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Gas chromatography of 4,4′-diphenylmethane diisocyanate in the workplace atmosphere[1]

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Abstract

A sensitive gas chromatographic procedure for the determination of 4,4′-diphenylmethane diisocyanate concentration in air is described. Traps containing 20–40-mesh silica gel coated with phosphoric acid are used. After the aspiration of the air, the silica gel is eluted with sodium hydroxide in methanol. The amine formed is then separated with a gas chromatograph and measured with a nitrogen–phosphorus detector. This can be performed in 7 min. Virtually no breakthrough occurs if an air concentration of up to 128 nmol in 20 l is sampled. The detection limit based on a 20-l air sample is 0.7 $\mu g/m^3$. Complete analysis requires about 30 min. The method was used to determine the concentration of 4,4′-diphenylmethane diisocyanate in working environments during spraying operations.

1. Introduction

The aromatic diisocyanates, toluene diisocyanate (a mixture of the 2,4- and 2,6-isomers) and 4,4′-diphenylmethane diisocyanate (MDI) are widely used raw materials in the production of polyurethane foams and coatings. They are the essential building blocks for the manufacture of flexible and rigid polyurethane foams, respectively. They are also involved in the production of other industrial substances, such as synthetic rubbers and elastomers, moulded products for marine and automotive purposes and polyurethane resins for paint and varnish formulations [1]. In recent years, the demand for MDI has increased, mainly owing to its low vapour pressure, which decreases the likelihood of inhalation exposure in its various applications. However, exposure to MDI does occur during production and application processes. The symptoms resulting from inhalation of vapour aerosol or fine particles of isocyanate include eye and mucous membrane irritation, coughing fits and dyspnea [2,3]. Chronic exposure may lead to allergies such as asthma. Although sensitization does not occur in all individuals, exposure to very low concentrations can trigger this reaction.

The threshold limit value for MDI according to the American Conference of Governmental Industrial Hygienists as a time weighted average (TLV-TWA) is 51 $\mu g/m^3$ [4]. The National Institute for Occupational Safety and Health (NIOSH)-recommended exposure limit (REL) is

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50 $\mu g/m^3$, with a 200 $\mu g/m^3$ ceiling (TLV-C) [5]. This represents the exposure level that should at no time be exceeded during the workday, not even instantaneously. The Occupational Safety and Health Administration (OSHA) only recommended a ceiling of 200 $\mu g/m^3$ [6]. Therefore, sensitive methods are required to determine this low threshold limit in the environment.

The most common sampling method involves bubbling of the air sample through an absorbing solution [7]. Impinger sampling, however, is cumbersome for workers. Because toluene or xylene is used as an absorbing solution [8], other drawbacks include possible spillage during sampling and the evaporation of organic solvents at high airflow sampling rates. Evaporation can be a limiting factor for the total air volume pumped and can present the risk of solvent exposure for workers.

The original procedure developed for the determination of the aromatic diisocyanates collected [9] has been modified in several studies [10–13]. Spectrophotometric methods are not specific: if mixtures of isocyanates are present, these methods only indicate the total concentration of the substances. Several chromatographic methods for determining isocyanates in air, including gas chromatography [14,15], thin-layer chromatography [16,17] and high-performance liquid chromatography [18–22], have been published. This paper describes the preliminary results of a promising method, which is quick and simple, for the determination of MDI in air. The isocyanate was collected by reaction in a solid acid medium, and the corresponding amine, after separation with gas chromatography, was measured with a nitrogen–phosphorus detector.

2. Experimental

2.1. Reagents and standards

MDI (97% pure) was purchased from Kodak (Rochester, NY, USA) and 4,4'-diaminodiphenylmethane (DAPM) (99% pure), a derivative of MDI hydrolysis, from Merck (Darmstadt, Germany). All other chemicals were of analytical-reagent grade.

Stock solutions of MDI were prepared at 10 mmol/l by diluting a known amount of the isocyanate with the appropriate amount of acetone, and stock solutions of DAPM were prepared at the same concentration by weighing a known amount of amine and dissolving in the appropriate amount of acetone. Working standard solutions of 0.3 μmol/l MDI and DAPM were prepared by serial dilution with acetone. MDI solution is not stable and must be prepared daily; DAPM solution is stable for 10 days when stored at 4°C.

2.2. Equipment

A Perkin-Elmer (Norwalk, CT, USA) Model 8500 gas chromatograph, equipped with a nitrogen–phosphorus detector (range 1×8) and an automatic on-column injector, was employed. After injection, the sample was routed through a 2 m × 4 mm I.D. glass column containing 1.5% OV-17 + 1.95 QF-1 on Chromosorb W HP (100–200 mesh) from Supelco (Bellefonte, PA, USA). Helium was used as the carrier gas at a flow-rate of 35 ml/min. The separation was performed with the injector at 250°C, the detector at 270°C and the oven at 220°C. Chromatograms were recorded and the peaks integrated on a Shimadzu (Kyoto, Japan) CR GA integrator (attenuation 3, speed 5 mm/min).

2.3. Procedure

Glass tubes (85 mm × 5 mm I.D.) used as traps were filled with 200 mg of H_3PO_4–silica gel prepared as described elsewhere [23]. These traps, closed at each end with glass-wool plugs, remain unaltered for at least 6 months if kept at room temperature [23]. Known concentrations of MDI were added to the trap using a microsyringe to prepare the calibration graph and to study the collection efficiency. This was done in accordance with the NIOSH evaluation of sampling parameters. Air samples were sucked through the trap using an MWG membrane pump (Neuberger, Freiburg, Germany). The

sampling rate was of the order of 0.5 l/min. The silica gel was then transferred from the trap into a glass test-tube and the DAPM was eluted with 600 μl of 1.7 mol/l sodium hydroxide in methanol. The mixture was first sonicated for 10 min and then centrifuged at 3300 *g* for 5 min. A vacuum centrifuge was used to concentrate the 600 μl of supernatant to 100 μl. Compared with a rotary evaporator, the vacuum centrifuge has two advantages: bumping is avoided and several samples can be handled at the same time. A 2-μl volume of the concentrated supernatant was then injected into the gas chromatograph.

2.4. Field studies

MDI values were obtained in a factory producing polyurethane-insulated pipes by the spray technique. Measurements were performed at various distances from the production machinery. The average temperature in the factory was 24°C and the relative humidity ranged between 40 and 50%. The flow-rate through the trap was maintained at 0.5 l/min. After 10 and 20 min of sampling the solid absorbers were analysed for MDI content. The experiment was repeated five times on the same day.

3. Results

3.1. Collection and recovery efficiency

The collection efficiency of the solid absorber medium for MDI was examined by using two traps in series. Increasing amounts of standard MDI were added to the first trap with a microsyringe while air at a flow-rate of 0.5 l/min was sucked through the traps. The air flow was continued for 40 min. After sampling, the absorbent medium in each trap was analysed for the MDI derivative using the reported method. The results are given in Table 1. There is 1.6% MDI breakthrough at the highest concentration studied. There is no breakthrough from the first trap at a concentration of 4 nmol, equivalent to 20 l of 50 μg/m^3 concentration (the current threshold limit value for MDI). This indicated that the trapping efficiency was essentially 100% and that only one trap is required for collection in the field. Tests performed with sampling tubes spiked with 3 μmol of MDI showed that virtually 100% of the DAMP was recovered using 600 μl of sodium hydroxide in methanol. Dharmarajan [24] has demonstrated that under normal operating conditions virtually all of the MDI in air is present as an aerosol and not in the gaseous form. The efficiency of MDI aerosol collection was studied by inserting a Teflon filter between the trapping system and the pump. After sampling, the filter was eluted with acidic methanol and the solution analysed for MDI content following our procedure. The concentration of MDI collected by the filter was less than 1.8% of the MDI collected by the trapping system in the workplace atmosphere. Our experimental procedure consisted of four runs, each repeated twice; the results ranged from 2.3 to 21.1 μg/m^3.

Table 1
Efficiency of the sampling procedure for the collection of MDI

Run[a]	MDI added (nmol)	MDI collected (nmol)	
		Trap 1	Trap 2
1	2.0	2.00	–
2	4.0	3.94	–
3	8.0	7.88	–
4	64.0	64.31	–
5	128.0	127.94	–
6	256.0	251.58	4.10

[a] Each run is the mean of three experiments.

3.2. Chromatographic analysis

Good separation of DAPM was achieved within 7 min under the experimental conditions described above. Typical chromatograms of a standard solution of MDI and of an air sample are shown in Fig. 1. Quantification of DAPM was performed using a calibration graph. The calibration graph was prepared by introducing 1.0, 3.0, 5.0, 7.0 and 10.0 μl of working standard solution (0.3 μmol/l MDI) with a microsyringe

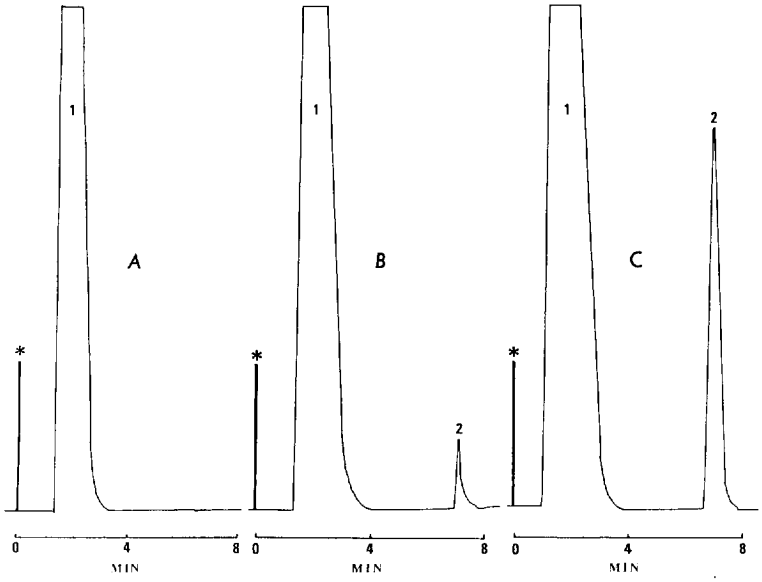

Fig. 1. Gas chromatogram of methanolic eluate of the absorber: (A) untreated, i.e. used as a blank, (B) with a standard solution of 0.3 nmol of MDI and (C) after air sampling of a concentration of 20.7 $\mu g/m^3$. Peaks: 1 = front; 2 = DAPM; * = injection.

into the traps, thereby obtaining standards of 3.75, 11.25, 18.75, 26.25 and 37.50 $\mu g/m^3$, respectively (for a 20-l air sample). Analysis of the standard gave a calibration graph $y = 4.5x$, where y is the amount of MDI and x is the peak area. The resulting function was used to calculate the amount of MDI in a sample. The calibration function was checked at regular intervals by injecting 1.0, 5.0 and 10.0 μl of working standard solution.

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

The absolute retention time was reproducible within 6%. Reproducibility was also determined for quantitative analyses via the calibration graph. Triplicate injections of standard sample at the five different concentrations gave an R.S.D. of less than 5%. The linearity of the assay was verified by determining increasing amounts of MDI standards (up to 3 nmol). The response was linear over the range investigated.

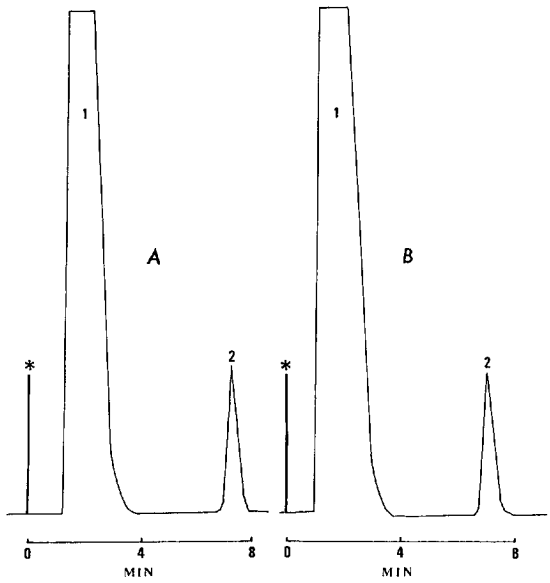

Fig. 2. Gas chromatogram of (A) 0.6 nmol of MDI standard solution added to the trap and (B) 0.6 nmol of DAPM standard solution injected directly into the column. Peaks: 1 = front; 2 = (A) MDI or (B) DAPM; * = injection.