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## Note

### Gas chromatographic determination of free toluene diisocyanate in flexible urethane foams

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Toluene diisocyanate (TDI) is currently used throughout the world in the production of urethanes, the biggest proportion of which is represented by flexible foams, mainly manufactured by continuous slabstock technology. After manufacturing, flexible foams are generally cured at room temperature for 24–28 h, cut into slabs, contoured to shape, etc. They are used in the production of bedding, furniture, etc.

It is well known that TDI presents a health hazard, and therefore it is of interest to ascertain the presence of free TDI in a flexible foam after its production\*. In order to measure low isocyanate levels a suitable analytical procedure must be used. Some quantitative methods are described in literature, but they are insensitive to small amounts of toluene diisocyanate or other isocyanates cause interference.

By means of infrared spectroscopy<sup>1,2</sup>, based on the N=C=O stretching vibration, it is possible to detect the percent of N=C=O groups independently of the molecular structure; the same occurs in procedures based on the reaction with an excess of dibutylamine and titration with a standard acid<sup>3</sup>, or colorimetric determination<sup>4</sup>. Other methods are based on the reaction with ethanol to form urethane and subsequent analysis by gel permeation chromatography<sup>5,6</sup>.

In the ASTM D-2615 method<sup>7</sup> the free TDI is isolated by vacuum distillation with a carrier solvent and determined colorimetrically after conversion with sodium nitrite–Cellosolve reagent. Free TDI in adducts with polyols<sup>8,9</sup> or in oligomers<sup>10</sup> can be determined by gas chromatography (GC) and in polyurethane prepolymers by high-performance liquid chromatography<sup>11</sup>. None of these methods can be used for determining ppm amounts of unreacted TDI in solid products such as foams.

Thus, we have developed a quantitative method involving extraction with *o*-dichlorobenzene and GC determination using a flame ionization detector (FID).

#### EXPERIMENTAL

Extraction of unreacted TDI in the foam is performed in the glass apparatus shown in Fig. 1. About 2 g of foam were weighed to an accuracy of 1 mg and placed in A. Ten millilitres of *o*-dichlorobenzene, dried under molecular sieve 5 A, free from

\* This work was performed within the safety program of the International Isocyanate Institute.

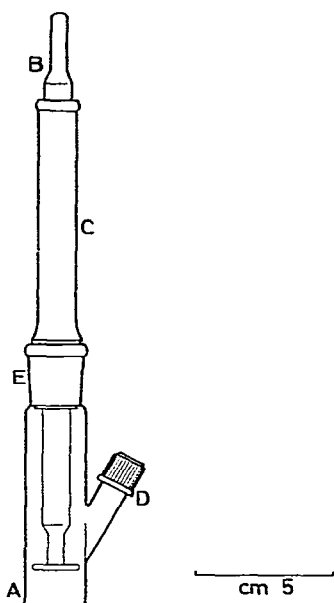


Fig. 1. Extraction apparatus. A = Vessel; B = piston; C = ground glass syringe; D = screw-capped septum; E = 19/26 cone adaptor.

impurities which have the same chromatographic retention time as TDI, were added and the sample was alternately compressed by plug B (syringe C) for about 10 min. Using a microsyringe, a quantity of solvent was drawn out through septum D and immediately analyzed under the following conditions: Carlo Erba Fractovap Series 2300 gas chromatograph or equivalent; glass column, 2.8 m  $\times$  3 mm I.D., packed with 10% OV-101 on Chromosorb W AW DMCS (80–100 mesh); nitrogen carrier gas, inlet pressure 172 kPa, rate 95 ml/min; FID, hydrogen flow-rate 65 ml/min, air flow-rate 320 ml/min; detector temperature 200°C, injector 200°C, column 170°C; sample size: 3  $\mu$ l; Leeds & Northrup Speedomax recorder, Model W or equivalent, 1 mV and 1 sec full scale, chart speed 30 in.

Calculations were made by the external standard method, using calibration solutions of TDI in dry *o*-dichlorobenzene and multiplying by the dilution factor (solvent amount/sample amount).

A typical flexible foam was prepared by using 100 parts Glendion FG 3501\* (triol, mol.wt. 3500, OH number 43.7), 4.8 parts water, 0.3 parts amine catalyst, 0.15 parts stannous octoate, 56.4 parts (*i.e.*, 5% more than the stoichiometric amount) Tedimon 80\* (TDI having a 2,4/2,6 isomer ratio of 80/20). The foam was analyzed both 1 h and 24 h after its production; in the last case the foam was kept either in ambient air (relative humidity 70%) or in a dry atmosphere (under P<sub>2</sub>O<sub>5</sub>). It appeared from the analyses (Fig. 2B) that the fresh foam contained about 300 ppm of free TDI; samples drawn from the same foam after 24 h were TDI-free (<5 ppm, *i.e.*, less than the value detectable by the analytical method used) (Fig. 2D).

A check for the presence of toluenediamine (TDA) was made; the retention

\* Montedison tradenames.

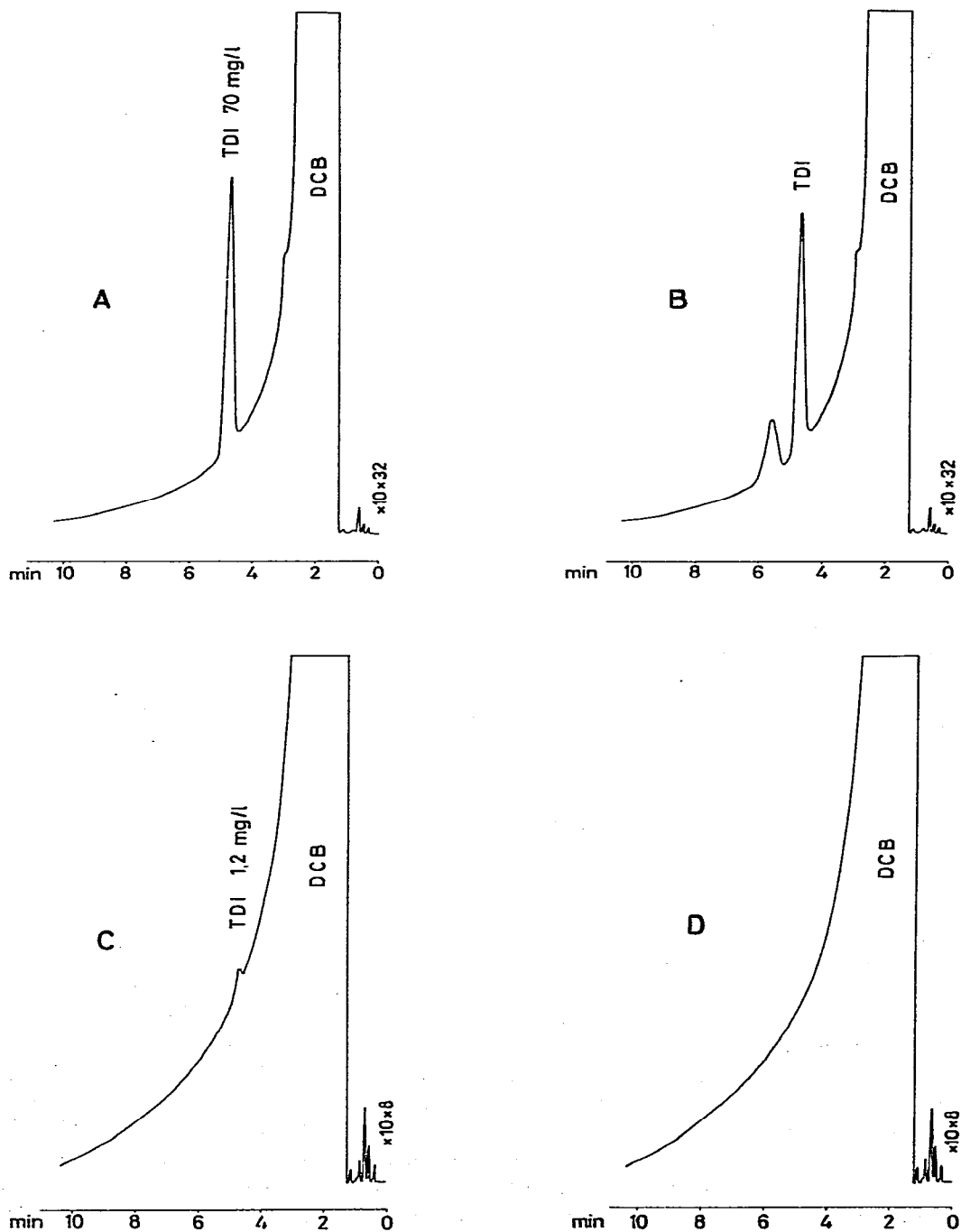


Fig. 2. GC analysis of: A, calibration solution of 70 mg/l toluene diisocyanate (TDI) in dry *o*-dichlorobenzene (DCB); B, extract from foam 1 h after production; C, calibration solution of 1.2 mg/l toluene diisocyanate (TDI) in dry *o*-dichlorobenzene (DCB); D, extract from foam 24 h after production.

time in the blank was found to be 1.06 relative to TDI. No TDA was observed in the samples examined (Fig. 2B and D).

#### DISCUSSION

Flexible slabstock foams are normally almost totally of open-cell structure; moreover, the crushing of the foam during extraction ruptures any cell windows still present<sup>1,2</sup>. For these reasons it seemed very likely that *o*-dichlorobenzene, which is a good solvent for TDI, would extract all of the unreacted monomer.

The use of a Soxhlet extractor did not appear suitable since it requires a great quantity of solvent (*ca.* 50 times the mass of the foam) with a consequent decrease in sensitivity in determining TDI; moreover, it requires a period of time sufficiently long to allow TDI to react with other compounds. We observed that the extracted solution must be immediately analyzed since the TDI content is not constant, probably due to reaction of TDI with other extracted compounds. Free TDI, which is present at levels of *ca.* 300 ppm in the fresh foam (1 h after production), disappears after 24 h under all storage conditions (both ambient and dry air).

The suggested method is simple and rapid and its sensitivity can be increased by using a nitrogen specific detector.

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