Chapter 1

Metrology Organic Solvents in the Shoes Industry in Sfax City (Tunisia)

Imed Gargouri and Moncef Khadhraoui

Additional information is available at the end of the chapter

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Abstract

In spite of the importance to the use of organic solvents in the shoes industry, exposure data of the employees at these solvents in this sector are absent in Tunisia. The objective of this study is to establish a biotoxicological supervision of exposure in shoes manufacturing companies. After the inventory of the most dominant solvents (acetone, cyclohexane, hexane and methylethylketone, toluene) in the preparations used in shoes manufacturing, 18 voluntary companies benefited from 55 dynamic atmospheric samplings realized on a duration of 4 hours. The exposure index some mixture ranged between 0.1 and 8.8 and presented an average value superior to 1, mainly in the partly industrialized process. These values reached, respectively, 1.7, 2.5 and 4.5 for the posts of finishing, shoes collector and glues dispatcher. The atmospheric average concentrations of certain solvents exceeded the limit value of professional exposure mainly for the hexane with a value of 214 mg/m^3 in certain posts. The chronic exposure to organic solvents in a shoes industry and to establish a first report on the profiles of exposure to these solvents in this sector. Hence, an approach of evaluation of the professional risk by the biotoxicological supervision of exposure is established in Sfax city.

Keywords: solvents, shoes, evaluation of the risk, metrology of atmosphere

1. Introduction

Organic solvents constitute a set of varied chemicals whose essential chemical properties are a solubilizing power associated with a generally high-volatility [1]. These properties make them products of use that are difficult to circumvent in various industrial sectors such as footwear manufacturing [2–4]. Among the chemical agents identified in this sector in Tunisia, organic solvents play a major role in the quantities used and the number of employees exposed.

However, employee exposure data for organic solvents in this sector are almost absent. The prevention of occupational risks (POR) and more particularly the chemical risk is based on the risk assessment (RA) according to procedures established by regulatory texts [4–6]. However, the Tunisian occupational health regulations [7, 8], did not provide any obligation for companies to perform RA requiring metrology of work environments, and biotoxicological dosages. The study objective is to establish a biotoxicological exposure metrology for solvent mixtures, composed mainly of acetone, cyclohexane, n-hexane, methyl ethyl ketone (MEK), and toluene used in the shoes industry of a pilot study to generalize it in all industrial sectors of Sfax city.

2. Methods

2.1. Manufacturing processes for shoes and workstations exposed to solvents

The shoe industry, despite the mechanization, remains a labor industry with 150 operations needed to make a pair of shoes. Three types of manufacturing techniques exist: welded, Goodyear sewn, and direct injected [9].

We limited ourselves in our study: (i) to the "welded" manufacturing process. It is the most widespread technique in Sfax city, and the most exposed to glue and solvent preparations (after creation, modeling, patronage, cutting and stitching, welded is the phase during, which the sole is fixed by gluing to a rod mounted on the base) and (ii) the three main positions exposing the solvents, which are the tiller station (mounting and gluing), the foundry station (display and welding), and the finishing station (cleaning, potting and packing) [10].

2.2. Sampling of shoe companies

Shoe manufacturing companies in the Sfax region have been classified and classified in three groups according to their manufacturing processes: industrial (26 companies and 751 employees), semi-industrial (6 companies and 46 employees) and handicraft (60 companies and 350 employees). The artisanal process has been divided into two categories: type 1 (foundry post and separate tiller station) and type 2 (the two spots are made by the same person in two steps).

Twenty-two companies using the "welded" process: 6 industrial, 6 semi-industrial and 10 artisanal with a workforce of 122, 48 and 60 employees (230 employees in total) were selected for this biometric study.

2.3. Selection of solvents to measure

Following a tracking of the solvents present in the composition of the products handled (glues, thinners and paint removers) in the shoe manufacturing companies during the first half of 2008, according to the simplified method of the National Institute for Research and Security (INRS) chemical RA, which mainly includes three phases: (i) inventory of products and materials used in the facility, in a workshop or workstation, (ii) prioritization of potential

risks and (iii) RA [4]; we have identified five predominant solvents: acetone, cyclohexane, hexane, methyl ethyl ketone and toluene [4, 11–14].

2.4. Methods

The exposure evaluation to these 5 solvents was carried out over 15 weeks from May 20 to September 15, 2010, divided into two periods, each comprising two components [4, 5, 15, 16]: (i) an observation of the different workstations with the help of the head of the company and the oldest employees and (ii) ambient metrology of solvents and glues.

2.4.1. Biometric measurements

In order to measure the concentration of solvents in the atmosphere, individual and/or stationary samples were taken (**Figure 1**): the sensors were placed close to the airways (personal sampling system) or installed at medium height of the tracks. Above ground level (stationary system), and consisted of a sampling pump (Poket Pump: Pump SKC® 210–1002 TX) with a regular flow rate of 100 (± 5%) cm^3/min and an activated carbon trapping tube (SKC® Tube 226-16: 800 and 200 mg). The sampling was set up for a half-workstation or duration of 4 hours. The samples were taken in the middle of the week: Wednesday or Thursday depending on the type of manufacturing process of the companies and their places of installation. Solvent concentrations were determined by gas chromatography after desorption of sampled sample tubes [17–21].

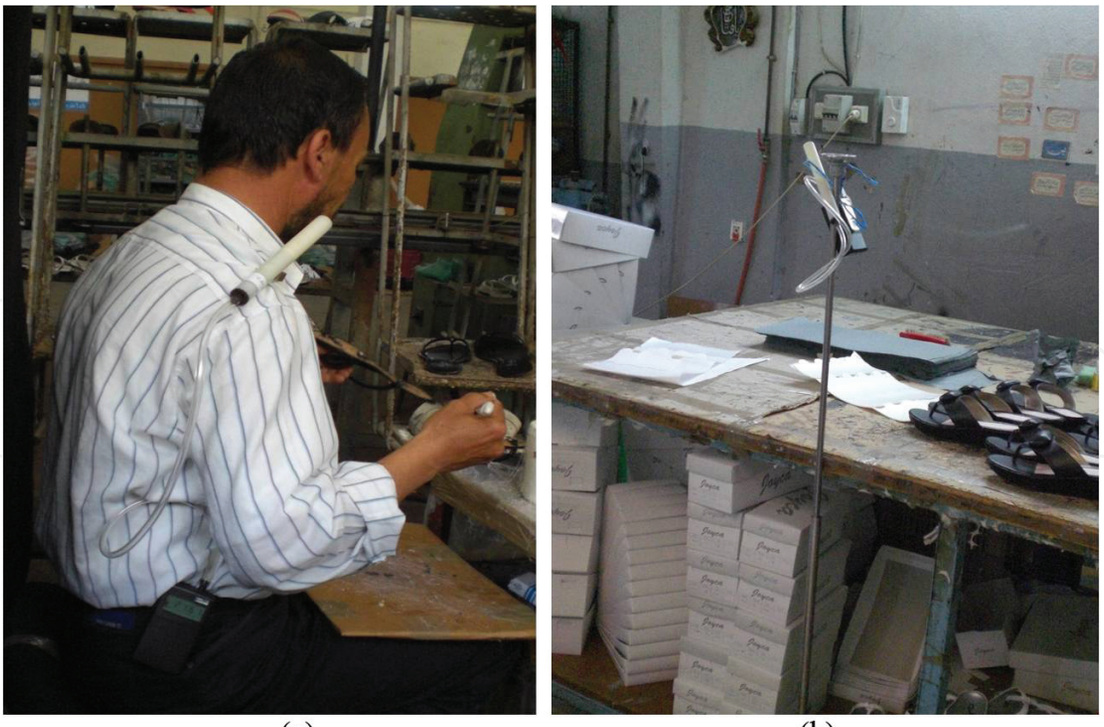

Figure 1. Atmospheric metrology in a semi-industrial shoe manufacturing company. (a) Individual sampling at the "uppers preparation workstation and (b) ambient sampling at the "finishing workstation.

Solvent	N° CAS[1]	France *UE*[2]		USA *ACGIH*[3]		Allemagne *MAK*[4]		Sfax study *Values selected*	
		VME[5]		TLV-TWA[6]				AEV adopted	
		ppm[7]	mg.m^{-3}	ppm	mg.m^{-3}	ppm	mg.m^{-3}	ppm	mg.m^{-3}
Acetone	67–64-1	500	1210	500	—	500	1200	500	1200
Cyclohexane	110–82-7	200	700	300	—	200	700	200	700
n-Hexane	110–54-3	20	72	50	—	50	180	20	72
Methylethylketone (MEK)	78–93-3	200	600	200	—	200	600	200	600
Toluene	108–88-3	50	192	50	—	50	190	50	190

[1]CAS: Chemical Abstract Service.

[2]UE: Union Européenne.

[3]ACGIH: American Conference of Governmental Industrial Hygienists.

[4]MAK: Maximale Arbeitsplatz-konzentration.

[5]VME: Average Exaposure Value (Valeur Moyenne d'Exposition) calculated in relation to a reference period of 8 working hours per day and 35 hours per week.

[6]TLV-TWA: Time-Werghted Average (Valeurs Weighted average values over 8 hours per day and 40 hours per week).

[7]ppm: parts-per million and volume of air.

Table 1. Occupational exposure limit values [7, 8, 11, 15, 23, 25, 26].

2.4.2. Biometric exposure limit values

The measurements results were compared with the 's (AEV) of solvents calculated for a reference period of 8 working hours/day and 39 hours/week (**Table 1**) [7, 9, 11, 22, 23]. In the absence of Tunisian exposure limit values (ELV) [9, 10], we have referred to international values (French, American and German), adopting the most restrictive values (**Table 1**) [11, 22, 24–26, 27].

Since glues are a mixture of solvents, we have conventionally used an exposure index (I.exp) for individual samples that are used as a comparison with limit values [11, 28]. This I.exp. is equal to $C_1/AEV_1 + C_2/AEV_2 + \ldots\ldots\ldots\ldots + C_n/AEV_n$ (C_n and AEV_n being, respectively, the concentration and the limit value of the pollutant n). If I.exp. is greater than 1, the limit value is considered exceeded. Calculated from a fixed-rate levy, this index is called pollution index (I.pol).

3. Results

3.1. Participating shoe companies

Eighteen companies out of the 22 companies contacted agreed to participate (participation rate of 81.8%), including four manufacturing shoes using an industrial process, five using a semi-industrial process, and nine using an artisanal process. They were divided into two

groups according to the level of activity and the planning of the realization of the interventions: the first period, from May 28 to July 21, 2010, was a period of average activity (end of the preparations of the collection of summer); and the second period, from August 27 to September 12, 2010, a period of significant activity (preparations for the winter collection, the return to school, and the holiday season after Ramadan). A total of 55 atmospheric samplings of which 33 individual and 22 fixed samplings: 17 industrial enterprises, 23 semi-industrial enterprises, and 15 artisanal enterprises.

3.2. Atmospheric dosages of solvents

Employee exposures according to the industrial process show high levels of I.exp., especially in semi-industrial and artisanal type 1 enterprises during the two periods of activity, particularly during the period of high-activity (**Table 2**).

The atmospheric concentrations according to the workstation shows I.exp. and/or I.pol exceedances for the exhibitor stations (tigers, foundries, and finishes) in the processes: industrial, semi-industrial and artisanal type 1 (**Table 3**). At the silkscreen station in the industrial process, occupied by a young woman of childbearing age, the I.exp. is equal to 9.4.

The set of atmospheric measurements carried out in the different companies shows that the solvent exposure varies from one process to another and from one station to another (**Table 4**). The average atmospheric concentrations of hexane were particularly high with exceedances of the AEV including the position of the tiller, the melter, and the finish in all processes with the exception of the artisanal process type 2. With the exception of MEK at the uppers preparation

Process	Company	Samples						
		Number	Individual			Ambience		
			Exposure index (I.exp)			Pollution index (I.pol)		
			n	min-max	average	n	min-max	average
Industrial	1	5	3	0.3–1.1	0.7	2	0.5–0.8	0.6
	2	2	1	—	**1.8**	1	—	0.3
	3	5	4	0.9–9.4	**3.7**	1	—	0.8
	4	5	4	0.8–19.8	**6.8**	1	—	0.0
Semi-Industrial	1	5	3	0.4–1.2	0.7	2	0.0–0.3	0.1
	2	5	4	0.5–2.0	1.0	1	—	0.4
	3	4	2	0.2–2.5	**1.3**	2	0.2–0.4	0.3
	4	5	4	0.9–2.4	**1.7**	1	—	0.1
	5	4	1	—	**5.6**	3	4.3–8.8	**6.8**

Process		Company	Samples						
			Number	Individual			Ambience		
				Exposure index (I.exp)			Pollution index (I.pol)		
				n	min-max	average	n	min-max	average
Artisanal	Type 1	1	2	1	—	0.1	1	—	0.4
		2	1	/			1	—	0.7
		3	1	/			1	—	0.8
		4	3	2	0.4–1.7	1.1	1	—	**1.6**
		5	2	1	—	**1.5**	1	—	0.9
		6	2	2	1.6–3.4	**2.5**	/		
		7	2	1	—	**6.4**	1	—	**5.1**
	Type 2	8	1	/			1	—	0.5
		9	1	/			1	—	0.6
			Total = 33				**Total = 22**		

First Period: May 28 to July 21, 2008.
Second Period: from August 27 to September 12, 2008.
n: number of measurements taken.

Table 2. Atmospheric exposure of employees according to the manufacturing process in the 18 companies.

Process	Workplace	Samples						
		Number	Individual			Ambience		
			Exposure index (I.exp)			Pollution index (I.pol)		
			n*	Min–Max	Average	n	Min-Max	Average
Industrial	Cutting	1	/			1	—	0.0
	Stitching	1	/			1	—	0.8
	Uppers preparation	4	3	0.9–19.8	**8.4**	1	—	0.5
	Founder	7	5	0.3–3.5	1.5	2	0.3–0.8	0.5
	Finishing	3	3	0.9–1.8	1.2	/		
	Serigraphy	1	1	—	**9.4**	/		
Semi-industrial	Uppers preparation	8	4	0.5–2.5	**1.6**	4	0.1–7.2	**2.5**
	Founder	12	10	0.2–5.6	1.8	2	0.2–8.8	**4.5**
	Finishing	3	/			3	0.3–4.3	1.7
Artisanal	Uppers preparation	5	2	0.1–1.6	0.9	3	0.9–5.1	**2.5**
	Founder	8	5	0.4–6.4	**2.7**	3	0.4–0.7	0.6
	Uppers preparation/ founder	2	/			2	0.5–0.6	0.6
		Total = 33				**Total = 22**		

*Number of samples.

Table 3. Employee exposure index by workstation.

Process	Workplace	n*	Acetone (mg/m³)		Cyclohexane (mg/m³)		n-Hexane (mg/m³)		MEK (mg/m³)		Toluene (mg/m³)	
			Min–Max	Average	Min–Max	Average	Min–Max	Average	Min–Max	Average	Min–Max	Average
Industrial	Cutting	1	—	0.0	—	0.0	—	0.0	—	0.0	—	0.0
	Stitching	1	—	0.0	—	160.5	—	36.8	—	0.0	—	6.8
	Uppers preparation	4	0.0–1652.0	413.0	0.0–183.8	66.8	28.1–975.0	**300.1**	0.0–2656.9	**776.6**	13.6–321.0	103.5
	Founder	7	0.0–3077.3	439.6	0.0–72.1	21.2	14.3–139.3	51.9	0.0–121.4	17.3	0.0–71.9	21.3
	Finishing	3	—	0.0	0.0–34.2	12.9	53.8–86.6	66.8	0.0–165.3	108.7	56–43.7	20.8
	Serigraphy	1	—	0,.0	—	**1281.1**	—	**401.8**	—	**1090.8**	—	38.6
Semi-industrial	Uppers preparation	8	0.0–114.3	16.1	—	118.5	0.0–204.0	57.4	0.0–509.5	113.4	4.4–500.0	106.6
	Founder	12	0.0–989.1	222.0	—	94.0	0.0–214.1	58.6	0.0–622.5	134.2	4.0–615.9	121.6
	Finishing	3	0.0–474.3	158.1	—	3.9	0.0–116.0	43.8	0.0–350.3	136.2	10.3–329.0	130.4
Artisanal	Uppers preparation	5	0.0–217.6	43.5	—	111.5	0.0–112.8	52.9	0.0–334.5	124.0	7.8–480.0	138.5
	Founder	8	—	0.0	—	112.2	3.3–147.3	58.6	0.0–442.5	150.8	0.4–578.1	115.0
	Uppers preparation / founder	2	00–43.4	21.7	—	26.6	21.6–27.2	24.4	—	0.0	27.7–35.9	31.8
		Total = 55										

*Number of samples.

Table 4. Average atmospheric concentrations of the solvents dosed.

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and screen printing stations in the industrial process, the concentrations of the other solvents measured (acetone, cyclohexane, and toluene) were relatively high without exceeding the AEVs.

4. Discussion

This study is the first active sampling approach in the field of occupational health in Tunisia. It initiates the implementation of a structured approach in occupational toxicology and the environment by our laboratory in the theme of the impact of hazardous substances on the environment and human health. It required the acquisition of sampling equipment, which is of great interest to develop this type of toxicological measures and to carry out new measurement campaigns in Sfax city.

We had to experience a delay in carrying out our atmospheric sampling due to the various difficulties related to the development of the solvent analysis protocols. Indeed, we have carried out bibliographic research and repeated laboratory tests in the absence of technology transfer (North–South) methods of analysis [16, 29, 30].

For about 10 years the use of solvents is in full revolution, because of the constraints of PRP, but mainly because of regulatory requirements of the protection of the environment. These regulatory changes lead to changes in the nature of the solvents applied and in the way, they are used [11, 23, 31]. In addition, the number of employees exposed continues to increase in Tunisia. In France, the summer 2003 survey showed that the number of employees exposed to solvents has increased since 1994, from 12.2 to 14.7%, mainly in the chemical industry [2].

If these atmospheric metrology and toxicological analyzes were made for the first time in the footwear manufacturing sector in Sfax, they interested a sample of companies from the three footwear manufacturing processes (industrial, semi-industrial and artisanal) and were preceded by a preliminary RA with a post-study and an inventory of the products handled [5, 6]. This RE could be improved by the experience we have gained and with the best knowledge of this sector and its risks.

All samples taken from companies indicate that employee exposure to organic solvents varies widely depending on the task performed. Exposure indices were greater than 1 with VME overruns, particularly at the most exhibiting positions: the tiller, the smelter, and the finish. In our study, hexane levels were particularly high with averages ranging from 24.4 to 300.1 mg/m^3; while toluene levels were relatively high in some measurements but averages were below the VME range of 21.3–138.5 mg/m^3. In Spain and according to Cardona [32, 33], in his studies on the manufacture of footwear in the process the welded, by means of passive sampling (by badge) the average atmospheric concentration of hexane and toluene at the positions of founders, and the finish was, respectively, 47 and 86 mg/m^3 with a range of 4–652 and 2–1143 mg/m^3, respectively.

5. Conclusion

This study allowed us to know the chronic exposure to solvents in Tunisian shoes industry and to establish the first report on solvent exposure profiles in this sector. This exposure is not

constant over time and varies according to the task performed and the manufacturing process. Therefore, the study of exposure to the workplace requires not only the average exposure to the AEV but also to identify the polluting phases to determine the short-term exposure to the AEV.

Following the phase of identification of solvents and the demonstration of exceedances of the limit values of certain solvents, the presence of women has increased in the shoe manufacturing companies, which encourages us to explore the reprotoxic nature of certain preparations. An approach to assess occupational risk through exposure bio-toxicological monitoring has thus been implemented in Sfax city in various sectors exposing solvents for a better POR.

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Conflict of interest

The authors declare that they have no conflict of interest in relation to this article.

Author details

Imed Gargouri[1,2]* and Moncef Khadhraoui[1,3]

*Address all correspondence to: imed.gargouri@fmsf.rnu.tn

1 Laboratory of Environmental Engineering and EcoTechnology (LR16ES19), Sfax University, Tunisia

2 Medical School, Sfax University, Tunisia

3 Higher Institute of Biotechnology of Sfax, Sfax University, Tunisia

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