ORIGINAL ARTICLE

Field protection effectiveness of chemical protective suits and gloves evaluated by biomonitoring

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Objectives: To determine the effectiveness of protective suits and gloves by biomonitoring.

Methods: Fifteen male spray painters at a ship coating factory were studied for two weeks. Workers wore no protective clothing during the first week and wore protective suits and gloves during the second week. Sampling was conducted on four consecutive working days each week. Ethyl benzene and xylene in the air were collected by using 3M 3500 organic vapour monitors. Urine was collected before and after each work shift.

Results: Urinary mandelic acid (MA) and methyl hippuric acid (MHA) levels were divided by the personal exposure concentrations of ethyl benzene and xylene, respectively. Mean (SE) corrected MA and MHA concentrations in the first week were 1.07 (0.18) and 2.66 (0.68) (mg/g creatinine)/(mg/m³), and concentrations in the second week were 0.50 (0.12) and 1.76 (0.35) (mg/g creatinine)/(mg/m³) in the second week, respectively. Both MA and MHA concentrations in the second week (when spray painters wore protective suits and gloves) were lower than in the first week, respectively ($p < 0.001$, $p = 0.011$). Mean decrease in MA and MHA biomarkers were 69% and 49%, respectively.

Conclusion: This study successfully evaluated the effectiveness of chemical protective suits and gloves by using biomarkers as urinary MA and MHA. This method is feasible for determining the performance of workers wearing personal protective equipment. Moreover, the experimental results suggest that dermal exposure may be the major contributor to total body burden of solvents in spray painters without protective suits and gloves.

Surface treatment is a very common industrial process, and spray painting is the most common application method. However, serious health hazards arise without effective protective measures such as water curtains, ventilation systems, and personal protective equipment. Among them, the effectiveness of personal protective equipment, such as protective suits and gloves, is often unclear.

Effectiveness in protecting wearers from chemical exposure is the most important consideration when selecting protective suits and gloves. Two major factors should be considered when evaluating the effectiveness of protective clothing: breakthrough time and steady-state permeation rate.^{1–3} Nevertheless, laboratory permeation test methods may not accurately represent the actual conditions in typical workplaces. Workplace temperature and humidity as well as permeability and comfort of protective clothing can influence the consistent use of such clothing. Thus, the actual effectiveness of protective suits and gloves provided to field workers cannot be fully understood simply by measuring breakthrough time and steady-state permeation rate with laboratory permeation tests.

Xylene and ethyl benzene, two of the most commonly used solvents in spray painting, are toxic to the central nervous system and can cause acute irritation of skin, eyes and mucous membranes.^{4–6} According to the American Conference of Governmental Industrial Hygienists and Deutsche Forschungsgemeinschaft, percutaneous absorption of xylene and ethyl benzene may increase systemic exposure. Xylene is mainly metabolised as methyl hippuric acid (MHA) and secreted into urine.⁷ The major metabolite of ethyl benzene in urine is mandelic acid (MA).⁸ Because they frequently work in a confined or poorly ventilated spaces, spray painters are often exposed to environments with high concentrations of solvent vapours, and the paints may contaminate their clothes or skin. Thus, wearing chemical protective suits and gloves can be an

important protective measure for reducing solvents hazards. The aim of this study was to assess the effectiveness of protective suits and gloves by biomonitoring.

METHODS

Study subjects

Fifteen male spray painters working at a ship coating factory in southern Taiwan were recruited for this study. The spray painters routinely wore air purifying, half-face respirators with organic vapour filtering canisters (Shigematsu Works Co, Ltd, Japan) but did not wear chemical protective suits and gloves. The painters used an airless spray gun to apply paints and the workplace provided no paint mixing room or exhausters. Subjects provided demographic information (for example, age, education, years worked), lifestyle factors (for example, alcohol and tobacco use) and use of personal protective equipment (for example, respirators, chemical protective suits and gloves).

Study design

Subjects worked without protective suits and gloves the first week and with suits and gloves the following week. All workers wore respirators during spray painting throughout the two-week period of the study. Sampling was conducted on four consecutive working days each week. Personal air samples and pre- and post-shift urine samples of subjects were collected. Notably, the paints used in the first and second weeks differed. The bulk samples were analysed by GC/MS. The major content of solvents were xylene and ethyl benzene. In the first week, ethyl benzene concentrations were 1.26 times xylene in the

Abbreviations: BDF, biomarker decreasing factor; GC/FID, gas chromatography/flame ionisation detector; HPLC, high performance liquid chromatography; MA, mandelic acid; MHA, methyl hippuric acid

thinner. In the second week, xylene concentrations were 2.84 times ethyl benzene in the thinner.

Protective suits and gloves provided

The airtight chemical protective suits were made of two layers of polyethylene (Shigematsu Works Co, Ltd). The breakthrough time for toluene was less than 5 min and the steady-state permeation rate was 3.3 mg/m²/second. The thickness of the suits was 0.36 mm. The chemical protective gloves (37 cm long and 0.65 cm thick) were MAPA ultranitrile 491 (MAPA Spontex, Inc, Columbia, TN, USA) and made of acrylonitrile. The protection grade was A for xylene, and B for toluene. According to the chemical protection grading system provided by the manufacturer, A denoted "excellent to good," B "average" and C "not recommended". New chemical protective suits and gloves were provided daily for subjects. Moreover, spray painters wore new organic vapour filters daily and changed the organic vapour filter whenever they experienced irritation during their work shifts.

Air and urine sample collection

Ethyl benzene and xylene were collected using 3M 3500 organic vapour monitors. Subjects wore the samplers during their work shift for at least six hours of the day, and sampling covered the entire working period involving solvent contact. The analysis of samples was performed within one week. Urine samples were collected before and after each work shift. Each urine sample was stored in a plastic bottle and frozen at -20°C until analysis.

Analysis of air ethyl benzene and xylene

Two ml carbon disulfide was added to the air sampler to desorb organic vapours. One µl of the extract was analysed by gas chromatography with flame ionisation detector (GC/FID) in a capillary column (DB-WAX; 30 m in length, 0.53 mm in inner diameter and 1.0 µm in film thickness). The column oven was initiated at 50°C, heated at 25°C/min to 230°C and kept at 230°C for 1 min. The carrier gas was nitrogen and the flow rate was at 1.72 ml/min. Each analysis required at least 23 min. Total xylene concentration was calculated by summing concentrations of the ortho-, meta- and para-isomers.

Urine analysis for MA, MHA and creatinine

Urine samples were pretreated and analysed following the procedures described elsewhere.⁹ The urinary concentrations of mandelic and methyl hippuric acids were measured by high performance liquid chromatography (HPLC) with UV detector.

Frozen urine samples were thawed and homogenised by vortex. The pH values of urine samples (1 ml) were adjusted to 2.0 with 85% phosphoric acid and applied to the top of a strong anion exchanger column, the MAX extraction cartridge (30 µm particle size, 1 cc/30 mg, Waters Co, Milford, MA, USA) which had been preconditioned with 1.0 ml acetonitrile and 1.0 ml water. After application, the sample was washed with 1 ml sodium acetate (pH = 9.5), and the adsorbed compounds on the cartridge were eluted with 2 ml solution of 100 mM phosphoric acid (50 parts) and acetonitrile (50 parts). Washing and elution proceeded under a vacuum manifold. Twenty five µl of elute was injected into the HPLC injector. The chromatography column was 250×4 mm ID, 5 µm RP18-Lichrospher 100 column (E Merck, Darmstadt, Germany). The mobile phase was a mixture of acetonitrile (15 parts) and pH = 5.6, 34 mM phosphate buffer (85 parts) containing 8.5 mM tetrabutyl ammonium hydrogen sulfate, and the flow rate was 0.8 ml/min. Urinary creatinine concentration was measured with a Hitachi model U-2000 spectrophotometer (Hitachi Instruments, Inc, Tokyo, Japan) using the Jaffe reaction.¹⁰ Creatinine was used to correct metabolite concentration in urine.

Calculation of biomarker decreasing factor

The biomarker decreasing factor (BDF) was calculated by the following formula:

$$\text{BDF} = [(Cu_1/Ca_1) - (Cu_2/Ca_2)] / (Cu_1/Ca_1) \times 100\%$$

Cu₁, urinary post-shift metabolite concentration in the first week; Ca₁, personal contaminant exposure concentration in the first week; Cu₂, urinary post-shift metabolite concentration in the second week; Ca₂, personal contaminant exposure concentration in the second week.

Statistical analysis

Data were analysed using the statistical software package SAS, release 9.1 (SAS Institute, Inc, Cary, NC, USA). Descriptive data for age, years worked and level of education were obtained. The medians and interquartile ranges (25th–75th percentiles; Q₂₅–Q₇₅) of the personal ethyl benzene and xylene exposure were determined for all subjects. Urinary creatinine-adjusted MA and MHA concentrations (mg/g creatinine) were used in all analyses. A cross-shift change in MA and MHA was calculated by subtracting the pre-shift concentration from the post-shift concentration. Because of the repeated measurement design, linear mixed models were used to compare pre-shift and post-shift MA and MHA concentrations. The corrected concentrations of metabolites in the first and second weeks were also examined by linear mixed models. The level of significance for all analyses was set at 0.05.

RESULTS

Table 1 shows the characteristics of study subjects. Median age was 38.3 years (range 27.5–54.1 years). On average, the subjects worked for five years (range 0.63–11 years). Most subjects were junior and senior high school graduates. Ten (66.7%) and 11 (73.3%) of 15 workers drank alcohol and

Table 1 Characteristics of study subjects

	n (%)
Highest level of education	
Elementary	5 (33.3)
Junior high	7 (46.7)
Senior high	3 (20.0)
Drank alcohol	
Yes	10 (66.7)
No	5 (33.3)
Smoked cigarettes	
Yes	11 (73.3)
No	4 (26.7)
Felt skin irritated during work	
Yes	15 (100)
No	0
Got skin allergies during work	
Yes	8 (53.3)
No	7 (46.7)
Age (years)*	38.3 (27.5–54.1)
Years worked*	5 (0.63–11)

*Age and years worked are presented as median (range).

Table 2 Summary of ethyl benzene and xylene 8-h time-weighted average concentrations in the first and second weeks (unit: ppm)

Contaminant	First week (n = 51)*	Second week (n = 48)*
Ethyl benzene	32 (9.65–70)	119 (36–197)
Xylene	18 (6.92–35)	171 (53–315)

*Median (Q₂₅–Q₇₅). Sample sizes vary by exposure measure because workers were absent.

Table 3 Urinary MA and MHA concentrations in the first week (unit: mg/g creatinine)

	n	Pre-shift*	Post-shift*	Difference*†	p Value‡
MA	51	70 (6.86) (10–26)	106 (12) (11–472)	36 (11)	0.008
MHA	51	82 (11) (14–364)	108 (12) (22–413)	26 (15)	0.123

*Mean (SE) (range).

†Post-shift minus pre-shift.

‡By linear mix model test.

smoked cigarettes, respectively. All spray painters experienced skin irritation while paint spraying whereas eight spray painters (53.3%) experienced skin allergies.

Air sampling results showed that ethyl benzene and xylene were the major solvents used on site. Table 2 shows personal 8-h time-weighted average (TWA) exposure to ethyl benzene and xylene. Median ethyl benzene concentration was 32 ppm during the first week with an interquartile range of 9.65–70 ppm. Xylene was 18 ppm with an interquartile range of 6.92–35 ppm for all subjects. During the second week, the median ethyl benzene was 119 ppm with an interquartile range of 36–197 ppm whereas xylene was 171 ppm with an interquartile range of 53–315 ppm for all subjects.

In the first week, pre-shift urinary MA and MHA concentrations for all subjects were compared with post-shift samples. The mean (SE) pre-shift MA and MHA concentrations were 70 (6.86) and 82 (11) mg/g creatinine, respectively. Post-shift MA and MHA concentrations were 106 (12) and 108 (12) mg/g creatinine, respectively. Cross-shift MA and MHA changes were 36 (11) and 26 (15) mg/g creatinine, respectively. Pre-shift MA concentrations significantly differed from post-shift samples ($p = 0.008$) (table 3).

During the second week, pre-shift MA and MHA concentrations were 75 (7.79) and 141 (14) mg/g creatinine, respectively. Post-shift MA and MHA concentrations were 103 (8.97) and 472 (45) mg/g creatinine, respectively. Cross-shift MA and MHA changes were 27 (8.83) and 331 (37) mg/g creatinine, respectively. Pre-shift MA and MHA concentrations significantly differed from post-shift samples ($p = 0.008$; $p < 0.001$, respectively) (table 4).

The American Conference of Governmental Industrial Hygienists recommends MA and MHA as biological exposure indices for ethyl benzene and xylene exposure, respectively. Pearson correlation coefficients between urinary post-work shift MA concentrations and ethyl benzene exposure in the first and second weeks were 0.261 and 0.376, respectively ($p = 0.064$; $p = 0.01$). Pearson correlation coefficients between urinary post-work shift MHA concentrations and xylene exposure in the first and second weeks were 0.481 and 0.697, respectively ($p < 0.001$; $p < 0.001$). Therefore, observing the variation in urinary MA and MHA before and after workers wore protective suits and gloves was appropriate for evaluating the field effectiveness of chemical protective suits and gloves.

To correct for changes in urinary MA and MHA concentrations caused by exposure to different levels of ethyl benzene and xylene, urinary post-shift MA and MHA concentrations (mg/g creatinine) were divided by ethyl benzene and xylene

levels (mg/m³), respectively. Corrected MA and MHA concentrations during the week without protective suits and gloves were 1.07 (0.18) and 2.66 (0.68) (mg/g creatinine)/(mg/m³), respectively whereas concentrations were 0.50 (0.12) and 1.76 (0.35) (mg/g creatinine)/(mg/m³) during the week of using protective suits and gloves, respectively. Corrected MA and MHA concentrations during the week the spray painters wore protective suits and gloves were lower than during the week without protective suits and gloves ($p < 0.001$; $p = 0.011$) (table 5). Notably, calculation of corrected MA and MHA concentrations was based on a linear relation between air exposure and metabolite levels.

Mean MA and MHA BDFs of subjects wearing protective suits and gloves were 69.2 % (range 14.6–94.9) and 49.0% (range 3.8–82.6), respectively. These experimental results indicate that with protective suits and gloves, urinary MA and MHA concentrations could be reduced by an average of 69.2% and 49%, respectively.

DISCUSSION

The findings of this study indicate that the providing protective suits and gloves effectively reduces dermal exposure to organic solvents and is a feasible for minimising the hazards of organic solvents in spray painters. As evaluated by the biomonitoring method, spray painters wearing protective suits and gloves can reduce urinary MA and MHA by 69% and 49%, respectively. Thus, when workers did not wear protective suits and gloves during the second week, mean urinary MA and MHA concentrations were increased from 104 to 334 mg/g creatinine (104/(1–0.69)) and from 472 to 926 mg/g creatinine (472/(1–0.49)), respectively. Several recent studies have concluded that exposure through the skin is becoming a more common mode of chemical exposure.^{11 12}

Jacobson *et al* studied low level occupational xylene exposure in 20 workers.¹³ Correlations between xylene and post-shift and increased (post-shift minus pre-shift) MHA concentrations were examined. Xylene showed a slightly closer correlation with the increased MHA than post-shift MHA. In the current study, correlations between xylene and increased MHA concentrations in the first and second weeks were 0.312 and 0.412, respectively ($p < 0.026$; $p < 0.004$). Correlations between ethyl benzene and increased MA concentrations in the first week and second weeks were 0.195 and 0.219, respectively ($p = 0.169$; $p = 0.134$). Increased MA and MHA levels revealed no improvement in r values compared with post-shift samples.

Increased MA and MHA concentrations (post-shift minus pre-shift) are divided by ethyl benzene and xylene exposure

Table 4 Urinary MA and MHA concentrations in the second week (unit: mg/g creatinine)

		Pre-shift*	Post-shift*	Difference*†	p Value‡
MA	47	75 (7.79) (0.18–251)	103 (8.97) (40–387)	27 (8.83)	0.008
MHA	47	141 (14) (35–511)	472 (45) (97–1578)	331 (37)	<0.001

*Mean (SE) (range).

†Post-shift minus pre-shift.

‡By linear mix model test.

Table 5 Comparison of corrected MA and MHA concentrations between the first and second weeks (unit: (mg/g creatinine)/(mg/m³))

Corrected metabolites*	First week (n=44)†	Second week (n=44)†	p Value‡
MA (n=44)	1.76 (0.35)	0.50 (0.12)	<0.001
MHA (n=44)	2.66 (0.68)	1.07 (0.18)	0.011

*The urinary post-shift MA and MHA concentrations were divided by personal ethyl benzene and xylene exposure levels, respectively.

†Mean (SE).

‡By linear mix model test.

levels, respectively. Corrected MA and MHA concentrations in the first week were 0.86 (0.22) and 1.62 (0.57) (mg/g creatinine)/(mg/m³), but were 0.28 (0.11) and 0.57 (0.08) (mg/g creatinine)/(mg/m³), respectively, in the second week. Mean MA and MHA biomarker decreasing factors reached 72.4 % (range 15.5–91.0) and 53.6% (range 12.7–78.7). These analysis results were similar to those calculated by post-shift MA and MHA levels.

Besides material, the behaviour of wearers significantly affected the effectiveness of protective outfit. For instance, one subject did not wear the protective clothing through the entire spray painting task because he felt they were too hot. In this case, the BDF showed that providing protective suits was ineffective in reducing exposure. Evidently, using the break-through time and steady-state permeation rate provided by the manufacturers of the chemical substances was insufficient for showing a complete picture of field effectiveness. Therefore, biomonitoring was more accurate in detecting metabolite reduction in urine before and after spray painters wore the protective outfits in order to detect actual exposure.

Most work in coating ships is performed manually, and reducing exposure by replacement or automation is difficult. Therefore, the use of personal protective equipment is currently the most feasible method of reducing exposure. This study was conducted at an average temperature of 23°C and an average humidity of 70%. Most spray painters who wore protective suits and gloves expressed a willingness to wear the protective gear and believed it effectively protected them from exposure to

organic solvents. However, an investigation of the acceptance of protective suits and gloves by spray painters working during the summer indicated that most expressed a willingness to wear the protective gloves but not the suits. Further studies of worker compliance should be conducted during the summer when temperatures reach 32°C.

Xylene and ethyl benzene levels were notably lower than in the second week due to the lighter workload of spray painters during the first week. Additionally, air sampling results were associated with the type of paint used by spray painters. Ethyl benzene exposure was highest in the first week whereas xylene exposure was highest in the second week.

In conclusion, biomonitoring methods were useful for evaluating the effectiveness of protective suits and gloves worn by workers. However, the reductions in biomarkers for spray painters wearing protective suits and gloves differed widely. Influential factors included style and duration of wear, work posture, degree of cooperation and work environment (for example, confined space). This study demonstrates that protective suits and gloves effectively reduce the risk of absorbing organic solvents through the skin. In addition to respirators, protective suits and gloves are strongly recommended for spray painters in the shipbuilding industry.

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Main messages

- Biomonitoring methods were useful for evaluating the effectiveness of personal protective equipment worn by workers.
- Wearing protective suits and gloves can significantly reduce dermal exposure to solvents.
- Dermal exposure may be the major contributor to the total body burden of solvents in spray painters with respirators only.

Policy implications

- As components of paints appear to be absorbed through the skin, techniques to reduce dermal exposure are needed.
- In addition to respirators, protective suits and gloves are strongly recommended for shipyard spray painters.