-diisocyanatodiphenylmethane (MDI) in TDI and MDI prepolymers, respectively, by high-performance liquid chromatography

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Isocyanates in the form of vapour or fine particles may irritate the eyes and mucous membranes and, if inhaled, cause attacks of coughing and dyspnoea, and possibly delayed attacks of asthma. The asthmatic response is thought to be caused by the isocyanates combining with protein in the body to induce tissue sensitization¹. If this is allowed to occur, affected persons show these symptoms at extremely low concentrations of isocyanate in air.

Isocyanate vapours or mists are mainly produced in two ways: (1) *by heating*. When isocyanate-containing materials for polyurethane coatings are heated *e.g.* for curing purposes in a stoving oven or tunnel, isocyanate vapour can be produced. It is important to know the percentage of free monomeric isocyanate present in the coating material, as the monomeric species is much more volatile than the prepolymer itself, and hence the airborne concentration depends largely on the monomer content. 4,4'-Diisocyanatodiphenylmethane (MDI)-based prepolymers are sometimes supplied in flake form; a vapour hazard may arise when they are heated to about 60° to bring them to a liquid form for use. (2) *by spraying*. The chief toxic hazard in spray application of these coatings lies in the inhalation of any form of isocyanates in the fine aerosol droplets: the percentage of free monomeric isocyanate present is not necessarily relevant. If paints containing isocyanate prepolymer are applied by brush or roller, the vapour inhalation hazard is minimal, unless heating is involved, provided that the monomer content of the commercial prepolymer is kept below 0.5%.

Isocyanates are also used in industry in the production of polyurethane foams, adhesives, varnishes, fabric coating preparations etc. The potential isocyanate inhalation hazard presented by such applications, assuming no spraying is involved, depends on the operating temperatures and the proportion of free monomer in the polymers.

Most methods for the determination of organic aromatic isocyanates are based on the original procedure of Marcali² for the determination of toluene diisocyanate (TDI). This method was later modified by Meddle *et al.*^{3,4}. This paper describes a method modified from that of Heinekey⁵ which enables free monomeric TDI and MDI in their respective prepolymers to be accurately determined. The method employs conversion to the ethyl urethane derivative and subsequent high-performance liquid chromatographic (HPLC) analysis.

EXPERIMENTAL

Chromatographic apparatus and conditions

The liquid chromatograph comprised a Waters 6000A constant-flow, reciprocating diaphragm pump, a stopped-flow injection system, and a Cecil Instruments CE212 ultraviolet monitor as detector. Spherisorb S5 ODS (5 μm average particle size, Phase Separations, Queensferry, Great Britain) was packed into a stainless-steel column, (150 \times 4.5 mm I.D.) by a high-pressure slurry technique⁶. The mobile phase was methanol-water (3:2), which had been previously deaerated and was pumped at ambient temperature through the column at a flow-rate of 1 ml/min. 246 nm was chosen as the monitoring wavelength to work at. (λ_{max} of 2,4-TDI urethane was found to be 240 nm; λ_{max} of MDI urethane was found to be 248 nm.)

Preparation of standard urethane derivatives

About 3 ml of the appropriate isocyanate was boiled under reflux with 100 ml of ethanol in a round-bottomed flask for 15 min. The flask was cooled and the ethanol was removed by rotary evaporation; the urethane produced was dried at 60°, and recrystallized in water and ethanol. Standards containing 0.08, 0.16, 0.20 and 0.40% (w/v) of the urethane derivatives were prepared by dissolving 0.02, 0.04, 0.05 and 0.10 g in 25 ml of ethanol in standard flasks.

Preparation of samples

A 1-g amount of prepolymer sample was dissolved in 25 ml of ethanol in a 250 ml round-bottomed flask and the contents boiled under reflux for 20 min. The flask was cooled, the contents transferred to a standard flask and made up to 50 ml with ethanol. If on cooling a precipitate formed (due to the presence of trimeric isocyanate), it was redissolved by making up to 50 ml with chloroform, instead of ethanol. The trimer is insoluble in ethanol.

RESULTS AND DISCUSSION

Chromatography was performed with constant-composition mobile phase of methanol-water (3:2). The urethane derivatives of the 2,6- and 2,4-isomers of TDI gave slightly better separation with methanol-water (1:1), but here the retention time for MDI was >25 min.

Before the 2,4- and 2,6-toluene diisocyanate isomers present in the prepolymers could be measured a standard had to be prepared from these two components. A commercially available (Fluorochem) grade of TDI containing *ca.* 80% 2,4- and 20% 2,6-TDI was used, the peak heights were measured for these components for a 2- μl injection. From the peak heights of the 2,4- and 2,6-TDI derivatives in the sample, the amount of isocyanate could be calculated. For MDI only a single peak was obtained and hence standard preparation was straightforward. The 2,6-urethane derivative is less soluble in the mobile phase than the 2,4-derivative, therefore the observed peaks produced do not give a direct measure of the ratios of these two isomers (Fig. 1).

The percentage recovery of free isocyanates from commercial hardeners was determined by "spiking" with either TDI or MDI at different concentrations (Figs. 2 and 3). Yields ranging from 92–109% (mean 102%) were obtained. Fig. 4 shows a chromatogram of a commercial hardener that contains both TDI and MDI.

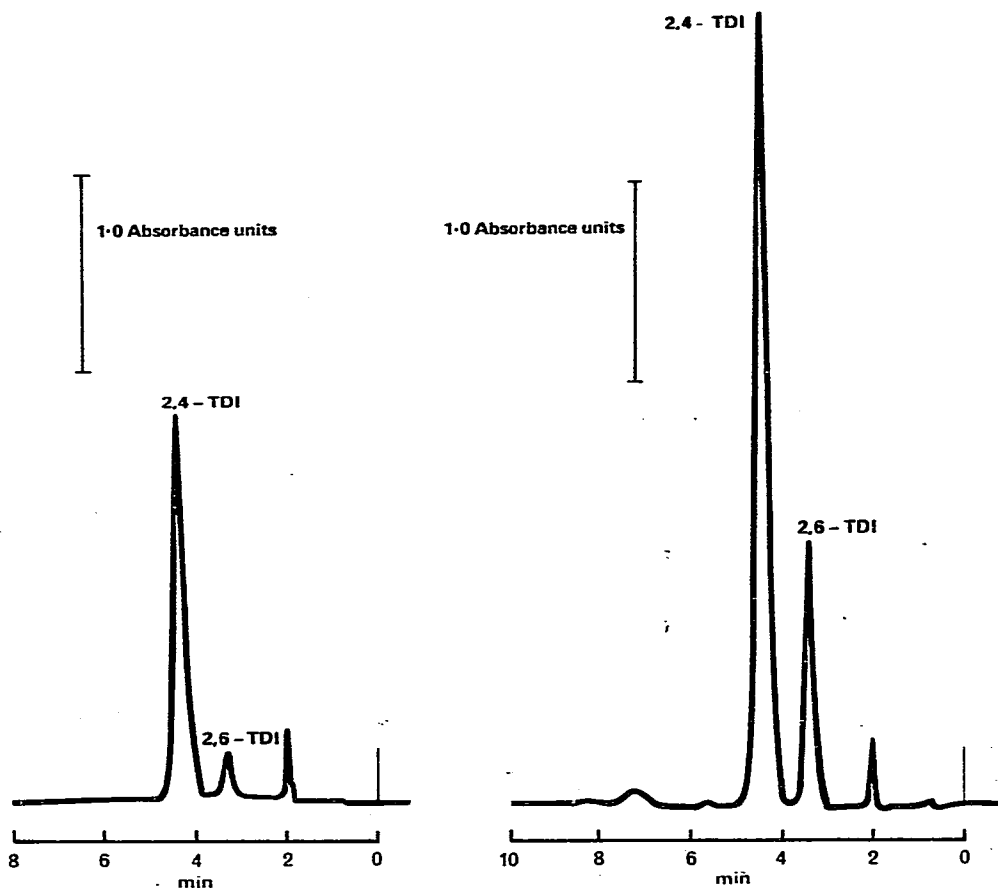


Fig. 1. Chromatogram of TDI standard.

Fig. 2. Chromatogram of a commercial hardener spiked with 0.24% TDI. Column, Spherisorb S5 ODS (150 × 4.5 mm I.D.); mobile phase, methanol-water (3:2); temperature, ambient; detection, 246 nm; sensitivity, 1.0; flow-rate, 1.0 ml/min; amount injected, 2 μ l.

Other compounds that may be present in commercial samples include toluene, xylene and cellosolve acetate, commonly used as solvents. These do not interfere with the analysis for free isocyanate. Other high molecular weight impurities, if present, can be eluted rapidly from the column if necessary (where their retention times are considerably in excess of those of the urethanes present) by a "step gradient" to a more or a less polar mobile phase where the analysis time is shorter.

Table I shows that MDI is not pure enough to be used to prepare the ethyl urethane directly as a standard. The urethane derivative has to be separately prepared for this purpose.

A stable baseline down to 0.02 a.u.f.s. was normally obtained with the equipment used in this work. Analysis was usually carried out with a sensitivity between 0.1 and 1.0 a.u.f.s. When no interference arose, the detection limit for a sample of 1.0 g was 0.001 %.

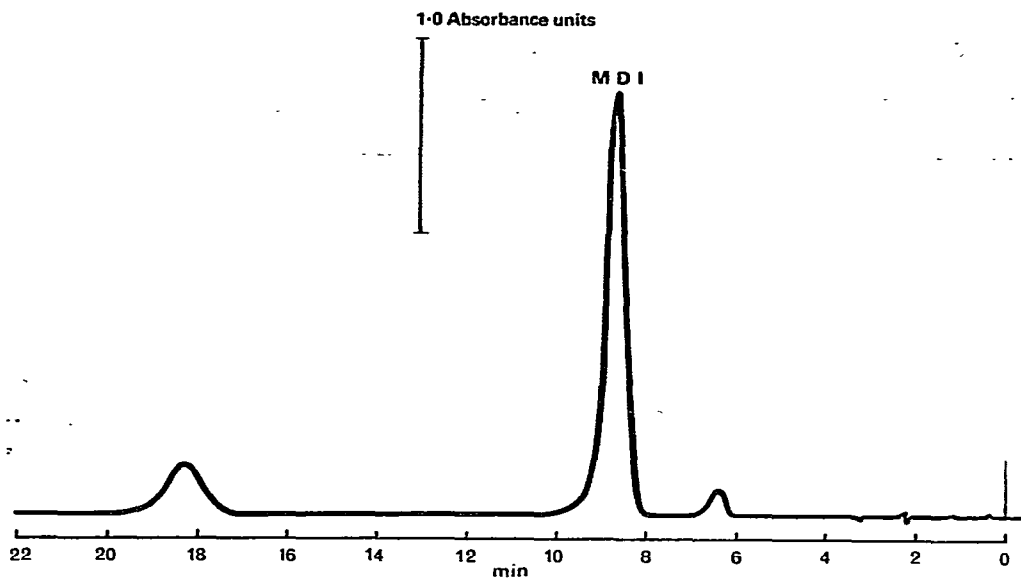


Fig. 3. Chromatogram of a commercial hardener spiked with 0.16% MDI.

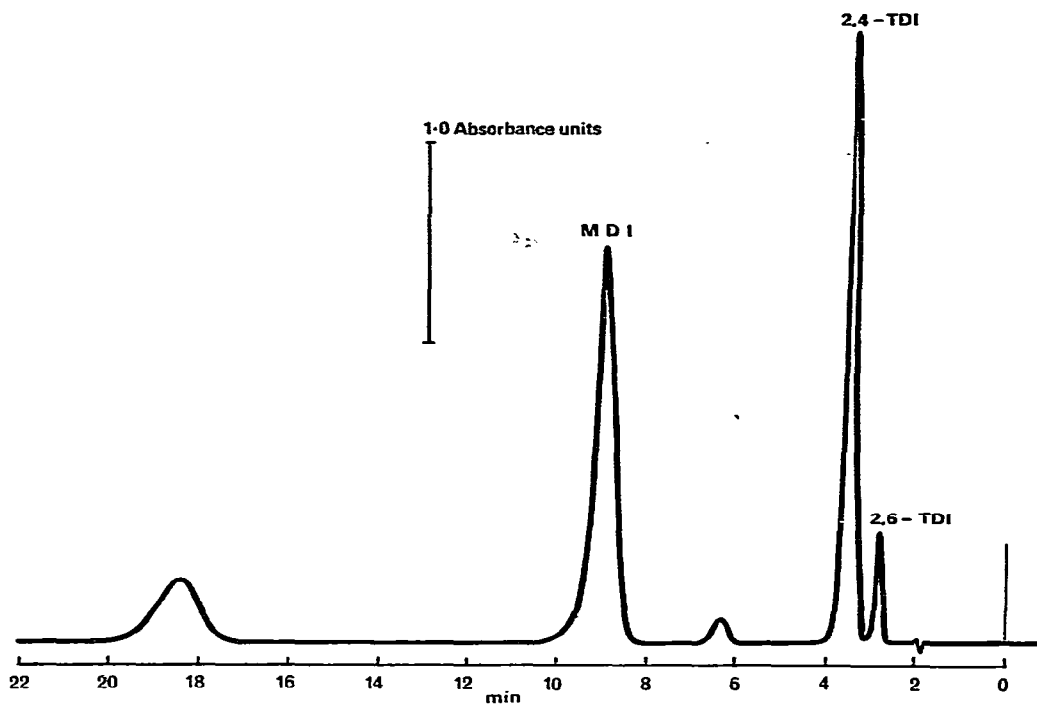


Fig. 4. Chromatogram of a commercial hardener containing both TDI and MDI.

TABLE I
 PURITY OF COMMERCIALY AVAILABLE ISOCYANATES

Isocyanate	Source	Approx. purity (%)		
		Total	2,6-	2,4-
TDI	Fluorochem	93	22	71
MDI	Flake (I.C.I.)	75		
MDI	Brown liquid (Merck)	42		
MDI	Brown liquid (sample)	33		

CONCLUSION

The method described is a modification of an existing HPLC method for the determination of free monomeric TDI. The modifications permit the determination of both free monomeric TDI and MDI in prepolymers, either separately or together, with a high degree of accuracy.

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