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Evaluation of a modified Marcali technique with high-performance liquid chromatography–ultraviolet detection for the determination of 2,4-toluene diisocyanate in air

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ABSTRACT

This work describes an method for the determination of 2,4-toluene diisocyanate concentration in air. Traps containing 20–40 mesh silica gel coated with phosphoric acid are used. After the aspiration of air, sodium hydroxide is added to the silica gel, which is subsequently eluted with methanol. The amine formed is then separated on a C_{18} column using a mobile phase of phosphate buffer–methanol (60:40, v/v). This can be performed in less than 4 min. The effluent is monitored with a UV detector at 235 nm. The detection limit based on a 20-l air sample is 0.2 $\mu g/m^3$. Complete analysis requires about 30 min.

INTRODUCTION

Polyurethanes, produced from toluene diisocyanate monomers, are used extensively in the coating and plastic industry. In fact, sprayed-in-place polyurethane foam has become a popular form of thermal insulation in the construction industry. These foams are used in the building of roofs, storage tanks, barns, walk-in coolers and new homes. Consequently, a large number of different types of workers are potentially at risk of occupational isocyanate exposure. They include polyurethane foam producers, textile processors, foam converters, wire-enamelling workers, paint sprayers, diisocya-

nate resin production workers, organic chemical synthesizers, and workers in the rubber, varnish and adhesive industries [1]. As a result of their widespread use, respiratory problems and allergic reactions have been reported by workers exposed to isocyanates. The symptoms resulting from the inhalation of vapour, aerosol or fine particles of isocyanate include eye and mucous membrane irritation, coughing fits and dyspnoea [2]. Chronic exposure may lead to allergies such as asthma. Sensitization reactions do not occur in all individuals, but they can be observed with exposure to very low concentrations.

The treshold limit value (TLV) of the American Conference of Governmental Industrial Hygienists [3] for 2,4-toluene diisocyanate (TDI) as time-weighted average (TLV-TWA) is 36 $\mu g/m^3$ with a

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140 μg/m^3 short-term exposure limit (STEL). The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is 40 μg/m^3, similar to the above limit, with a 150 μg/m^3 action level [4].

In addition to spectrophotometric methods [5,6], used also in band-type monitors for continuous monitoring [7,8] a number of other procedures based on chromatographic techniques (HPLC, GC, TLC) have been developed to determine isocyanate content in air [9–13]. Most of these procedures, however, are both long and tedious, which severely limits their use in routine monitoring of industrial environments and controlled atmospheres where a rapid response is necessary to ensure air quality.

This paper describes the preliminary results of a promising method, which is simple and quick, for the analysis of TDI in air. The isocyanate was collected by reacting in an acid medium, like that of the traditional Marcali procedure [5], and the corresponding amine, after separation by reversed-phase liquid chromatography, was measured with a UV detector. The goal for the detection limit for a 20-l air sample was two orders of magnitude below the isocyanate TLV-TWA. This corresponded to 0.36 μg/m^3.

EXPERIMENTAL

Reagents and standards

TDI, 98% pure, was purchased from Kodak (Rochester, NY, USA), whereas 2,4-toluene diamine (TDA), 99% pure, a derivative of the hydrolysis of TDI, was purchased from Merck (Darmstadt, Germany). Methanol and water were of HPLC grade (Merck), while all other chemical were of analytical-reagent grade.

The mobile phase was phosphate buffer–methanol (60:40, v/v). The buffer was composed of 10 mmol/l dipotassium hydrogenphosphate adjusted to a pH of 7.0 with 1 mol/l phosphoric acid. Stock solutions of TDI were prepared at 1 mmol/l by diluting a known amount of the isocyanate with the proper amount of acetone, while stock solutions of TDA were prepared at the same concentrations weighing a known amount of amine with the proper amount of acetone. Working standard solutions of 0.3 mmol/l TDI and TDA were prepared by serial dilutions with acetone. TDI solution is not stable

and must be prepared daily; TDA solution is stable for 10 days when stored at 4°C.

Equipment

The liquid chromatograph consisted of a Perkin-Elmer series 400 pump, a Perkin-Elmer Model ISS 100 autosampler, a Merck 25 cm × 4.6 mm I.D. RP-18 column with 5-μm particles and a Perkin-Elmer Model LC 95 (3-μl cell) detector that monitored at 235 nm. Chromatograms were recorded and the peaks integrated on a Shimadzu Model CR 6A (attenuation 3, speed 5 mm/min) integrator.

Procedure

The absorber medium was prepared by mixing 0.6 ml of 10% H$_3$PO$_4$ (v/v) orthophosphoric acid with 200 mg of silica gel. After water evaporation at 75°C in a rotary evaporator (30 min), the silica gel was dried overnight in an oven at 80°C. Glass tubes, 85 mm × 5 mm I.D., were filled with 200 mg of the acidified absorber medium and closed at each end with glass wool plugs. Prepared traps will remain unaltered for at least 6 months if kept at room temperature. To prepare the calibration curve and to study the collection efficiency, known concentrations of TDI were added to the trap using a microsyringe. This was done in accordance with the NIOSH evaluation of sampling parameters. Air samples were sucked trough the trap using an MWG (Neuberger, Freiburg, Germany) membrane pump. The sampling rate was of the order of 0.5 l/min.

The contents of the trap were transferred to a glass test tube, while 0.5 ml of methanol and 100 μl of 10 mol/l sodium hydroxide were added to the silica gel. The mixture was first sonicated for 10 min and then centrifuged at 3300 g for 5 min. The supernatant was concentrated to 100 μl. A 20-μl volume was then injected into the HPLC system. The separation of the amine was carried out at a flow-rate of 1 ml/min.

RESULTS

The trapping efficiency of the orthophosphoric acid absorber medium for TDI was assessed by using two traps in series. To the first trap, 0.3 μmol of TDI were added with a microsyringe, while 20 l of air were sucked through both traps. In three differ-

ent experiments TDI was not detected in the second trap. This indicated that the trapping efficiency was essentially 100%, and that only one trap would be required for collection in the field.

Test performed with sampling tubes spiked with 3 μmol of TDI showed that virtually 100% of the TDA was recovered using 500 μl of methanol. To concentrate this volume to 100 μl, a vacuum centrifuge proved very useful. In comparison with a rotary evaporator, the vacuum centrifuge has two advantages: bumping is avoided and several samples can be handled at the same time.

Under the experimental conditions described above, good separation of TDA was achieved within 4 min. Typical chromatograms of a standard solution of TDI and of an air sample are shown in Fig. 1. Quantitation of TDA was performed using a calibration curve based on the measured absorbance at 235 nm.

In order to prepare the calibration curve, 1, 3, 5, 7 and 10 μl of working standard solution (0.3 mmol/l TDI) were introduced with a microsyringe in the traps. In this manner, standards of 2.6, 7.8, 13.0, 18.2, 26.0 μg/m^3 (for a 20-l air sample) were obtained. Analysis of the standard gave a calibration curve with $y = 4.5$ x, where y is the quantity of TDI and x is the peak area.

Fig. 2. HPLC profiles of 0.6 nmol of TDI standard solution added to the trap (A) and 0.6 nmol of TDA standard solution injected directly into the column (B). Peaks: 1 = front; 2 = TDI (A) or TDA (B).

Fig. 2 shows a chromatogram of 0.6 nmol of TDI added to a trap and that of the same amount of TDA added to another trap. The retention times and the areas of the peaks are identical, thus confirming the complete transformation of TDI into TDA.

The absolute retention time was reproducible within 4%. Reproducibility was also determined for the quantitative analyses of the calibration curve. Triplicate injections of standard sample at the four different concentrations gave an R.S.D. of less than 3%. The precision of the method was evaluated with both within-run assays (twelve equal samples of a standard solution added to the traps and analysed on the same day) and between-run assays (sample of equal concentration added to traps and analysed on ten consecutive days). These results are reported in Table I.

As is customary, the detection limit of the procedure was defined as the concentration derived from a signal three times the noise level. With an air sample of 20 l, the TDI derivative (TDA) showed a detection limit of 0.2 μg/m^3.

The linearity of the assay was verified by determining increasing amounts of TDI standards (up to 3 nmol). The response was linear over the range
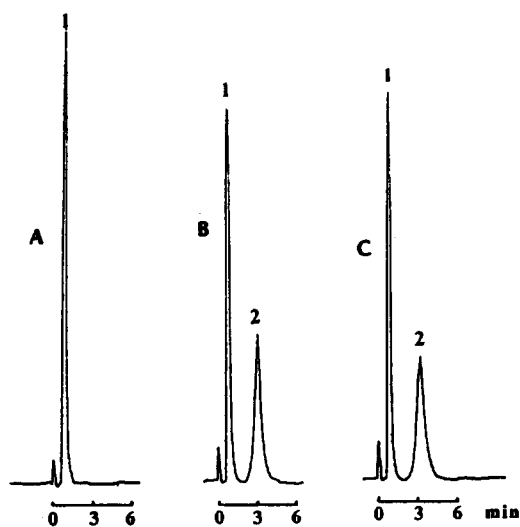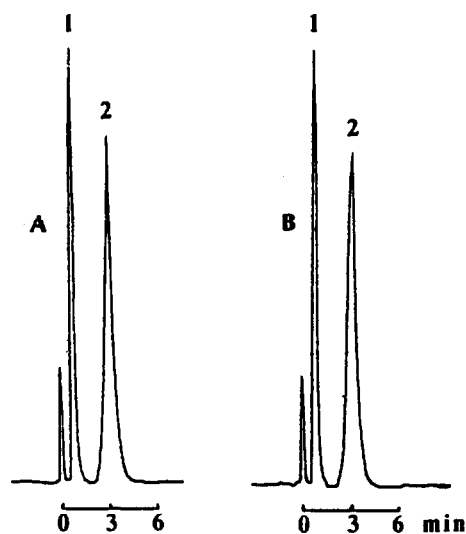

Fig. 1. HPLC profiles obtained by injecting methanolic eluate of the absorber: not treated, i.e. used as a blank (A), with a standard solution of 0.3 nmol of TDI (B), and after air sampling of a concentration of 2.5 μg/m^3 (C). Peaks: 1 = front; 2 = TDA.

TABLE I

PRECISION OF THE TDI ASSAY

n	x (nmol)	S.D.	R.S.D. (%)
Within-run precision			
12	0.3	0.013	4.2
12	1.5	0.046	2.9
Between-run precision			
12	3	0.023	7.0
12	15	0.080	4.9

investigated. Often it is not practical to analyse a sample for a number of days. In the present case, storage studies indicated that samples should be desorbed within 10 days for maximum recovery when they are stored at 4°C in the dark. Losses up to 5% can occur after 15 days. Recovery of TDA was unchanged up to 10 days for refrigerated desorbed solutions.

DISCUSSION

The principal advantage of this method is its considerably reduced sample handling prior to the chromatographic step. This can be done without significant sacrifice in sensitivity (30 pmol). The simplicity of the method is the result of the very rapid and complete one-step sample preparation as well as the fact that unreacted orthophosphoric acid does not interfere in the subsequent chromatographic step. Our method is linear up to at least 3 nmol, which is 100 times above the detection limit. Complete determination, including sample preparation and analysis, can be performed in less than 30 min.

The equipment required is relatively inexpensive and readily available. This enables on-site analysis to be carried out by most factories.

Since TDA is also present in the environment it can be trapped in the silica gel as well. As a result,

its presence can simulate that of TDI. In order to determine the environmental level of TDI alone, we took advantage of the fact that TDI does not collect on silica gel without acid. This was done by preparing two type of traps: one containing acid, which collected both TDI and TDA, and another without acid, which collected only TDA.

Other amines (hexamethylendiamine; 4,4'-diaminodiphenylmethane) and 2,6-toluene diisocyanate do not interfere since they have different retention times. We feel that the present method could be extended to other isocyanates (4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate) found in polluted air if the accuracy of the quantitative determination of the compounds can be confirmed.

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