

Emission of diisocyanates in indoor air

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ABSTRACT

The objective of this study was to measure the amounts of emissions of diisocyanates from polyurethanes. The amounts of primary emissions of diisocyanates from urethane adhesive, painting and varnish were measured as equilibrium concentrations in a desiccator after 1.0, 3.0, 6.0 and 24 h from the start of the experiment. The amounts of secondary emissions of diisocyanates by interactions between polyurethanes and diluted gas-phase acetone (0, 15.2 and 841 ppm) or α -pinene (0, 0.704 and 7.04 ppm) were measured as flux rates. Diisocyanates were collected in filters coated with 1-(2-pyridyl)piperazine, which selectively reacts with diisocyanates and becomes high boiling derivatives. Toluenediisocyanate, hexamethylenediisocyanate and methylenebisphenyldiisocyanate were analysed by high performance liquid chromatography. The primary emissions were not observed. The secondary emission of toluene-2,4-diisocyanate was identified at 841 ppm of acetone.

INDEX TERMS

Polyurethane; Diisocyanate; Primary emission; Secondary emission

INTRODUCTION

Polyurethanes consist of polymers of diisocyanates and polyols and are used as thermal insulating materials, paints, adhesives, synthetic fibres and so on. Thus, they exist indoors all the time. Toluenediisocyanate (TDI), which represents diisocyanates as sources of the polymer, is suspected to be the cause of occupational asthma in polyurethane factories (Werner, 2002). Moreover, odour thresholds of diisocyanates are as much 100 times that of the time weight average (TWA) of diisocyanates. For example, the odour threshold of TDI is 0.4 ppm while its TWA is 0.005 ppm (Beliles *et al.*, 1994). Residents might not be aware of the exposures to diisocyanates and are badly affected. Pollutants such as volatile organic compounds (VOCs) and carbonyls in indoor air are emitted from building materials as primary emission and secondary emission (Wolkoff, 1999). Diisocyanates as well as VOCs may be emitted. Methylenebisphenyldiisocyanate (MDI) was measured as residues in commercial rigid polyurethane and laminate food packages (Andrew *et al.*, 1995). Hexamethylenediisocyanate (HDI) was emitted from coating materials after 5.0, 48 and 72 h

after the application (Salthammer *et al.*, 1999). Total volatile organic compounds (TVOCs) from urethane adhesives in test chambers were observed at high concentration (Kumagai *et al.*, 1997). Urethane paints are stored in bulk during indoor renovations. Thus, diisocyanates during renovations might be in high concentration. Secondary emissions of diisocyanates might happen by interactions between polyurethane and acetone or α -pinene which exist indoors all the time. Acetone is used as a solvent and dissolves diisocyanates. α -pinene is emitted from woods and relatively more reactive than other indoor compounds. The objective of this study is to measure the amounts of diisocyanates by primary emissions from polyurethane and secondary emissions by the interactions between polyurethanes and acetone or α -pinene.

METHODS

The amounts of primary emissions of toluene-2,6-diisocyanate (2,6-TDI), toluene-2,4-diisocyanate (2,4-TDI), 1,6-hexamethylenediisocyanate (1,6-HDI) and 4,4-methylenebisphenyldiisocyanate (4,4-MDI) from urethane adhesive, paints and varnish were measured by using set-ups shown in Figure 1. Four petri dishes (90 mm) coated with adhesive, paint or varnish were set in a desiccator. Pure air was injected into the desiccator at 0.20 L/min, 25°C and 0.10 MPa. The gas phase in the desiccator was collected for 30 min after 1.0, 3.0, 6.0 and 24 h from the start of the experiment and the concentrations of diisocyanates were measured.

Secondary emissions of 2,6-TDI, 2,4-TDI, 1,6-HDI, and 4,4-MDI by interactions between rigid polyurethane and gas-phase acetone and α -pinene were measured by using the set-up shown in Figure 2. Rigid polyurethanes were cut into pieces (10 mm \times 10 mm \times 10 mm). These pieces were put into a glass column (50 mm). The glass column was set in an incubator (FUKUSHIMA). Revised gas, acetone or α -pinene diluted by pure air was continuously controlled by a flow controller (Permeater, Gastec) at constant concentrations. Revised gas was injected at 0.20 L/min, 25°C, and 0.10 MPa. Rigid polyurethanes were exposed to revised gas for 6.0 h. The concentrations of revised gases were calculated from emission amounts of liquid-phase acetone or α -pinene used as the sources of revised gases in the Permeater. Fourier transform infrared spectrometry (FTIR, JASCO) was used to monitor whether the concentrations of revised gases were constant. Emissions of diisocyanates were measured as flux rates from the surfaces of rigid polyurethanes. Changes of the flux rate were measured by changing the concentrations of acetone or α -pinene.

Diisocyanates were collected in glass fibre filters impregnated with 1-(2-pyridyl)piperazine (1-(2PP)) (ORBO-80 Filter, Supelco) that selectively reacts with diisocyanates and becomes a high boiling point derivative. After the sampling, derivatives were extracted into a mixed solution such as acetonitrile : dimethylsulfoxide = 90 : 10 (v/v) and analysed by high performance liquid chromatography (HPLC, Hewlett Packard). Table 1 shows the analysis conditions. A standard solution of the derivatives of 2,6-TDI, 2,4-TDI, 1,6-HDI and 4,4-MDI

were used to make calibration curves. Tables 2 and 3 show the detection limits and the quantification limits of the experiments. The detection limits and the quantification limits were calculated as three times and 10 times the standard deviation, respectively.

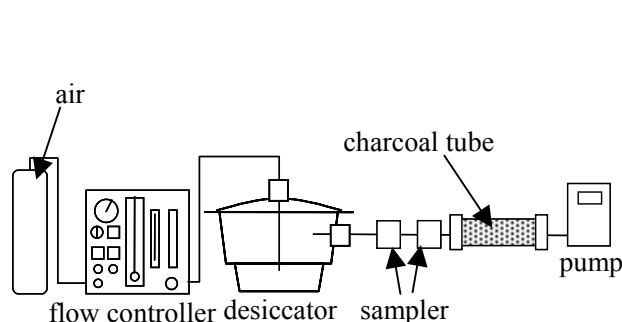


Figure 1 Experimental set-ups for measurement of primary emission

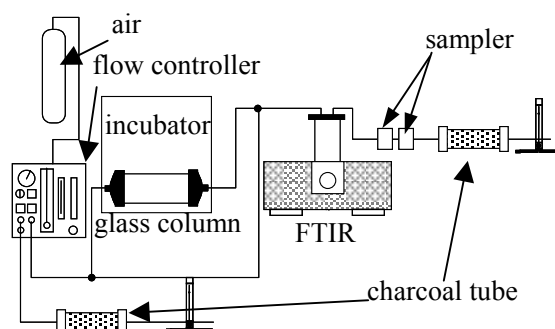


Figure 2 Experimental set-ups for measurement of secondary emission

Table 1 Analysis conditions of HPLC

Instrument	Condition
HPLC	HP1100
Column	Supelcosil LC-8-DB(7.5 cm * 4.6 mm μ m)
Mobile	0.010 M Ammonium Acetate : Acetonitrile = 65 : 35
Flow rate	1.0 mL/min
Injection	5.0 μ L
Column	40 °C
Detector	Diode Array Detector(DAD) 254

Table 2 Detection limits and quantification limits of diisocyanates as equilibrium concentrations [μ g/m³].

	2,6-TDI	1,6-HDI	2,4-TDI	4,4-MDI
Detection limit	2.55	1.95	3.33	5.79
Quantification limit	8.49	6.49	11.1	19.3

Table 3 Detection limits and quantification limits of diisocyanates as flux rates [$\mu\text{g}/\text{m}^2/\text{h}$]

	2,6-TDI	1,6-HDI	2,4-TDI	4,4-MDI
Detection limit	0.0530	0.0406	0.0695	0.121
Quantification limit	0.177	0.135	0.231	0.402

RESULTS AND DISCUSSION

Table 4 shows the results of equilibrium concentrations of 2,6-TDI, 2,4-TDI, 1,6-HDI and 4,4-MDI. These concentrations were below the detection limits. Thus, the primary emissions of diisocyanates were not confirmed.

Table 5 shows the results of flux rates of 2,6-TDI, 2,4-TDI, 1,6-HDI and 4,4-MDI. The flux rates of 2,6-TDI, 1,6-HDI and 4,4-MDI were below the detection limits for all conditions of the concentrations. Flux rate of 2,4-TDI was over the detection limit and below the quantification limit at 841 ppm of acetone. Thus, it was assumed that secondary emission of 2,4-TDI was a result of the interaction between rigid polyurethane and gas-phase acetone. For example, if 2,4-TDI was emitted from the surfaces of rigid polyurethanes at $0.116 \mu\text{g}/\text{m}^2/\text{h}$, which is a half of the quantification limit, the equilibrium concentration of 2,4-TDI was calculated to be 4.28×10^{-2} ppb in Japanese houses (Table 6). This concentration is as much 1/100 of TWA of 2,4-TDI, and may be as much as the guideline limit for indoor air. The guideline limits for other compounds indoors are usually set at 1/10–1/100 of the TWA limit.

Table 4 Equilibrium concentrations of diisocyanates as primary emission [$\mu\text{g}/\text{m}^3$]

	Time [h]											
	Urethane adhesive				Urethane painting				Urethane coating			
	1	3	6	24	1	3	6	24	1	3	6	24
2,6-TDI	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1,6-HDI	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2,4-TDI	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
4,4-MDI	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Table 5 Flux rates of diisocyanates from polyurethane by the interactions of polyurethane/acetone or α -pinene interaction

	Concentration[ppm]					
	Acetone			α -pinene		
	0	15.2	841	0	0.704	7.04
2,6-TDI	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
1,6-HDI	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2,4-TDI	N.D.	N.D.	< 0.231	N.D.	N.D.	N.D.
4,4-MDI	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Table 6 The average sizes of Japanese houses (Construction Research and Statistics Division, Information and Research Department, Policy Bureau, Ministry of Land, Infrastructure and Transport, 2000)

Floor area [m ²]	97.5
Height [m]	2.4
Ventilation ratio [/h]	0.5

CONCLUSION

- Primary emissions from three kinds of samples were not confirmed.
- Secondary emission of 2,4-TDI by the interaction between polyurethane and 841 ppm of acetone was identified.

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