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Exposure to organic solvents has been reported to increase the risks for acute and chronic health effects among shoe industry workers. In developing countries, protection against chemical exposures is often not provided. The study was conducted to identify working conditions and estimate the concentrations of organic solvents used in shoe factories and workshops in Hebron City. Personal interviews containing questions related to personal protective equipment (PPE) were used to identify working conditions, and samples collected from factories and workshops were analyzed using gas chromatography. Geometric means (GMs) were calculated for the solvents. Six major organic solvents were detected in the factories. Acetone (GM = 51.5 mg/m^3, GSD = 3.82) was common in gluing tasks. Dichloromethane (GM = 47 mg/m^3, GSD = 2.62) was common in cleaning tasks. Heptane, methylethyl ketone, *n*-hexane, and toluene were common in gluing tasks. Four major organic solvents were detected in the workshops: acetone (GM = 32.3 mg/m^3, GSD = 6.33), toluene (GM = 70.3 mg/m^3, GSD = 3.06), *n*-hexane (GM = 19.4 mg/m^3, GSD = 2.65), and methylethyl ketone (GM = 130 mg/m^3, GSD = 1.5). 81% of the factory workers had never used respiratory protective equipment, and 92% had never used work clothes. 97% of the workers in the workshops had never used respiratory protective equipment, 94% had never worn gloves, and 90% had never used work clothes. Exposures to solvents in the absence of personal Protective equipment, tasks barriers, and mechanical ventilation can adversely affect health. *Key words*: organic solvents; gas chromatography; TLV; protective equipment; geometric mean; work tasks.

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Organic solvents, which have been used in industry in large and increasing quantities during the last 50 years, are considered to be the main risk factor for many occupational diseases among workers.[1-3]

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Workers who have histories of exposures to organic solvents have been shown to have neurologic abnormalities,[4,5] poorer neurobehavioral performances,[6] impaired memory, and concentration problems.[7] The types of neurologic damage are closely related to the structures of the chemical agents involved, while the degrees of impairment and the extents of reversibility are related to agent potency and dose and duration of exposure.[8]

n-Hexane is well known to produce peripheral nervous system degeneration.[9-11] High concentrations of commercial n-hexane found in glue samples and solvents collected from the residences of home workers and from factories in Italy were associated with the appearance of polyneuropathy among the workers.[12,13] Coexposure to methylethyl ketone (MEK) may enhance the neurotoxicity of *n*-hexane.[14,15]

Organic solvents are a major component of products used in the shoe industry. Gas chromatographic analysis of 43 kinds of glues and 22 solvent products used in footwear manufacture showed the presence of acetone, cyclohexane, and methylethyl ketone, but *n*-hexane was detected only in a few cases.[16] Samples of solvents and glues collected from five shoe factories in Italy contained paraffinic hydrocarbons such as n-hexane, pentane, and heptane.[17]

Workers in Hebron City shoe factories (Nijem et al., unpublished data) and workshops[18] had reported several health complaints related to solvent exposure. Absence of true safety measures at the factories and workshops could increase the effects of solvents.

The objectives of the present study were to determine working conditions at shoe factories and workshops, including the availability of personal protective equipment (PPE), and to identify organic solvents used in the shoe manufacturing industry, in both shoe factories and workshops, as well as to estimate the concentrations of the solvents used.

MATERIALS AND METHODS

Study Population

Hebron City, which is located in the southern part of the West Bank, 40 km from Jerusalem, contains many shoe factories and workshops that were developed during the Israeli occupation of the West Bank and the Gaza Strip

(Hebron Chamber of Commerce, personal communication). Most of these factories and workshops were established without implementing compliance with minimum standard requirements, such as barriers between working tasks and mechanical ventilation systems, in the absence of labor-inspection authority and legal regulations. Most of the shoe-manufacturing workers had little education (Nijem et al., unpublished data) and lacked knowledge about the compounds they used at work. During past years, they had not received any information about possible adverse effects of the compounds with which they worked, and thus had taken no precautions to protect themselves.

Process of Manufacturing in Hebron Shoe Factories

Shoe manufacturing consists of four major working tasks, including sole molding, cleaning, gluing, and varnishing.

In the sole-molding task, polyvinylchloride or polyurethane pellets are injected into a molding machine, which heats and reshapes the pellets to form the shoe sole. After the removal of the sole, the plates are sprayed with solvents to remove residual plastics. In the gluing task, workers adhere the plastic sole to the upper leather portion (Figure 1), which involves contact with rubber-paste adhesives. Finally, in the varnishing task, the workers spray (Figure 2) the shoes or insert them into a tank containing solvents for coloring and polishing.

Shoe workshops are smaller than the factories, employ fewer workers, and are less productive. They do not have plastic-molding machines, and thus the main activity in the workshops is to adhere the plastic soles to the upper leather portions of shoes. Plastic soles are brought from shoe factories. Shoes are occasionally inserted into containers containing fixatives and varnishing solvents.

Sampling and Solvent Measurements

The study was conducted by sending an invitation letter to the owners of 27 factories and 30 workshops. Owners of 20 factories and 30 workshops agreed to participate in the study and allowed us to interview personally a total of 167 male shoe factory workers (aged 17–64 years) and 103 male workshop workers (aged 15–56 years) (Nijem et al., unpublished data[18]). Female workers were not seen. The interview included questions related to symptoms representing neuropsychiatric and mucous membrane irritations (Nijem et al., unpublished data[18]) and to the use of personal protective equipment (respiratory protective equipment, gloves, goggles, head coverings, special shoes, and special work clothes).

Four factories and four workshops were randomly selected and invited to participate in organic solvent measurements. The selected factories met the following criteria: the manufacturing process composed of four steps: plastic molding, cleaning, gluing, and varnishing; they employed more than ten workers; and they lacked true barriers between working tasks.

The selected workshops met the following criteria:

Figure 1—Adult worker and two children in the gluing task are using adhesive compounds to adhere the plastic sole to the upper leather part.

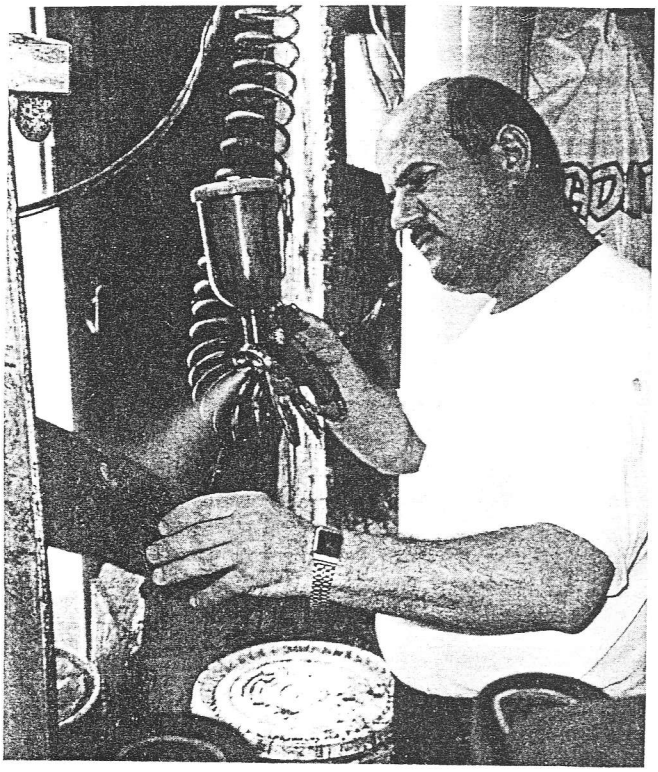

Figure 2—Worker using spraying machine to spray the shoes with fixative and varnishing solvents at the varnishing task.

absence of the plastic-molding process; employing fewer than ten workers; and lack of barriers between working tasks.

Owners of the selected factories and workshops agreed to participate in the study; four workers from each factory and two workers from each workshop were selected to represent different factory/workshop tasks (molding plastic, cleaning, gluing, and varnishing). Each worker was asked to wear a gas dosimeter for four separate days. Two students from Hebron University were trained to fix the dosimeters close to breathing zones of the workers at the starting hours of the workday and then to remove them at the end of the workday. The dosimeters were collected and analyzed at the university lab.

Exposure Assessment

Seventeen workers from four factories and nine workers from four workshops were selected based on working tasks and asked to wear a passive personal air sampler. Totals of 61 samples from factories and 34 samples from workshops were collected. For each worker, the concentrations of organic solvents were monitored continuously throughout the working day, i.e., 8 hours with 3M-3500 personal diffusive samplers attached to the clothing within the breathing zone during exposure. Towards the end of the shift, the sampler was removed and immediately capped. The samplers were sent to the laboratory at Hebron University and kept in a refrigerator before analysis. The solvents in the sampler were extracted with 3 mL carbon disulfide for 12 hours. The carbon disulfide extracts were analyzed by gas chromatography (Shimadzu, Class-GC10) equipped with two parallel capillary columns and two flame-ionization detectors. Each sample (injection volume 2 μL) was thus analyzed simultaneously on two different columns in the same run (total run time 30 minutes). Mineral spirits (white spirits) consisting of complex mixtures of hydrocarbons and appearing as multiple peaks in the chromatogram were excluded from the study, since they presented difficulties during compound identification.

Occupational exposures and the additive effects for most of the solvents were calculated in different tasks and were evaluated using the threshold limit values (TLVs) of the American Conference of Governmental Industrial Hygienists (ACGIH). TLVs are hygienic limits used for the regulation of the working environment and are defined as the highest airborne concentrations of particular substances under which the risk of adverse effects if sufficiently low for safety.[19] Hygienic effect of a compound is defined as the ratio between the actual concentration of the compound and its TLV. For an estimation of the hygienic effect caused by several compounds with similar effects (additive effect), the calculation $C_1/G_1 + C_2/G_2 \ldots + C_n/G_n$ was carried out, where C = the actual concentration of the compound and G = the TLV of the compound.

Statistical Analysis

Exposures were measured during all working tasks in the factories and during the main task (gluing) in the workshops. Frequencies of detection, geometric means (GMs), and geometric standard deviations (GSDs) were calculated for the organic solvents detected in association with each task.

RESULTS

Six major compounds of organic solvents were detected in Hebron City shoe factories, including acetone, dichloromethane, heptane, *n*-hexane, methylethyl ketone (MEK), and toluene (Table 1). In 18 measurements in the gluing task, acetone was the solvent most often present (detected in 14 measurements; the GM of its concentrations was 51.3 mg/m^3 (GSD = 3.82). In cleaning and plastic-molding tasks 14 measurements were taken and dichloromethane was found the most often. It was detected in 13 measurements made during cleaning tasks, in a concentration higher than those found for the other tasks (GM = 47 mg/m^3, GSD = 2.62), while in the plastic-molding task it was detected in 12 measurements. In two measurements the concentration of this compound exceeded the ACGIH TLV (Table 1).

Heptane was often detected in most of the tasks (Table 1), especially those involving plastic. Its maximum con-

TABLE 1 Concentrations of Organic Solvents Associated with Work Tasks in Shoe Factories in Hebron

	Acetone	Dichloro-methane	Cyclohexane	Heptane	*n*-hexane	Methylethyl Ketone	Toluene	Additive Effect Relative to ACGIH§
TLV (ACGIH)	1,187 mg/m³	174 mg/m³	1,033 mg/m³	1,639 mg/m³	176 mg/m³	590 mg/m³	188 mg/m³	
Plastics work								
(n/N)*	7/14	12/14	0	10/14	2/14	2/14	10/14	
Concentration								
GM†	18.3 mg/m³	21.1 mg/m³	0	15.3 mg/m³	2.3 mg/m³	14.3 mg/m³	14.5 mg/m³	0.21
GSD‡	2.3 mg/m³	1.9 mg/m³	0	2.9 mg/m³	3.1 mg/m³	1.2 mg/m³	2.6 mg/m³	1.69
Min	4.8 mg/m³	11.1 mg/m³	0	6.6 mg/m³	1.0 mg/m³	12.4 mg/m³	2.7 mg/m³	0.07
Max	50.8 mg/m³	61.5 mg/m³	0	232.6 mg/m³	5.1 mg/m³	16.6 mg/m³	48.4 mg/m³	0.38
Cleaning								
(n/N)*	4/14	13/14	2/14	12/14	2/14	3/14	10/14	
Concentration								
GM†	19.3 mg/m³	47.3 mg/m³	10.7 mg/m³	44.9 mg/m³	3.6 mg/m³	17.6 mg/m³	5.8 mg/m³	0.35
GSD‡	2.3 mg/m³	2.6 mg/m³	1.6 mg/m³	2.34 mg/m³	1.3 mg/m³	1.1 mg/m³	3.0 mg/m³	2.24
Min	5.9 mg/m³	15.8 mg/m³	7.9 mg/m³	14.0 mg/m³	2.9 mg/m³	16.2 mg/m³	1.5 mg/m³	0.14
Max	36.5 mg/m³	298.1 mg/m³	14.6 mg/m³	173.6 mg/m³	4.5 mg/m³	20.1 mg/m³	23.9 mg/m³	1.82
Gluing								
(n/N)*	14/18	7/18	1/18	15/18	9/18	8/18	17/18	
Concentration								
GM†	51.3 mg/m³	19.6 mg/m³	9.5 mg/m³	6.9 mg/m³	15.2 mg/m³	14.3 mg/m³	37.9 mg/m³	0.32
GSD‡	3.8 mg/m³	1.4 mg/m³	0	1.8 mg/m³	2.5 mg/m³	1.6 mg/m³	3.8 mg/m³	4.51
Min	9.6 mg/m³	14.3 mg/m³	9.5 mg/m³	2.9 mg/m³	4.5 mg/m³	4.7 mg/m³	2.6 mg/m³	0.01
Max	2,235.0 mg/m³	33.4 mg/m³	9.5 mg/m³	16.4 mg/m³	11.0 mg/m³	18.3 mg/m³	238.0 mg/m³	3.18
Varnishing								
(n/N)*	10/11	6/11	0	5/11	2/11	5/11	11/11	
Concentration								
GM†	74.1 mg/m³	14.7 mg/m³	0	9.4 mg/m³	3.6 mg/m³	11.5 mg/m³	37.1 mg/m³	0.35
GSD‡	4.4 mg/m³	1.2 mg/m³	0	1.2 mg/m³	1.7 mg/m³	1.3 mg/m³	3.4 mg/m³	2.37
Min	7.1 mg/m³	11.7 mg/m³	0	7.5 mg/m³	2.5 mg/m³	8.0 mg/m³	8.5 mg/m³	0.10
Max	499.0 mg/m³	17.8 mg/m³	0	11.7 mg/m³	5.1 mg/m³	16.4 mg/m³	236.0 mg/m³	1.70

*Frequency of detection/total measurements.
†Geometric mean.
‡Geometric standard deviation.
§Additive effect = $C_1/G_2 + C_2/G_2 \ldots + C_n/G_n$, where C = the actual concentration of the compound and G = the TLV of the compound.

centration was 232 mg/m³. *n*-Hexane (GM = 15.2 mg/m³, GSD = 2.46) and MEK (GM = 14.3 mg/m³, GSD = 1.57) were most often found in the gluing task.

Exposures to toluene were common in all of the factory tasks, with a high concentration in the gluing task (GM = 37.9 mg/m³, GSD = 3.84).

In shoe workshops, 34 measurements were performed, detecting four major organic solvents, acetone, n-hexane, MEK, and toluene (Table 2). Toluene was found the most often (GM = 70.3 mg/m³, GSD = 3.06); its concentration exceeded the ACGIH TLV in 11 measurements. Acetone (GM = 32.3 mg/m³, GSD = 6.33) and

TABLE 2 Concentrations of Organic Solvents Associated with Gluing in Shoe Workshops in Hebron City, 1997–1998

	Acetone	*n*-hexane	Methylethyl Ketone	Toluene	Additive Effect Relative to ACGIH§
Threshold limit value (ACGIH)	1,187 mg/m³	176 mg/m³	590 mg/m³	188 mg/m³	
Gluing					
(n/N)*	30/34	30/34	6/34	34/34	
Concentration					
GM†	32.3 mg/m³	19.4 mg/m³	130 mg/m³	70.3 mg/m³	0.53
GSD‡	6.3 mg/m³	2.7 mg/m³	1.5 mg/m³	3.1 mg/m³	2.90
Min	0.7 mg/m³	2.2 mg/m³	65.6 mg/m³	8.0 mg/m³	0.06
Max	399.0 mg/m³	85.1 mg/m³	173.0 mg/m³	290.0 mg/m³	2.52

*Frequency of detection/total measurements.
†Geometric mean.
‡Geometric standard deviation.
§Additive effect = $C_1/G_2 + C_2/G_2 \ldots + C_n/G_n$, where C = the actual concentration of the compound and G = the TLV of the compound.

TABLE 3 Use of Personal Protective Equipment in Shoe Factories in Hebron City, 1997–1998

	Never		Sometimes		Always	
	No.	%	No.	%	No.	%
Gloves	113	67.7	18	10.8	36	21.5
Filter masks	136	81.4	13	7.8	18	10.8
Goggles	160	95.8	5	3.0	2	1.2
Head covers	164	98.2	2	1.2	1	0.6
Special shoes	161	96.4	2	1.2	4	2.4
Working clothes	154	92.2	2	1.2	11	6.6
Any type*	104	62.3	14	8.4	49	29.3

*The use of at least one type of personal protective equipment.

TABLE 4 Use of Personal Protective Equipment in Shoe Workshops, Hebron City, 1997–1998

	Never		Sometimes		Always	
	No.	%	No.	%	No.	%
Gloves	97	94.2	2	1.9	4	3.9
Filter masks	100	97.1	2	1.9	1	1.0
Goggles	102	99.0	0	0.0	1	1.0
Head covers	102	99.0	0	0.0	1	1.0
Special shoes	93	90.3	0	0.0	10	9.7
Working clothes	84	81.6	0	0.0	19	18.4
Any type*	78	75.7	2	1.9	23	22.3

*The use of at least one type of personal protective equipment.

n-hexane (GM = 19.4 mg/m^3, GSD = 2.65) were also common (30 of 34). The frequency of detection for MEK was slightly less than those of the other solvents (6 of 34); its GM was 130 mg/m^3 (GSD = 1.5).

According to the ACGIH standards, the GMs of the additive levels in the shoe factory tasks were below the TLVs. However, the cleaning, gluing, and varnishing tasks were found to have maximum additive levels exceeding the TLVs (1.82, 3.18, 1.69, respectively). In workshops, the GM of the additive levels in the gluing task was also below the TLV, although the maximum additive level (2.5) exceeded it.

Workers in shoe factories and workshops have rarely used personal protective equipment; 62% of the workers in the factories (Table 3) and 76% of those in the workshops (Table 4) had never used any protective equipment at any time during their working hours. Furthermore, 81% of the factory workers and 97% of the workshop workers had never used respiratory protective equipment, and 92% of the factory workers and 81% of the workshop workers had never worn special work clothes during their work.

In the absence of work regulation, the architecture of the factories, especially factories built during the Israeli occupation of the West Bank, is primitive: 94.7% of them are located outside the Hebron City industrial zone (Chamber of Commerce and Industry, personal communication). These buildings lack standard safety features such as task barriers, rooms for storing raw materials, and mechanical ventilation.

DISCUSSION

Organic solvents detected in shoe factories are considered to be the main risk factor for occupational diseases among the workers.[20] Chronic neurologic symptoms as well as neurophysiologic abnormalities attributed to exposures to industrial solvents have been found among shoe workers.[12] Exposures to glue solvents in shoe factories have been found to cause chronic airway impairment, with nonspecific bronchial hyperresponsiveness.[21]

In the present study, six organic solvents were detected in association with the different shoe factory tasks (plastic molding, cleaning, gluing, and varnishing). This finding is similar to other findings worldwide.[17,22,23] These solvents were present during all tasks.

The factories lack barriers that separate the tasks from each other; thus the solvents can freely diffuse across the factory. The frequencies of detection of the solvents varied among factory tasks, however, each task was associated with particular solvent that was often found and was mainly related to the task activity, i.e., dichloromethane was prevalent in association with cleaning tasks.

Toluene was the organic solvent most often present in association with all the tasks; it was mainly detected in gluing and varnishing in maximum concentrations that often exceeded the ACGIH TLV. Although toluene is used as a safer replacement for benzene in solvent applications,[24] nevertheless it may have adverse effects on health, such as throat irritation,[25] headache, dizziness, feeling of intoxication,[26] prenarcotic symptoms,[27] and optic neuropathy and retinopathy.[28] Also, exposure to toluene may increase the risks of various gastrointestinal cancers.[29]

Acetone was also detected in high concentrations in association with gluing and varnishing. Neurobehavioral performances of workers exposed to high concentrations of acetone have been reported to be less than those of unexposed workers.[30] The concentrations present in the gluing and varnishing tasks were mostly below the TLV using the additive-effect formula based on the ACGIH exposure limit, but the maximum concentrations exceeded the TLV.

Dichloromethane (DCM) was mainly used in cleaning; it was used to remove plastic residues from the sole plates after the molding process. The close association between the cleaning and plastic-molding tasks resulted in the appearance of high concentrations of DCM in the plastic-molding tasks. A high concentration of DCM may cause neurotoxicity.[31] The additive effect in this task was below the TLV, but the maximum exceeded it.

Exclusion of mineral spirits from the study could have reduced the apparent additive effects found for some factory tasks. However, they were excluded from the calculation because of difficulties that arose during compound identification.

In a previous study, shoe factory workers engaged both in gluing and in varnishing had reported high prevalences of breathing difficulties, while workers in the cleaning and plastic-molding tasks had reported high prevalences of tingling of limbs and sore eyes. These health effects were associated with exposures to solvents and plastic compounds (Nijem et al., unpublished data).

Heptane was the second most common solvent in terms of frequency of detection. It was found in association with all factory tasks in concentrations below the TLV. Its effect on the peripheral nervous system is less toxic than that of *n*-hexane, and it could therefore be used as a substitute for *n*-hexane.[13]

Although the owners of the factories in the study agreed to participate in the entire study, some factories did not sustain their commitments to the end of the study. One of these factories did not allow us to take measurements on the last day, which may have been due to expected high levels of exposure. Thus, our results could underestimate true exposure. Other factories changed some of their workers' jobs, which obliged us to include new workers in the study.

Three major solvents related to gluing activities were used in the workshops: acetone, *n*-hexane, and toluene. However, the absence of the plastic-molding and cleaning tasks in these workshops and the lower prevalence of varnishing activities resulted in the detection of fewer solvents. The detected solvents were mainly associated with adhesive activities, which were the main task of the workers.[18]

The workshop workers had reported painful tingling of limbs, which was associated with exposures to solvents such as *n*-hexane in the gluing task.[18] Toxicity of *n*-hexane increased in the presence of other organic solvents such as methylethyl ketone.[14,15] Other compounds related to the plastic-molding and cleaning activities, such as dichloromethane and isocyanates, were not found in these workshops.

The absence of heptane in the workshops could be an indication that the workshops were using adhesive compounds that contained high percentages of *n*-hexane; this was not the case in the shoe factories.

The workers in these shoe factories and workshops had rarely used personal protective equipment such as respiratory protective equipment, gloves, and work clothes. They had usually relied on dust masks to reduce or prevent exposure. A few workers were using gas masks that had expired or nonfunctional gas filters. They had never replaced the filters and did not know that the filters should be replaced periodically. The workers had rarely used gloves, although a few had used unsuitable plastic gloves, which probably are easily penetrated upon contact with solvents.

The fact that the workers did not wear special work clothes during their work could create health hazards for their household members; upon returning home, the workers' contaminated clothes could transmit organic solvents to food and water in their houses and thus affect family members. this situation is possible since most of the workers have no knowledge about the potential adverse effects of such compounds. In the past, workers did not receive any information about any possible health effects or diseases they might get as a result of heavy exposures to organic solvents, and they had to work in unregulated conditions.

The buildings housing the factories and workshops are not suitable for shoe manufacturing since they were built to be dwellings in crowded areas. No safety regulations govern these factories and workshops. Raw materials are stored in open containers in close proximity to the workers. These containers normally lack labels and instructions about the health effects of the chemicals inside, or what to do upon contact. Even when such labels were found in this study, they were not in Arabic language, and most of the workers could not understand them. The potential for fires in these workplaces is very high, since some of the workers smoke while working.

The only ventilation in the shoe factories and workshops was open doors and windows (passive ventilation). Mechanical ventilation is not seen in the majority of these factories. Thus the solvents persisted in the working areas for long periods, making the indoor air heavily polluted by solvent vapors. The different tasks are performed very close to one another without true barriers, so the solvents easily and freely diffuse between working areas.

The raw materials used in the Hebron City workshops were found to contain commercial n-hexane (considered to be main causative factor for polyneuropathy) above the recommended value of less than 5%, and MEK was detected in combination with *n*-hexane; thus the neurotoxicity of *n*-hexane would have been greater even in concentrations below the TLV.[14,15,32] The high prevalence of painful tingling of limbs among the shoe workshop workers found by Nijem et al. (2000) could have been the result of such a combination.

CONCLUSION

This study describes the working conditions and the main organic solvents found in the materials used in the process of shoe manufacturing in Hebron City. Concentrations of the solvents were mainly below TLVs in most of the measurements. However, the bad working conditions, the absence of safety measures, and the lack of regulation probably will increase the health effects of these solvents. Awareness of the actions of such compounds and the use of personal protective equipment are essential to reduce or even prevent any further adverse health effects.

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