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Sampling Time Effect on 2,4-Toluene Diisocyanate Concentration by using Different Samplers

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Sampling Time Effect on 2,4-Toluene Diisocyanate Concentration by using Different Samplers

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Abstract: In order to understand the sampling time effect on the 2,4-TDI (Toluene diisocyanate) concentrations, laboratory and field tests were conducted in this study. An ADS (annular denuder sampler) and two OFFCs (open face filter holders) with different filters were tested for 1 to 120 minutes in the laboratory using 2,4-TDI gas. In the field study, the standard sampling method, the dual filter the triple filter and

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annular denuder systems were used at two workplaces to study the change of 2,4-TDI concentrations with sampling time from 15 to 60 minutes. The test results in both laboratory and field studies 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 very significantly.

Keywords: Toluene diisocynanate, sampling method, denuder sampler, filter sampler

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INTRODUCTION

Toluene diisocyanate (TDI) is a major isocyanate compound used commercially in surface coating, adhesives, resins, elastomers (esp. polyurethane foams), binders, and sealants (1). 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 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. 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. 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-hour work-shift, and 0.02 ppm as a ceiling for any 10-minute 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 workplace 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 containing a glass fiber filter (GFF) coated with 0.1 mg of 1-2PP to collect airborne total TDI (1, 6–9). The modified closed-face cassette sampler was found to collect 21% more 2,4-TDI than the open-face design (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 absorbs 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 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). The laboratory test with sampling time of 15 minutes 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.

MATERIAL AND METHODS

The ADS, and two OFFCs (using coated GFF and uncoated Teflon filter, respectively) were used in the laboratory study and the TFS, ADS, DFS,

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open- and closed-face filter cassettes (OFFC, CFFC) samplers were used in the field study.

The TFS sampler was designed previously (16) which consists of three filters: two 37-mm 2.0-μm Teflon filters (Zefluor^{TM}, PTFE, Pall Co., Ann Arbor, Mich., 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 (1-(2-pyridyl)-piperazine) 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. 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:

$$M_a = M_1 - (M_2/M_3)(M_2 + M_3) \quad (1)$$

$$M_g = (M_2/M_3)(M_2 + M_3) + M_2 + M_3 \quad (2)$$

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 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, N.C., 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 following annular denuder section consists of inner and outer glass cylinders with an annular spacing of 2 mm in between. The outer diameter of the denuder tube is 13 mm, and the length is 75 mm. The final stage of the sampler is a 25-mm Teflon filter pack containing a GFF impregnated with 1 mg of 1-2PP. The diffusion coefficient of the denuder for TDI was estimated to be 0.061 cm^2/s at 25°C using the method of Tucker and Nelken (21). The penetration of TDI through the denuder was calculated to be 1.9% (or the efficiency is 98.1%) at 1.7 L/min flow rate using the Possanzini equation (22).

The closed-face 37-mm filter cassette (CFFC, Gilian, N.J., USA) includes an inlet cover, a spacer, a coated glass-fiber filter, a back-up pad, and a bottom. If the inlet cover is removed, it becomes an open-face 37-mm filter cassette (OFFC). Both aerosol and gas-phase TDI are collected on the 37-mm diameter GFF impregnated with 1 mg of 1-2PP at the flow rate of 1.0 L/min.

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Laboratory Study

The laboratory test using artificially generated TDI gas was conducted using the ADS and two OFFCs, one of which used Teflon filter while other used GFF. Since uncoated Teflon is used as the first filter in both the DFS and TFS, no additional laboratory tests using these two samplers were conducted.

The schematic diagram of the gaseous TDI generating system is shown in Fig. 1. Gaseous and aerosol TDI were generated by a liquid TDI-containing impinger with a flow rate of 30 mL/min adjusted by a dynamic gas calibration system (Model 146, Thermo Environmental Instrument Inc., Franklin, MA, USA). The flow rate of dilution air was adjusted by a rotameter to generate the required TDI concentration. A zero air supply system (Model 111, Thermo Environmental Instrument Inc., Franklin, MA, USA) was used to supply clean and dry air in the TDI generating system. The TDI test stream was further conditioned to about 30°C by a water bath and the heating tapes attached to the Teflon tubes before the mixing chamber. The humidity of the test stream was increased by a bubbler containing deionized water at a flow rate of about 5 L/min. Flow rate of each sampler was controlled by portable air sampling pumps (Gilian Instrument Corp., Ringoes, USA). The flow rates of the pumps and air flow through the rotameter were calibrated using a bubble calibrator (PN#800268, Gilian Instrument Corp).

The reagents used were: 2,4-TDI in 1000 μg/ml standard solution—from Fluka (Buchs, Switzerland); urea derivative of TDI (2,4-TDIU) in 1000 μg/ml standard solution—from Supelco (Bellefonte, Pa., USA); 1-2PP—from Aldrich (Milwaukee, Wis., USA); acetonitrile (ACN) and methylene chloride—from J.T. Baker (Phillisburg, Pa., USA); dimethyl sulfoxide (DMSO), ammonium acetate, and glacial acetic acid—from Merck (Darmstadt, Germany).

In the mixing chamber, aerosol TDI was removed by using a Teflon filter allowing only pure TDI gas to enter the test chamber (L60 cm × W50 cm × H50 cm) where the ADS and 2 OFCCs were tested. The sampling time of 1,

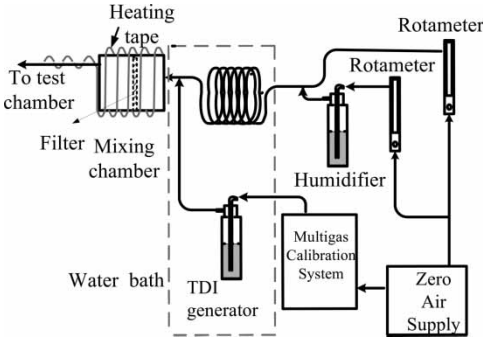

Figure 1. Laboratory setup for gas 2,4-TDI generation.

15, 30, or 60 min was used for the test. RH was maintained at 42.1 $\pm$ 0.5% or 83.1 $\pm$ 2.2%, and temperature was 28.3 $\pm$ 1.8°C. For each sampling condition, 6 samples were taken for each sampler.

Field Study

The field study was conducted at two workplaces. The first work place is a plant which makes flexible polyurethane (PU) foam with the raw material of 80/20 mixture of TDI. All processes were carried out manually. When the samplers were placed at a fixed stand very near (about 20 cm) the foaming tank, it was found that the TDI concentrations of different samplers were not uniform. Therefore it was decided to use only the ADS to study the gaseous and aerosol TDI concentrations at the fixed 15-min sampling duration at different distances from the foaming tank. Then the comparison test using 5 different samplers at different sampling durations (15, 30 and 60 minutes) was conducted at the breathing zone two meters from the foaming tank, where the aerosol TDI concentration was very low and only gaseous TDI existed as shown by the ADS. For the comparison test, 6 samples were taken for each sampler for each sampling duration. The temperature was 28.5 $\pm$ 1.9°C and RH was 42.2 $\pm$ 6.9% during the test.

The second field study was conducted in front of a painting booth for the surface finishing of furniture. The painting material used was fixed and it was polyo, 50% 2,4-TDI and toluene with the volume ratio of 1 : 1 : 2. The booth was well ventilated using an exhaust fan with the horizontal wind speed of about 0.5 m/s at the working zone of 2 m in height and 5 m in width. The comparison test was also conducted using five different samplers at different sampling durations (15, 30, and 60 minutes) about 1.5 m above the ground and at a distance of about 1 m away from the painting gun used. Six samples were taken for each sampler for each sampling duration. During the test, temperature was 23.8 $\pm$ 0.4°C and RH was 68.5 $\pm$ 2.2%.

Sample Preparation and Analysis

The glass-fiber filters and the annular denuders were coated with 1 mL of 1.0 mg/mL 1-2PP/methylene chloride solution and then dried by nitrogen. The Teflon filters were uncoated. After sampling, the GFFs were placed into a vial and extracted with 4 mL of 10/90 (v/v) DMSO/ACN solutions. The Teflon filters were immediately placed into an extraction vial containing 0.5 mL of 1.0 mg/mL 1-2PP/methylene chloride solution and 4 mL of the 10/90 (v/v) DMSO/ACN solutions. The vials were shaken in a shaker (Vortex-2 Genie, Scientific Industries, USA) for 5 min during extraction. 2 mL of 10/90 (v/v) DMSO/ACN solutions was added into the denuder tubes, then the tubes ends were capped and shaken by a shaker for 5 min.

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Each extract was then decanted into a vial containing 2 mL of 10/90 (v/v) DMSO/ACN solutions. All samples were stored in the refrigerator at 4°C. Before analysis, the extracts were filtered by passing through a 0.45 μm pore size polyvinyl filter (Millipore Millex-HV, Lisons, USA).

All samples were analyzed by a high performance liquid chromatograph system (HPLC) (LC-10AT, Shimadzu, Tokyo, Japan) within 24 hours of sampling. A fluorometric detector (Shimadzu Model RF551) with excitation at 240 nm and emission at 370 nm was used. Sample injection volumes were defined by a 10-μL sample loop at the flow rate of 1.0 mL/min. A Phenomenex RP-8 stainless steel column (i.d. = 4.6 mm, length = 25 cm) with 5 μm silica packing (Phenomenex, Torrance, USA) was used. The mobile phase consisted of 60% ACN and 40% 0.05 M aqueous solution of ammonium acetate, which was adjusted to pH = 6.2 with glacial acetic acid. The output of the detector was sent to a personal computer for on-line recording of the data. The precision of the analysis was determined to be good with the relative standard deviation of less than 5.1%. The recovery test of adsorbed TDI on the coated glass-fiber filter showed that the recovery efficiency was 96.6 ± 2.2%. In this study, the MDL (method detection limit) was determined to be 0.10 ppb (or 0.712 $\mu g/m^3$, at 20°C, 1atm) of the 2,4-TDI gas concentration when the sampling flow rate was 2.0 L/min and sampling time was 15 minutes.

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RESULTS AND DISCUSSION

Laboratory Test Results

The TDI concentration was measured in the laboratory to study the effect of sampling time and relative humidity with the time duration of 1 minute and 120 minutes. Figure 2 shows the TDI concentration at different sampling durations using different samplers at 42% and 83% relative humidity. The concentration of the absorbed or collected gaseous TDI is maximum when the sampling time is only 1 minute and also the difference between the concentrations measured by three different samplers is small. The TDI concentration decreases by about 50% as the sampling time is increased to 15 minutes for all samplers. It is important to note that concentration of absorbed gaseous TDI with uncoated Teflon filter decreases more rapidly with increasing sampling time as compared to that collected by the ADS or coated GFF.

This suggests that the standard sampling time of 15 minutes by the coated GFF may underestimate the gaseous TDI concentration as water vapor at low RH or high RH reacts with collected TDI molecules. The same situation may exist for the ADS.

Figure 2 also shows that there is no apparent difference between the sampled TDI concentrations at RH 42% and 83% at each sampling

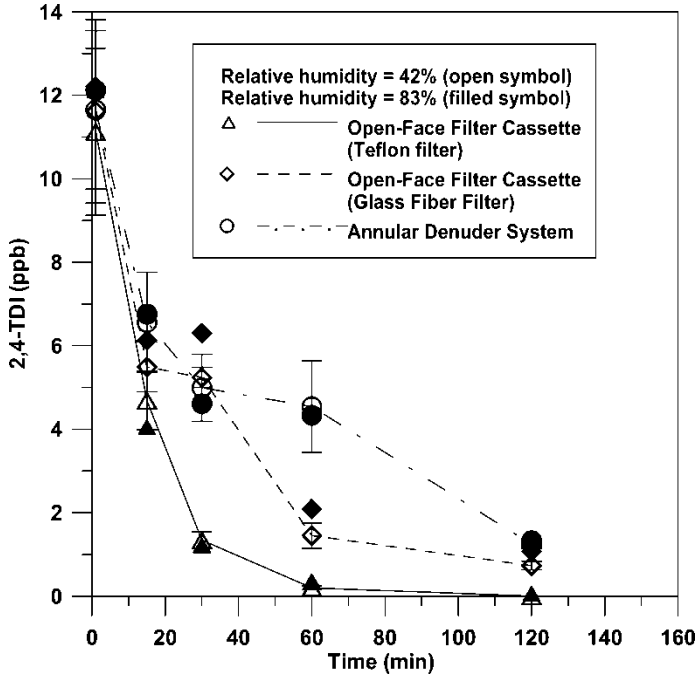

Figure 2. The gas 2,4-TDI concentration obtained using ADS and two OFFCs with different sampling durations at relative humidity of 42% and 83% in laboratory.

duration. This finding confirms the previous results on the relative humidity effect (18–19). The effect of sampling time on the TDI concentration is seen to be very important and should be considered in the TDI sampling method.

Field Test Results at PU Factory

The initial measurement at the PU factory showed that if the samplers were too close to the foaming tank (such as 20 cm from the foaming tank), TDI concentrations were not uniform among different samplers and the comparison of samplers was difficult. Therefore, the first attempt was to use only the ADS to sample both aerosol and gaseous TDI concentrations at 20 cm, and 2 m from the foaming tank. Figure 3 shows the gas- aerosol phase TDI concentration versus the total TDI concentration after 15 minute sampling while the sampler was kept at 20 cm and 2 m from the foaming tank. The total TDI concentrations greater than $100\,\mu g/m^3$ are the sampling results at 20 cm, while those less than $100\,\mu g/m^3$ are the results at 2 m from the foaming tank. The results show that the total TDI concentration varies very much from 51 to $483\,\mu g/m^3$. As the percentage of 2,4-TDI used was not

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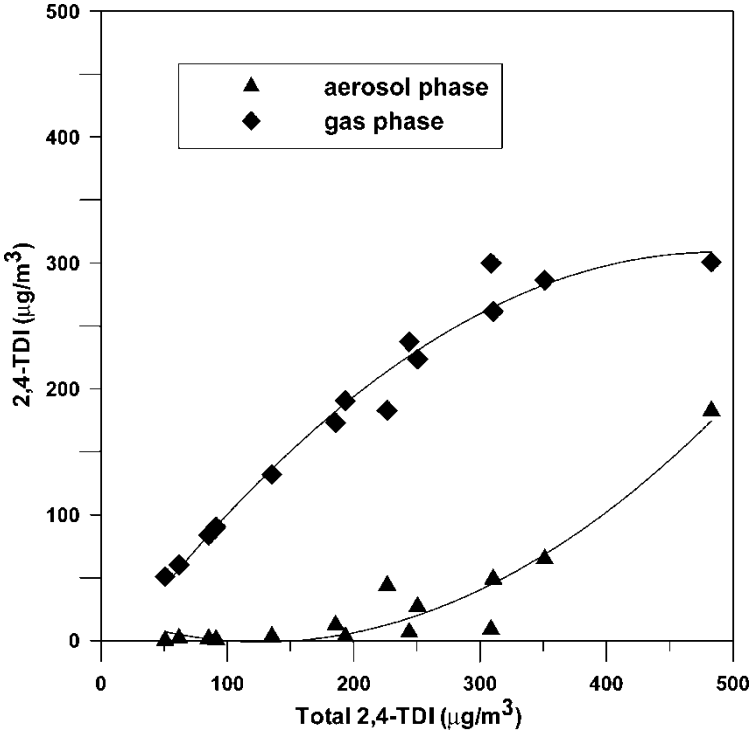

Figure 3. The aerosol–gas phase 2,4-TDI concentration using ADS sampler at the PU factory with a fixed sampling duration of 15 minutes. (for gas 2,4-TDI, 1 ppb = 7 $\mu g/m^3$) (20 cm from the tank: total TDI > 100 $\mu g/m^3$; 2 m from the tank: total TDI < 100 $\mu g/m^3$)

the same during each batch of production, which lasted for about 10 minutes, the TDI concentrations were not the same even at the same sampling location.

Figure 3 shows that when the total TDI concentration is less than 100 $\mu g/m^3$, the concentration of TDI in aerosol phase is negligible with the fraction of aerosol TDI concentration ranging from 0 to 2.81% only in the total TDI concentration. The predominant fraction of TDI is in the gas phase, and the fraction of TDI in aerosol phase increases with an increasing total TDI concentration with the maximum of 38% when the total TDI concentration is 480 $\mu g/m^3$.

Figure 4 shows the gas TDI measured using different samplers at a constant distance of 2 m from the foaming tank and varying sampling time of 15, 30, 60 minutes. Since only gas TDI is observed at 2 m from the foaming tank, the absorbed TDI by the Teflon filters of the TFS and DFS is counted as gaseous TDI concentration. The figure shows that although the standard deviation of the data point is large, which ranges from 2.5 to

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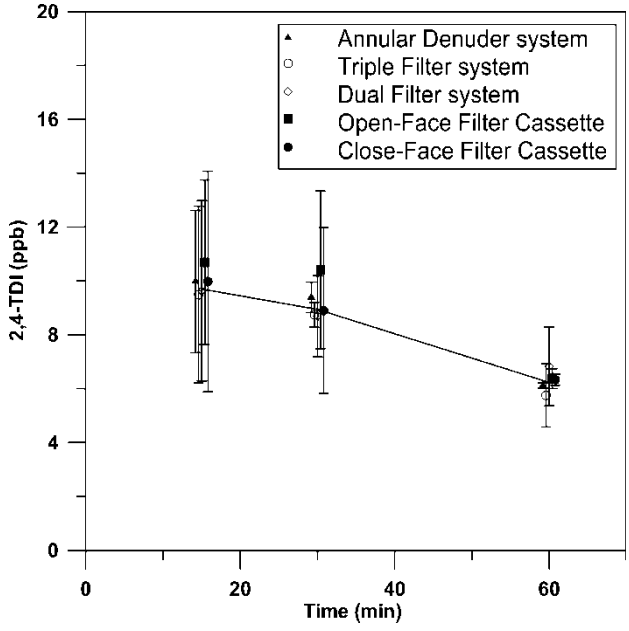

Figure 4. Comparison of gas 2,4-TDI concentration obtained using five different samplers at the PU factory with different sampling durations.

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37.8%, the average gaseous TDI concentration of each sampler at each sampling duration is nearly the same. Using the average TDI concentration of 9.7, 8.9, and 6.2 ppb at 15, 30, and 60 minutes of sampling time, respectively, as the reference value, the maximum difference in the measured concentrations of all samplers is about 16%.

The solid line in Fig. 4 represents the average gaseous TDI concentrations of all samplers. It shows that as sampling time increases, the sampled TDI concentration decreases. The decrease of about 36% is observed in TDI concentration as sampling time was increased from 15 to 60 minutes. This may be due to the chemical reaction of TDI with water vapor which turns into toluene diamine TDA (17) which was not determined in this study. Also it is quite possible that the reaction of airborne polyo with TDI occurs during the sampling process which reduces the measured TDI concentration.

It is to be noted that an appreciable amount of TDI gas was adsorbed in the Teflon filters of the TFS or DFS. For example, at the 15-min sampling duration, 40% of TDI was adsorbed by the Teflon filter of the DFS. Without the prior knowledge that TDI is in the gas phase, TDI on the Teflon filter will be mistaken for aerosol TDI by the DFS. In this case, the model developed for the TFS sometime also fails since the amount of TDI on the first Teflon filter is not always greater than that on the second Teflon filter.

Field Test Results at Painting Booth

The total TDI and aerosol TDI concentration obtained using different samplers at the painting booth are plotted against the sampling time in Fig. 5. The results shows that the standard deviation of the TDI concentration is very large, which ranges from 15.3 to 26.7%, and the average gaseous TDI concentration of each sampler at this workplace is more variable than the previous PU factory. This may be due to non-uniform concentration distribution in the painting booth. But the trend of decreasing total TDI concentration with 4an increasing sampling duration is persistent in this case. The decrease in the total TDI concentration ranges from 70 to 91% as sampling time increases from 15 to 60 minutes depending on the type of samplers.

The aerosol TDI concentration determined by the DFS is found to be much higher than that determined by the ADS and TFS at this sampling location, when the sampling time is the minimum, i.e.15 minutes. The aerosol TDI concentration measured by the ADS and TFS is only 3.6 and 3.9% of the total TDI concentration, respectively. When the sampling time

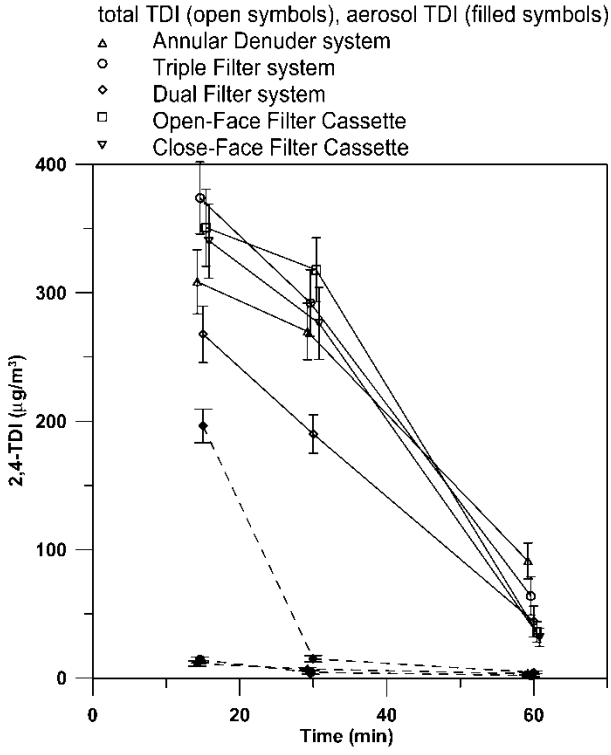

Figure 5. Comparison of total 2,4-TDI and aerosol 2,4-TDI concentrations using five different samplers at the painting booth with different sampling durations.

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is higher, i.e. 30 or 60 minutes, all three samplers show negligible amount of aerosol TDI.

CONCLUSIONS

The field study shows that the chemical reaction of TDI with airborne w ater vapor and polyo will result in the underestimation of sampled gaseous TDI concentration by all samplers (DFS, TFS, ADS and standard sampler) tested in this study. As sampling time increases from the standard 15 minutes, the sampled TDI concentration decreases. Laboratory test using pure gaseous TDI suggests that the reaction occurs right from the very beginning of sampling. The sampled gaseous TDI concentration at 1-min is much higher than that at 15 minutes and longer sampling time. The standard sampling time of 15 minutes by the coated GFF might have underestimated the gaseous TDI concentration as water vapor (low RH or high RH) reacts with collected TDI molecules. The same reaction may occur for the ADS.

The adsorbed TDI on the uncoated Teflon filter of the DFS will react with water vapor and makes the use of the sampler difficult. Further study is required to resolve this problem for DFS. It also suggests that the adsorbed TDI will be mistaken for aerosol TDI if only pure gaseous TDI exists in the workplace. When the adsorbed TDI on the first Teflon filter reacts faster than the second filter, such as in the PU factory, then the accuracy of the TFS for simultaneous determination of aerosol and gaseous TDI will also be in doubt.

The ADS has been shown to be a good sampler to determine the gaseous and aerosol TDI concentrations simultaneously with a sampling time of 15 minutes in the workplace, but the effect of sampling time on the measured concentrations also exists. If only gaseous TDI exists in the workplace, the standard sampling method using the coated GEF in the OFFC or CFFC measures TDI concentrations similar to those of the ADS. The adsorbed TDI on the Teflon filters of TFS and DFS can be added to that collected on the GFF to give a reasonable gaseous TDI concentration measurement. However, without the prior knowledge of the TDI phase, TDI adsorbed on the Teflon filter may cause wrong estimation of aerosol TDI by the DFS. The model developed for the TFS gives more reasonable aerosol and gaseous TDI concentrations, but it sometime also fails since the amount of TDI on the first Teflon filter can decay faster than that on the second Teflon filter in some instances.

In summary, the sampling time effect found in this study is seen to be very important and should be considered in the TDI sampling method. Shortening the sampling time is one of the possible solutions to this problem. Developing artifact-free sampling methods or real time monitors are worth further investigating.

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