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Determination of toluene-2,4-diisocyanate in environmental and workplace air by sampling onto Tenax-TA followed by thermal desorption and capillary gas chromatography using flame ionisation and ion-trap detection

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Abstract

This work describes a method for the determination of low levels of toluene-2,4-diisocyanate (TDI) in workplace air. Perkin-Elmer ATD-400 adsorbent tubes containing 200 mg of Tenax-TA (80–100 mesh) were used with low-flow personal sampling pumps. Following a period of sampling, the adsorbent tubes were sealed and returned to the laboratory for analysis within 24 h. The TDI content was determined by thermal desorption of the tubes followed by capillary column gas chromatography with simultaneous FID–ITD detection. The analytical run time was less than 30 min. Based on a nominal 1-l air sample volume, the detection limit was determined as less than 0.001 μg of TDI.

Keywords: Toluene-2,4-diisocyanate

1. Introduction

Isocyanates are basic constituent substances utilised in the commercial manufacture of polyurethanes. Urethanes are often produced by reacting dihydroxy alcohols with diisocyanates and are commonly used in the production of flexible or rigid foams, in synthetic rubber manufacture and in the industrial preparation of paints and varnishes [1].

Isocyanates are used in industry on a worldwide basis but may also be encountered in non-occupational environments (in organic substances sold for domestic, home repair (DIY) and hobby-related activities) [2]. As a consequence of acute and chronic exposure to isocyanates (and residual breakdown products associated with some polyurethanes) adverse health effects including respiratory and allergic sensitisation responses are increasingly common. In sufficiently high concentrations, isocyanates exhibit a primary acute irritant effect on the respiratory tract, and can cause mild symptoms such as dry throat, eye and throat irritation, coughing and further, more serious effects such as dyspnoea. Long-term (chronic) exposure to low levels of isocyanates are also implicated as causes of occupational asthma and other pulmonary and upper respiratory tract conditions [2].

Toluene diisocyanate (TDI) (molecular formula, $C_9H_6N_2O_2$) is perhaps the most volatile of the isocyanate compounds. In its commonest form TDI is a colourless to pale-yellow liquid consisting of a mixture of 2,4- and 2,6-diisocyanate isomers which

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will polymerise readily in air. However, in many industrial and laboratory applications it may be encountered as the 2,4-diisocyanate on its own. TDI is also highly implicated in the onset and development of occupational asthma in paint sprayers, foam manufacture workers and chemical process plant workers [3]. It presents a significant hazard with respect to its ability to enter airborne environments and constitute an inhalation risk. It has a high vapour pressure (0.025 mm Hg at 25°C; boiling point 115–120°C) and must be strictly controlled to prevent fugitive emission losses to atmosphere. TDI liquid(s) must be managed with care as at temperatures below about 8–14°C, the substance will begin to freeze, creating special problems for outdoor handling activities for much of the year. TDI is principally used to manufacture polyurethane foams although it is increasingly used as a blended component with aromatic, alkane and alcohol-based solvents in the synthesis of demulsifier packages for oilfield chemical applications [2]. In many instances it is premixed with solvents which have been heated up (e.g., to prevent chilling of the liquid and solidification in the inlet to the reactor vessel) prior to addition to the reaction vessel, enhancing the potential for operator exposure during the early stages of manual processing.

The threshold limit value (TLV) of the American Conference of Governmental Industrial Hygienists for TDI is 36 $\mu g\ m^{-3}$ (as an 8-h time weighted average, TWA) and 140 $\mu g\ m^{-3}$ (as a 15-min short-term exposure limit (STEL) [4]. In the UK, TDI has a stricter maximum exposure limit (MEL) of 20 $\mu g\ m^{-3}$ (as an 8-h TWA) and 70 $\mu g\ m^{-3}$ (as a 15-min STEL) [5].

TDI is commonly analysed through the use of a variety of spectrophotometric and specific detector methods and in band-type monitors for continuous exposure monitoring. Many other procedures based on sampling into impingers filled with a solvent absorbing medium or impregnated filters followed by HPLC or TLC analysis have been successfully developed to determine TDI in air [6–15]. A common disadvantage is that some of the procedures are necessarily long and tedious, incurring significant delays between the time of sampling and execution of the analysis. Moreover, many of these methods are designed to be used for a wide range of isocyanates, but will not yield information on other toxicologically significant compounds to which personnel may be co-exposed.

This paper describes the preliminary results of a relatively simple alternative method for the analysis of TDI in air. The TDI was collected by sampling directly onto an adsorbent tube packed with Tenax-TA, followed by thermal-desorption and capillary column gas chromatography with simultaneous flame ionisation (FID) and ion-trap (ITD) detection. We used the ITD to confirm the presence of TDI in sample chromatograms although in practice most analyses would be sufficiently well served by use of FID alone.

2. Experimental

2.1. Reagents and materials

Standards were prepared using high-purity toluene-2,4-diisocyanate (Aldrich, Wimborne, UK). Initially, TDI was spiked onto adsorbent tubes using hypodermic microsyringes calibrated to 0.01 μl (SGE, Milton Keynes, UK) according to a standard method outlined in the UK MDHS literature [16]. To verify the calibration data, TDI blends were then made up in pure anhydrous 99.8% toluene (Aldrich, Wimborne, UK) following the protocols described in EPA [17] and CONCAWE [18] methods and spiked onto adsorbent tubes.

Adsorbent tubes (stainless-steel, 90 mm×5 mm I.D.) obtained from Perkin-Elmer (Beaconsfield, UK) were packed with 200±5 mg Tenax-TA (60–80 mesh) (Phase Separations, Clwyd, UK) and retained by heat-treated silanised glass-wool plugs. In preliminary experiments, a second adsorbent tube was connected "in-series" to investigate the occurrence of breakthrough of analyte from the first tube to the second. The tubes were conditioned overnight (i.e., by passing a stream of ultra-pure helium at 100 ml min^{-1} through each tube for 8–12 h at 300°C). The tubes were then capped with Swagelok end-caps and stored in sealed glass jars immediately prior to use.

2.2. Sampling

For air sampling in the field, sample pumps [low

flow (AMETEK S205 Model) Shawcity, Oxon, UK] were attached to individual adsorbent tubes using 30 cm lengths of clear, inert polythene tubing suitable for low-level organic compounds (BDH Merck, Eastleigh, UK). Each pump and tube assembly was calibrated using a bubble flow meter (SKC UK, Blandford Forum, UK) in order to measure and adjust the sampling flow-rate precisely. The pumps were adjusted to provide a flow-rate of 50±2 ml min^{-1}. Samples (static and personal) were taken adjacent to an operation where TDI was being handled in the open air for periods ranging from 15–20 min to 8 h. On completion of field sampling, the tubes were sealed with Swagelok end-caps and returned to the laboratory. Samples were chilled to 2°C in a laboratory refrigerator and analysed within 24 h.

2.3. Instrumentation and capillary column

Samples were thermally desorbed using a Perkin-Elmer automated thermal desorber (ATD-400 Model) which was connected to a Perkin-Elmer 8700 gas chromatograph (GC) via a 1-m length of sealed, deactivated fused-silica transfer line, 0.22 mm I.D., held at 150°C. A full description of the ATD operating principle for the analysis of trace organics in air was given previously by Bianchi and Cook [19] and Bianchi and Varney [20]. The gas chromatograph was fitted with a cradle-mounted, 50 m×0.22 mm I.D. BP-1 wall-coated open-tubular (wcot) capillary fused-silica column, 1.0 μm film thickness (SGE). The exit point of the column was connected to a twin-hole split ferrule permitting 50% of the column eluant to be routed to a flame ionisation detector. The remaining 50% is swept via a second 1-m length of transfer line at 250°C into an ion-trap detector (Finnigan MAT).

2.4. Analytical operating conditions

The analytical operating conditions were generally similar to those already described in Bianchi and Varney [20] for airborne VOC analysis.

2.4.1. Carrier gas

Ultrapure helium 5.5 grade was used throughout (Air Products, Basingstoke, UK).

2.4.2. ATD400

Cold-trap packing, 20 mg Chromosorb-106 (60-80 mesh); cold-trap low temperature, −30°C; cold-trap high temperature, 250°C; valve temperature, 150°C; split ratio (combined), 50:1; desorption oven temperature, 250°C; adsorbent tube desorption time, 10 min; desorption gas-flow through tube, 10 ml min^{-1}; carrier gas pressure, 170 kPa.

2.4.3. Gas chromatograph

Detector temperature, 250°C; carrier gas flow-rate, 1 ml min^{-1}. Temperature programming conditions: oven temperature, 60°C; isothermal time, 7 min; ramp rate, 10°C min^{-1}; final temperature, 280°C; final hold time, 10 min.

2.4.4. Ion-trap detector

Ionisation voltage, 70 eV; s $scan^{-1}$, 0.5; mass range, 50–200 mass units; transfer line temperature, 250°C; multiplier delay, 300 s; mass defect, 100 molecular mass units (m.m.u.)/100 u; acquire time, 35 min.

3. Results

Sampling efficiency was examined by sequentially injecting varying concentrations of TDI onto adsorbent tubes which had been connected to the injector inlet of a Perkin-Elmer 8320 "packed column" gas chromatograph. The flow-rate through the injector assembly and tube was set at 50 ml min^{-1}. The effluent gas stream from the tube was connected to the FID detector of the GC and continuously monitored to identify elution of TDI (i.e., to determine "breakthrough"). Standards in the range of 0.01 to 100.0 μg were prepared to begin with. Using 10-l air sample volumes, sample concentration ranges between 0.001 to 10 μg l^{-1} were determined. Blank determinations were made repeatedly to check the absence of contamination and artefacts, and to ensure that complete desorption of TDI was obtained using the standard analytical conditions.

Breakthrough was defined as the point at which the effluent concentration was 5% of the applied test concentration. Experiments were carried out by varying the temperature levels (i.e., to maintain isothermally stable temperatures to ±1°C) inside the

GC oven such as to replicate environmental conditions. A carbon-dioxide cooling system was used to attain temperatures below 15°C inside the GC oven. The levels of breakthrough were examined at levels of relative humidity ranging from 30% to 80% relative humidity. Experiments were also carried out at temperatures ranging from −10°C to 40°C. Based on 15 determinations (each) of 1, 5, 10, 20, 35 and 50-l sample volumes, laboratory results indicated that breakthrough was not identified with air sample volumes less than 50 l or TDI concentrations (mass on the tube) exceeding 500 μg, within the range of temperatures and relative humidities examined. Aliquots of TDI injected into the gas chromatograph were not observed to freeze inside the injector at temperatures below the range of 8°C–15°C as might have been anticipated by their physicochemical characteristics [1,2].

TDI was found to chromatograph well on the BP-1 column, yielding a sharp, symmetrical peak shape for injections of pure liquid TDI and where airborne TDI vapour was co-present in a matrix of aromatic and alkane solvents in field samples. A specimen gas chromatogram of 0.05 μg of pure TDI obtained from the FID is shown in Fig. 1. The absolute retention time was reproducible within 5%. Reproducibility was also examined by making sequential calibration injections across the sample concentration range of interest. The precision was evaluated by making a series of multiple injections on the same day (i.e., within-run precision) and over an extended period of time spanning three months (between-run precision). The results of these experiments, measured as the R.S.D., %, are shown in Table 1. The response was linear over the range investigated. Recovery of TDI from the adsorbent tubes following thermal desorption was always greater than 99.5% (n=53).

The TDI component was clearly resolved among

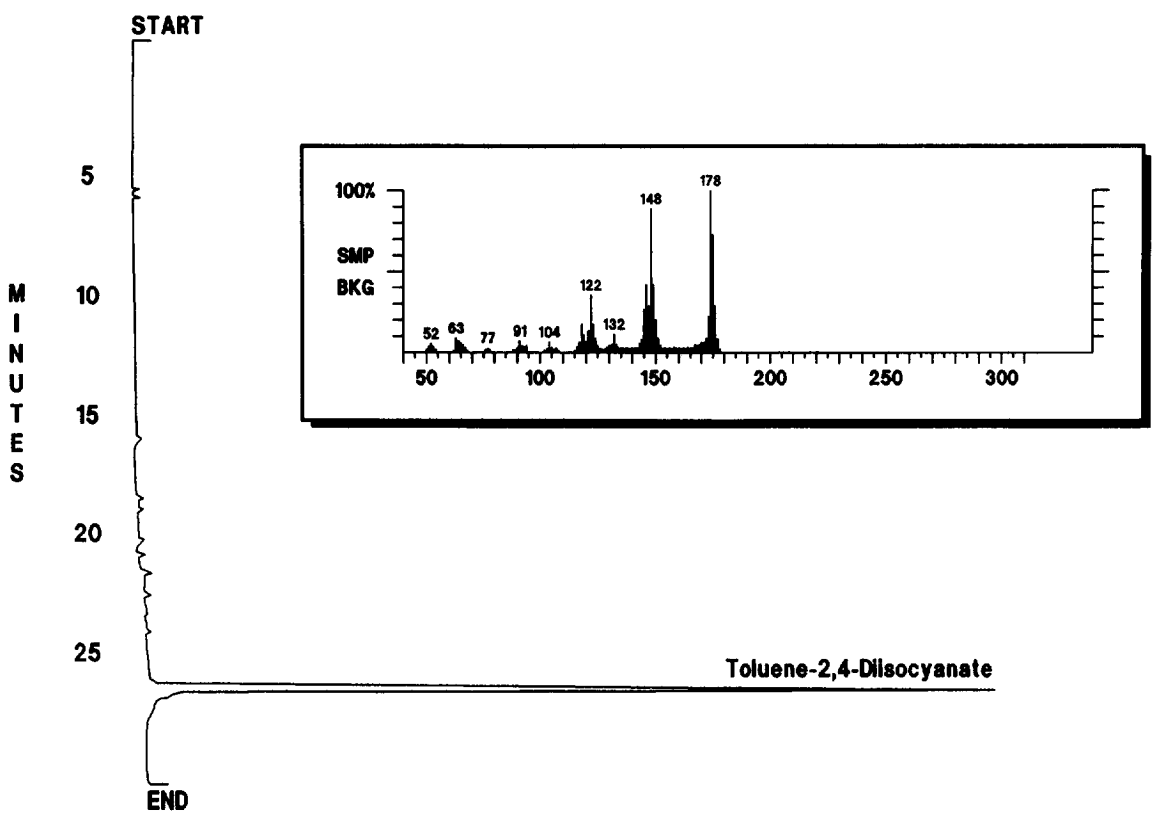

Fig. 1. Gas chromatogram (cGC–FID) of calibrant toluene-2,4-diisocyanate (0.05 μg) thermally desorbed from a Tenax-TA adsorbent tube. Diagram inset shows the mass-spectrum of toluene-2,4-diisocyanate obtained from the ion-trap detector.

Table 1
Precision of the TDI calibration experiments

n	Concentration of, 2,4-TDI on Tenax-TA adsorbent tube spikes ($\mu g\ l^{-1}$)	%R.S.D.
Within-run precision		
30	0.01	3.8
30	0.12	3.4
30	1.2	3.9
35	12.1	4.8
35	121	6.9
Between-run precision		
18		
18	0.01	4.4
18	0.12	4.9
18	1.2	5.2
18	12.1	5.1
18	121	7.0

Short term precision is expressed as the % relative standard deviation (R.S.D.).

alkane, kerosene, "white-spirit" and aromatic-based solvents in airborne field samples ($n=23$) obtained during solvent premixing operations. TDI produces a reproducible and consistently reliable mass-spectrum following the chromatographic step of the analysis, as shown in the inset within Fig. 1. The presence of TDI was confirmed by ion-trap detection in preliminary trials as a key part of risk assessment. For example, Fig. 2 shows a 3-dimensional diagram in which complete mass spectra are shown at designated points in a reconstructed total ion current chromatogram; the latter being a plot of recon-

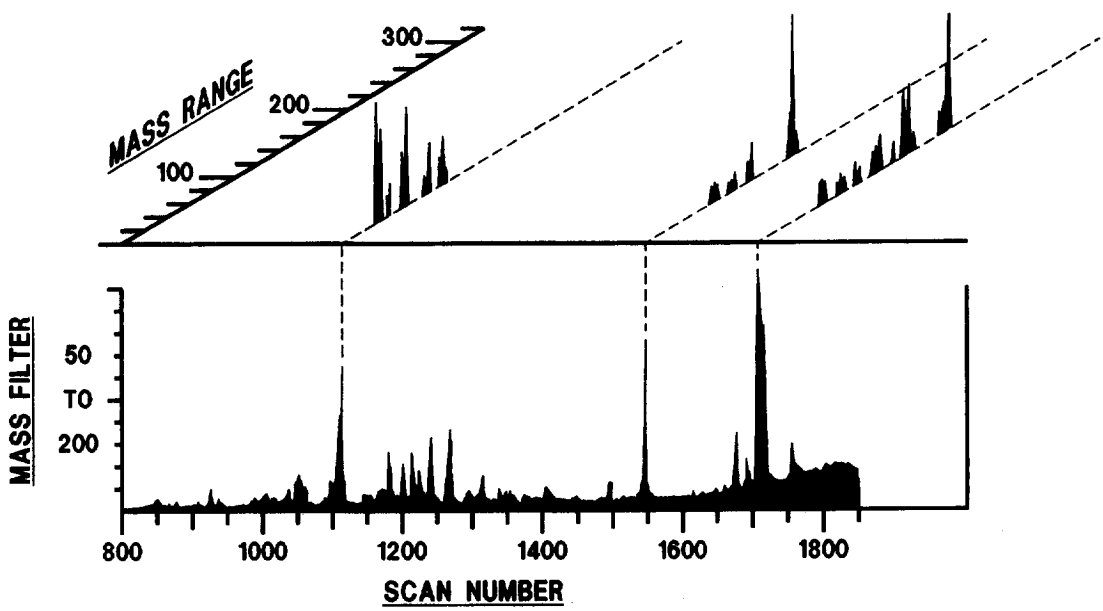

Fig. 2. Total ion current versus mass-spectra for volatile ion masses from 50 *m/e* to 200 *m/e*, showing the presence of TDI (toluene-2,4-diisocyanate) in a matrix of alkane and aromatic components including *n*-nonane and naphthalene. Scan number 1133=*n*-nonane, 1557=naphthalene, 1725=2,4-TDI.

structed total ion current versus scan number. This example was obtained from thermal desorption of an air sample taken adjacent to an "open-air" TDI handling facility during a drum transfer trial. Apart from the TDI component, the major components in the air sample are *n*-nonane and naphthalene.

The detection limit, taken as the concentration derived from a signal three times the noise level was less than 0.001 μg (mass of TDI on the tube) based on recovery from a standard 1 l air sample. This is approximately 1/20th of the maximum exposure limit (MEL) 8-h TWA for TDI (i.e., 20 μg m^{-3}), indicating that this method may be suitable for assessing compliance with personal exposure standards in the workplace.

Storage of TDI samples was investigated to determine the occurrence of losses, artefact formation or in-situ thermal or physical degradation. A range of standard samples (i.e., adsorbent tubes capped with Swagelok end-caps) were stored in the refrigerator at 2°C for up to 31 days. We observed that samples were stable for up to 10 days after which variable rates of TDI loss ranging from 5%–15% were measured. These findings were very similar to those documented by Colli et al. [13] for TDI in solution. These observations may suggest that some form of chemical degradation of the TDI inside the adsorbent tube is a key loss route. Further experiments will be required to ascertain the nature of this pathway.

4. Discussion

The key advantages of this method are its applicability to a capillary gas chromatographic separation technique and its relative experimental simplicity. Sample handling steps are considerably reduced, minimising the handling of absorbing solvents or delicate glassware in the field. For laboratories with the appropriate analytical equipment analysis turnaround times can be kept under 24 h, offering important advantages for assessing exposure controls and making decisions for employee health surveillance. The stainless-steel adsorbent tube and its attendant low-flow pump can be comfortably worn by the process or laboratory worker under a variety of conditions, without the risk of spillage or breakage.

The sampling technique pre-concentrates TDI effectively, and when used with thermal desorption offers a high degree of analytical sensitivity sufficient to assess exposure to levels well below current occupational exposure levels. Under modified sampling conditions, the method should also be applicable to environmental monitoring for trace levels of airborne TDI.

A further advantage of this method is that it offers the environmental scientist or occupational hygienist the ability to assess co-exposure to other toxicologically significant volatile organic substances in the inhalation matrix without requiring the need for separate sampling and analytical systems. Although this technique has not been experimentally evaluated for higher boiling isocyanates such as HDI and MDI, we believe the basic analytical approach described here for TDI should be worthy of evaluation by commercial and governmental regulatory health monitoring laboratories elsewhere.

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