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Measurement of 2,4-toluene diisocyanate concentrations by different samplers

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Abstract

The standard sampling methods for toluene diisocyanate (TDI) only collect total TDI without separating the aerosol and gas phases. There are few other samplers, such as the dual filter, triple filter and annular denuder systems (ADS), which are able to sample the aerosol and gas phases simultaneously. This field study was conducted at two workplaces to access the total 2,4-TDI and the gaseous and aerosol TDI concentrations by different samplers simultaneously. In addition to the standard sampling time of 15 min, sampling was done for 30 and 60 min to study the effect of sampling time on the measured 2,4-TDI concentrations. Test results at two workplaces show that gas-phase 2,4-TDI is the predominant species and the aerosol phase concentration is very small. The measurements using various samplers show that the sampling time influences the sampled TDI concentration considerably which may be due to reaction of TDI with water vapor and polyo in the sampling process. It is evident that as sampling time increases the TDI concentration decreases. Laboratory test was also conducted using pure gas-phase 2,4-TDI to confirm the sampling time effect on the measured concentrations found in the field study.
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1. Introduction

Toluene diisocyanate (TDI) is a major isocyanate compound used commercially in surface coating, adhesives, resins, elastomers (esp. polyurethane foams), binders and sealants [1]. The compound has two –N=C=O functional groups attached to a parent toluene. It is known as semi-volatile organic compounds (SVOC) with the vapor pressure of 0.025 mmHg (or 32.9 ppm) at 25 °C. There are two primary isomers of TDI, namely 2,4-TDI and 2,6-TDI. Commercial grades of TDI are usually mixtures of these two isomers, with the 80% of 2,4-TDI and 20% of 2,6-TDI mixtures being the most common. The 65–35% mixture is also frequently used. The earlier research showed that the exposure to TDI in the workplace may result in occupational asthma due to sensitization [2,3]. Less prevalent syndrome is contact dermatitis (both irritant and allergic forms) and hypersensitivity pneumonitis (HP) [2,3].

The Occupational Safety and Health Administration (OSHA) have established a permissible exposure limit (PEL) of 0.02 ppm for TDI based on toxicity, epidemiology, physical chemistry and industrial hygiene data. The National Institute of Occupational Safety and Health (NIOSH) has recommended an exposure limit of 0.005 ppm for the time-weighted average isocyanate concentration during a 10-h work-shift, and 0.02 ppm as a ceiling for any 10-min sampling period in 1978 [4]. In Taiwan, the maximum concentration for 15-min exposure to TDI is set at 0.005 ppm [5] as determined by a standard method similar to that of OSHA.

There are several TDI sampling methods used in the work place such as the NIOSH and OSHA methods which are suitable for measuring the total TDI sampling without separating gaseous and particulate phase. The OSHA 42 is a standard method which uses an open-face 37-mm filter cassette sampler

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containing a glass fiber filter (GFF) coated with 0.1 mg of 1-2PP (1-(2-pyridyl)piperazine) to collect airborne total TDI [1,6–9]. However, the open-face cassette was found to collect 21% less 2,4-TDI than the modified closed-face cassette where the inner surface was lined with a GFF coated with 1-2PP and the lined GFF was also analyzed for 2,4-TDI [10]. This test was performed using a known amount of 2,4-TDI liquid to generate 2,4-TDI gas in front of the open-face or closed-face cassette, and the collection efficiency was calculated based on the ratio of the amount of TDI collected by the cassette to total TDI generated [10]. Recently, it is found that the respiratory deposition site of inhaled TDI and health effects depends upon the physical state of airborne TDI, i.e. gas or aerosol phase [11]. Thus the knowledge of correct gas and aerosol phase TDI present in particular workplace is important.

The dual filter system (DFS, ISO-CHEK) [12] and the annular denuder are two methods currently used to separate TDI according to their physical state. The aerosol phase TDI is collected on an uncoated (or regentless) Teflon filter while gaseous TDI is collected on a reagent-coated GFF in the dual filter system [12,13]. The loss of isocyanate species in the aerosol fraction due to curing reactions occurs between the time of collection and postsampling derivatization. This problem would be expected to be greater for longer sampling time and more reactive isocyanate system [11]. The Teflon filter adsorbs some gaseous SVOCs along with the gaseous TDI in the dual filter system [14]. Thus it gives overestimation of aerosol phase TDI concentration. In the annular denuder system (ADS), the annular denuder tube is used for gas collection while a reagent coated GFF is used for aerosol collection [15]. The coating and extraction procedure of the annular denuder system is somewhat complicated.

The triple filter system (TFS) using two front uncoated Teflon filters and one coated GFF in series, was tested in the laboratory together with the ADS and DFS for simultaneous sampling of gaseous and aerosol TDI [16]. A model was developed to calculate the accurate amount of gaseous and aerosol TDI using the amount of TDI collected by each of the three filters. The model equations are the following:

$$M_a = M_1 - \left(\frac{M_2}{M_3}\right)(M_2 + M_3) \quad (1)$$

$$M_g = \left(\frac{M_2}{M_3}\right)(M_2 + M_3) + M_2 + M_3 \quad (2)$$

where M_a and M_g are the actual amount of aerosol and gaseous TDI; M_1, M_2 and M_3 are TDI collected on the first and second Teflon filters, and GFF, respectively. The laboratory test with sampling time of 15 min showed that the TFS is in good agreement with the reference ADS both in the gaseous and aerosol TDI concentrations [16]. The overestimation of the aerosol TDI concentration and underestimation of the gaseous TDI concentration in case of the DFS are minimized.

The measurement of ambient air at polyurethane production factory by Walker and Pinches [17] showed appreciable concentrations of toluene diamine (TDA). They concluded that TDA occurred as a hydrolysis product of TDI in the factory process. However, Holdren et al. [18] indicated that removal of gaseous TDI from air is not dependent on water vapor concentration, and in fact, the gas-phase reaction between TDI and H_2O appears to be quite slow. That is, TDA is not formed in significant quantities by gas-phase reaction between TDI and H_2O. A dynamic flow system was used to generate different humidity levels and TDI concentrations in laboratory studies by Dharmarajan [19]. The sampling medium consisted of a 13-mm binder-free glass fiber filter, coated with 1-2PP and diethylphthalate (DEP), mounted in a 13-mm filter cassette. The result showed that relative humidities (RH) ranging from 30 to 80% did not affect the TDI concentrations. Wang [20] reported that the SUPELCO ORBO-80 coated filters can collect 2,4-TDI efficiently under humidity levels up to about 80%, but the collection efficiencies will be decreased by about 20–30% under extremely humid conditions.

Although the effect of relative humidity on the TDI concentration measured using filter samplers has been studied in the past, the sampling time duration is an important factor which deserves further investigation for the reactive gas, such as TDI. The objective of this study is to measure the concentrations of 2,4-TDI using five kinds of samplers, at two workplaces to study the sampling duration effect on the total, aerosol and gaseous TDI concentrations of these samplers. The effect of sampling time on the measured gaseous TDI concentration was also examined in the laboratory at two different relative humidities.

2. Materials and methods

The TFS, ADS, DFS, open- and closed-face filter cassettes (OFFC, CFFC) samplers were used during the field study and the ADS, and two OFFCs (using coated GFF and uncoated Teflon filter, respectively) were used in the laboratory study.

2.1. Samplers

The TFS sampler was designed previously [16] which consists of three filters: two 37-mm, 2.0-μm Teflon filters (Zefluor™, PTFE, Pall Co., Ann Arbor, MI, USA) in series followed by a 1.0-μm, 37-mm GFF (type A/E, SKC Inc., Eighty Four, PA, USA) coated with 1 mg of 1-2PP according to the OSHA 42 [9]. The first Teflon filter is to collect aerosol-phase TDI, while the second is to calibrate the gas-phase TDI adsorbed by the first Teflon filter using the model of the triple filter system [16]. The GFF is used to collect the remaining gas-phase TDI. The sampling flow rate is maintained as 2.0 L/min.

The DFS cassette was designed by Lesage et al. [13]. The front filter is a Teflon filter that collects TDI in the aerosol form. The back filter is a GFF impregnated with 1 mg of 1-2PP to capture gas-phase TDI. The sampling flow rate is 1.0 L/min.

The ADS sampler (URG-2000-15T, Chapel Hill, NC, USA) consists of an annular denuder coated with 1 mg of 1-2PP in series with a size selective aerosol preseperator and a backup filter [15]. All components are made of borosilicate glass, Teflon®, or stainless steel. The inlet aerosol preseperator is a Delrin elutriator followed by an acceleration jet and a glass frit impactor with $D_{50} = 2.5$ μm at the sampling flow rate of 1.7 L/min. The

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