Exposure to styrene in the fiberglass reinforced plastic industry

Master project

Student: Snezana Nedeljkovic

University of Bergen

August 2020

Foreword

During the past two decades, to our knowledge there have been no published studies on exposure to styrene or acetone in the Norwegian FRP industry. The lack of information about the present occupational exposure to these chemicals was the motivation behind the choice of this study.

The study was part of a larger study that I had the honor to participated in. That study examined personal exposure levels to styrene, styrene oxide and acetone, styrene metabolites in urine, as well as hematological and immunological effects in peripheral blood, among workers in two fiberglass reinforced plastic companies in Norway and it was run by the Department Occupational Medicine, Haukeland University Hospital and Research Group for Occupational and Environmental Medicine, University of Bergen, Norway. The cooperation and support I received from my research colleagues and supervisors at the University of Bergen was of great help to me. Without their engagement and encouragement this study would not be fulfilled.

I would like to give my greatest gratitude and acknowledgements to:

- Magne Bråtveit; Main supervisor. Professor at the Department of Global Public Health and Primary Care, Occupational and Environmental Medicine, University of Bergen
- Bjørg Eli Hollund; Co-supervisor. Associate professor at the Department of Global Public Health and Primary Care, Occupational and Environmental Medicine, University of Bergen
- Jorunn Kirkeleit; Co-supervisor. Associate professor at the Department of Global Public Health and Primary Care, Occupational and Environmental Medicine, University of Bergen
- Management and all the workers who participated in this study

SUMMARY

OBJECTIVE: To characterize exposure to airborne styrene and acetone among workers in the fiberglass reinforced plastic (FRP) industry.

METHODS: Two full shift exposure measurements of airborne styrene and acetone were performed on 37 workers in two FRP companies (n=72). Urine samples were collected for the same workers pre- and post-shift on the first day for analysis of markers of exposure to styrene; Mandelic acid (MA) and phenylglyoxylic acid (PGA). Styrene and acetone concentrations were determinated by gas chromatography-mass spectrometry (GC-MS). Urinary MA+PGA was assayed by liquid chromatography with tandem mass spectrometry (LC-MS/MS).

RESULTS: The overall arithmetic mean (AM) value of exposure to styrene for all production workers in the two companies was 11.8 ppm, which is below the Norwegian Occupational Exposure Limit (OEL; 25 ppm). The overall AM mean exposure to acetone among the same group of workers in the two companies was 69.7 ppm, which is below the OEL for acetone (125 ppm). There was a statistically significant, but weak correlation between exposure to acetone and styrene ($r=0.375$, $p=0.001$, $n=72$). The overall AM value for the post-shift MA+PGA for the production workers was 116,8 mg/g creatinine, which is below the Biological Exposure Index (400 mg/g creatinine) from the American Conference of Governmental Industrial Hygienists (ACGIH). The correlation between exposure to styrene and post-shift MA+PGA was strong and statistically significant ($r=0.844$, $p<0.001$, $n=34$).

CONCLUSION: The exposure to airborne styrene and acetone is relatively high compared to the occupational exposure levels. Furthermore, for some of the workers post-shift urinary concentrations of the styrene metabolites MA+PGA were above the BEI.

KEYWORDS: Styrene exposure; Acetone exposure; Fiberglass reinforced plastic industry.

Table of Contents

1. Introduction

1.1 Background

Fiberglass reinforced plastic (FRP) industry

Fiberglass reinforced plastic (FRP) or fiber reinforced polymers are composite plastics used in a range of products such as leisure boats and storage tanks.

The first boat made of fiberglass in Europe was produced in Norway in 1953. The years after, and until 1970-80s the FRP industry was extensive in the Southern and Western part of Norway. The Norwegian industry exported plastic boats to Europe. Plastic boats were cheap and easy to produce and very popular because they were easy to maintain compared to wooden boats. Herwa Plast in Grimstad was the first company established in Norway in 1956. Later, new companies were established in the Southern part of Norway [1].

Production process

The lamination process mostly used are contact open molding techniques which are often manual and can involve hand lay-up or spray-up lamination to deposit styrene resin/polyester and fiberglass onto the surface of a prepared mold. Depending on the part and structure of the boat, series of layers are applied during lamination.

During the hand lay-up, the styrene resin is applied directly to the mold, after which it is covered with fiberglass mats by hand, and thereafter rolled manually to remove any entrapped air bobbles before curing [2] (Picture 1).

In spray-up operation, both the styrene resin from a styrene tank and fiberglass in form of a thread chopped by a hand-held machine are applied simultaneously to the mold by jet spray guns. Also after spray-up the laminate is manually rolled before curing (Picture 1).

The vacuum method (Picture 2) is a closed mold technique used for the parts with large and clean surfaces and implies that the resin is injected into a sheet of fiberglass in a mold, which is covered with a thin plastic film. As air is aspired from the space between the mold and the plastic film by a vacuum pump, polyester is spread through a network of small tubes into the fiberglass layer. This method will also press out air from the laminate. After this step, the part is left to dry (around 21h) under vacuum.

Picture 1. Rolling and spraying technique [31]

Picture 2. Vacuum technique [31]

Chemicals used in the process

At room temperature, the polyester is a liquid containing 40-60% styrene. During the process of laminating and curing, about 10% of the styrene may evaporate into the workplace air [3]. Workers are exposed to a mixture of fine fiberglass fibers and volatile organic compounds (VOC), mainly styrene from the resin and acetone which is used as a cleaning agent.

Styrene

Styrene C_8H_8 (*Chem. Abstr. Serv. Reg. No.*: 100-42-5, phenyl ethylene, vinyl benzene) is a colorless-to-yellowish, viscous liquid with a peculiar, sweetish, piquant odor. Because of the immense reactivity of its double vinyl-bond, styrene is easy to polymerize and copolymerize at room temperature [4]. This characteristic makes styrene an important commercial chemical. Styrene-based unsaturated polyester resins (UPR) are used to produce fiberglass reinforced plastic products (e.g. boats, tanks) with long service life for both indoor and outdoor applications [2].

Workers in the reinforced plastic industry are reported to have the highest occupational exposure to styrene [5] followed by workers involved in styrene polymerization and in the rubber industry. In the reinforced plastic industry styrene exposure mainly occurs by inhalation during hand lay-up and spray-up operations, lamination and curing steps [4, 6]. Exposure via skin contact is minor and the percutaneous absorption of styrene is not likely to significantly contribute to the body burden of workers in this type of industry [7].

The metabolism of styrene in humans is well characterized, where the first step in the major metabolic pathway is initiated by cytochrome P-450 enzymes with the oxidation of styrene to reactive metabolite styrene 7, 8-oxide (SO), further metabolized by hydrolysis to styrene glycol, then oxidized to mandelic (MA) and phenylglyoxylic (PGA) acids. These acids comprise, respectively, 85% and 10% of the total amount of absorbed styrene excreted in urine [8]. A small fraction of styrene escapes metabolic transformation and gets eliminated unchanged through the urine [9]. The total concentration of MA and PGA in urine are widely used as biomarkers for the biological monitoring of styrene exposure in humans.

Possible health effects connected to occupational exposure to styrene can be:

- Acute effects – are manifested as mild to severe mucous membrane irritation of upper respiratory organs and eyes. Also, symptoms as headache, dizziness and fatigue can be observed.
- Chronic effects – are manifested in the CNS [10].

International Agency for Research on Cancer [3] has classified styrene as probably carcinogenic to humans (group 2A).

Acetone

Acetone C_3H_6O (*Chem. Abstr. Serv. Reg. No.*: 67-64-1) is a colorless, volatile, flammable organic solvent. In humans, rapid absorption of acetone (within several minutes) occurs from oral, dermal and inhalation exposure (with relative uptake around 50%). Acetone is more evenly distributed in the body water, not selectively absorbed in any tissue. The metabolism of acetone in humans is well examined. Independent of the route of uptake, the metabolic fate of exogenous acetone, at low doses, involves three separate pathways with acetol (1-hydroxyacetone), methylglyoxal and 1,2-propanediol as intermediary products. An alternate pathway appears at high doses, which causes the splitting of 1,2-propanediol to acetate and formate. Acetone is effectively eliminated even at high internal doses. Elimination occurs via metabolic transformation to endogenous biochemicals, as vapour via airways and the skin, via exalation of CO_2 and via urine as acetone or acetol, methylgyoxal or as D-lactoyl-GSH [11].

Workers involved in manufacturing of reinforced plastic products may be co-exposed to acetone. Acetone is an inexpensive solvent and generally used in large quantities as cleaning agent for the work equipment used.

Acute health effect of acetone varies depending on the exposure level and the route of exposure. Airborne exposure can give symptoms from CNS as headache, dizziness, confusion, unconsciousness, also irritating effect on nose, throat, lung and eyes. Skin exposure can give irritation and damage to skin. Chronic exposure may result in dermatitis and nerve damage [12].

1.2 Literature review on exposure to styrene in the fiberglass reinforced industry

A review of styrene exposure for workers in the European FRP industry showed that the average styrene concentrations in the breathing zone of open-mold workers had decreased on average 5.3% per year during the period 1966-1990, with reported mean concentrations ranged up to 150 ppm. This review also showed that in the period between 1990 and 2002 the average styrene concentration decreased by only 0.4% per year, with mean values in the range 12-58 ppm [13].

A study by Geuskens *et al*., [14] of exposure to styrene and health complaints in the Dutch glass-reinforced plastic industry in 1992 also showed that the levels of exposure were high. Geometric mean values of 8-h TWA of measured airborne styrene ranged from 4-168 ppm during the open mold techniques regardless the fact that all examined plants had implemented control measures.

Lenvik *et al*., [15] analyzed statistically the measurement data of exposure to airborne styrene in Norway (234 enterprises) in the period 1972-1996. Their analyses showed that the median value decreased from 62 ppm (1970s) to 7.1 ppm (1990s), but it did not reveal any decisive impact of any single preventive measure enforced by the authorities to reduce the exposure.

Galassi *et al*., [16] performed biological monitoring of styrene exposure among Italian workers employed in the reinforced plastic in the period between 1978-1990. The measured concentrations of post-shift mandelic (MA) and phenylglyoxylic acid (PGA) showed that the most important predictor of styrene exposure is the type of the job performed by the workers i.e. hand laminators had the highest mean values (MA: 682 mg/g creatinine) while the lowest mean values were detected in non-process workers (MA: 186 mg/g creatinine).

In U.S. a survey report in the fiber reinforced plastic boat manufacturing industry from 2007 reported a significant difference between the job categories. Hull-rollers and gun-operators had significantly higher exposure (GM of 34.74 and 34.48 ppm, respectively) than the gel coaters (GM=17.89 ppm) [17].

Tranfo *et al.*, [18] compared the exposure to styrene between two different manufacturing processes in Italy in 2012. Workers engaged in the open mold process were exposed to higher levels of styrene (median value 31,1 mg/m^3 (7,3 ppm)) than in close mold process (median value 24,2 mg/m^3 (5,6 ppm)). They found a significant linear correlation between exposure to airborne styrene and the concentrations of MA+PGA in urine ((R=0.74).

A study by Polakova *et al.*, [19] from 2012 on urinary concentrations of styrene metabolites in fiberglass laminate production workers reported mean styrene exposure within the range 93.77-159.88 mg/m^3 (21.7-37 ppm), and it was concluded that the concentrations of mandelic acid (MA) in urine is a sensitive metabolic marker of styrene exposure without cumulative effect.

A Spanish study in fiberglass boat factories from 2002 found that workers exposed to both styrene (mean TWA=70.5 mg/m^3 (16.5 ppm)) and acetone (mean TWA=370.7 mg/m^3 (156 ppm)) had a mean concentration of excreted metabolites (MA+PGA) of 147.1 mg/g creatinine, and that this concentration decreased significantly when environmental concentrations of acetone increased [9].

In order to explore the factors that can influence the levels of styrene exposure biomarkers of the workers and the aspects that might interfere with the exposure assessment measures, such as the co-exposure to acetone, an Italian study was completed in 2015. The median values of measured styrene exposure in four different fiberglass reinforced plastic manufacturing plants were between 24.1-94 mg/m^3 (5.6-22.1 ppm), while the median values of post-shift MA+PGA were between 7.3-331.1 mg/g creatinine. They concluded that simultaneous exposure to acetone modify the styrene metabolism with a reduction in the levels of (MA + PGA) excreted [20].

Table 1. Overview of literature on exposure to styrene, acetone and styrene metabolites in urine (MA, PGA, MA+PGA) (1990-2019)

Reference	Location/collection data	Occupation description	No. workers/samples	Styrene (ppm)	Acetone (ppm)	MA; PGA; MA+PGA (mg/g creatinine)
Geuskens, R.B.M. *et al*. (1992)	Nederland, Four factories; NR	Hand laminating Spraying Filament winding	82 in total	[R TWA, 4-126] [R TWA, 11-142] [R TWA, 31-168]	NR	NR
Galassi, C. *et al*. (1993)	Italy, 118 factories; 1978-1990	Hand laminating Spraying laminating Rollers Semi-automatic process	4682 MA 1630 styrene exposure	[AM, 53.4] [AM, 31.5] [AM, 38.3] [AM, 20.0]	NR	[AM; MA, 682] [AM; MA, 404] [AM; MA, 327] [AM; MA, 243]
Lenvik, K. *et al*., (1999)	Norway, 234 enterprises; 1972-1996	NR	7011	[M, 62] 1970s [M, 7.1] 1990s	NR	NR
Prieto, M.J. *et al*. (2002)	Spain, Boat factory	NR	34	[AM TWA, 16.5]	[AM TWA, 156]	[AM; MA, 104.5] [AM; PGA, 42.6]
Carlo, R.V. *et al*., (2007) (Survey Report)	USA, US Marine Boat factory	Open-mold Closed-mold	NR	[AM,47.5] [AM, 3.22-4-78]	NR	NR
Van Rooij, J.G.M. *et al*. (2008)	EU 1966-2002	Open-mold Closed-mold Other Not reported	24145 air samples 6361 urine samples	[AM, 12-150] [AM, 2-21]	NR	NR
Tranfo, G. *et al*. (2012)	Italy, Two factories	Open-mold Closed-mold (Compression)	24	[AM, 7.3] [AM, 5.7]	NR	NR
Polakova, *et al*. (2012)	Slovakia, Not specified	Laminating Milling and finalizing Spraying Background support	11 11 6 7	[R, 21.7-37]	NR	[AM; MA, 1011.75] [AM; MA, 210.65] [AM; MA, 278.97] [AM; MA, 109.70]
Bonanni, R.C. *et al*. (2015)	Italy, Four factories	Open-mold (Factory A) (Factory B) (Factory D) Closed-mold (Factory C)	20 12 12 14	[M, 10.1] [M, 7.3] [M, 22.1] [M, 5.6]	NR	[M; MA+PGA, 7.3] [M; MA+PGA, 76.7] [M; MA+PGA, 331.1] [M; MA+PGA 33.8]

AM=arithmetic mean; **GM**=geometric mean; **M**=median; **R**=range; **TWA**=time-weighted average; **MA**=MA post-shift; **PGA**=PGA post-shift; **NR**=not reported

1.3 Rationale for the present study

Due to the acknowledged neurotoxic effects of styrene and the “Scandinavian solvent syndrome” [21] occupational exposure to styrene among workers in the reinforced plastic industry has been of special concern in Norway since the beginning of the 1970s. As late as 2019, styrene was classified as probably carcinogenic to humans (group 2A) by the International Agency for Research on Cancer (IARC, 2019), emphasizing a continued need for focus on exposure reducing measures in this industry.

In 2010, around 4000 workers were employed in this type of industry in Norway [22] and therefore exposed to styrene. Due to a sustained focus from the Labour Inspection on reducing the exposure levels of styrene and other solvents from the Norwegian FRP industry before year 2000, control measures were established in the production processes. Consequently, occupational exposure to styrene in Norway as well as in the other European countries dropped from the 70-ties to the mid 90-ties [15]. However, the exposure levels were still close to or above the present Norwegian occupational exposure limit (OEL) of 25 ppm, indicating that it was difficult to obtain adequate efficiency of the control measures in order to comply with the regulations [13]. To our knowledge there have been no published studies on exposure to styrene or acetone in the Norwegian FRP industry during the last 20 years. Thus, information about the present exposure is lacking. Although appropriate personal protective equipment is available for the FRP-workers, it is of importance to assess whether the present use of these devices provides adequate protection of the workers by studying the uptake of styrene in the body.

2. Objectives

The main objective was to characterize personal airborne exposure to styrene and acetone among workers in the glass fiber reinforced industry.

Specific objectives were to:

1. Characterize personal airborne exposure to styrene and acetone in order to compare it with the Norwegian Occupational Exposure Limits (OELs).
2. Assess the concentration of two major styrene metabolites (phenylglyoxylic (PGA) and mandelic acid (MA)) in urine.
3. Compare the levels of MA+PGA in urine with the ACGIH Biological Exposure Index (BEI) for these metabolites in post-shift urine.

3. Method

3.1 Organization of the master project

This master project is part of a larger study “Exposure to styrene in the fiber glass reinforced plastic industry” run by the Department Occupational Medicine, Haukeland University Hospital and Research Group for Occupational and Environmental Medicine, University of Bergen, Norway. The full study examined personal exposure levels to styrene, styrene oxide and acetone, styrene metabolites in urine, as well as hematological and immunological effects in peripheral blood, among workers in two fiberglass reinforced plastic companies. The study also comprised questions on health-related symptoms. The study was conducted over two days of one week in each company. During each of the two sampling days, personal full-shift air samples were taken for analysis of styrene, styrene-oxide and acetone. Furthermore, urine and blood samples were taken pre-shift and post-shift on the same two days for analysis of markers of exposure to styrene (MA and PGA) and effects on the immune-system, respectively. A detailed log sheet/diary was filled in on work activities/tasks and on use of personal protective equipment.

The present master thesis presents personal exposure levels to styrene and acetone on the two selected days of the week (Monday and Thursday) and urine concentrations of pre- and post-shift MA+PGA on the first day of the week (Monday).

3.2 Study setting

3.2.1 Selection of the study participants

The study population comprised full-time workers in the production lines in two fiberglass reinforced plastic industries, one in boat production (Company A) and the other one in water tank production (Company B).

From Company A, all production workers from the Foundry department (N=7), Assembly department (N=5), Vacuum department (N=7), Form department (N=2) and Finish-polish department (N=1) were defined as an exposed group. Office/shop workers (N=4) were defined as a low exposed group. Out of totally 26 workers, 23 were male and 3 were female. Two workers in Company A only participated the first day of the study, leaving 24 workers participating on both days.

From Company B, all production workers from the Foundry department (N=3) and Assembly department (N=6) were defined as the exposed group. Employees from the Office section (N=2) were considered as a low exposed group. All 11 workers from Company B were males.

3.2.2 Production facilities

I. Company A:

Company A, a boat factory, was established in 1988. They produce recreational yachts from 8-12m in length. Yearly production is around 80 boats.

1. <u>Factory layout</u>

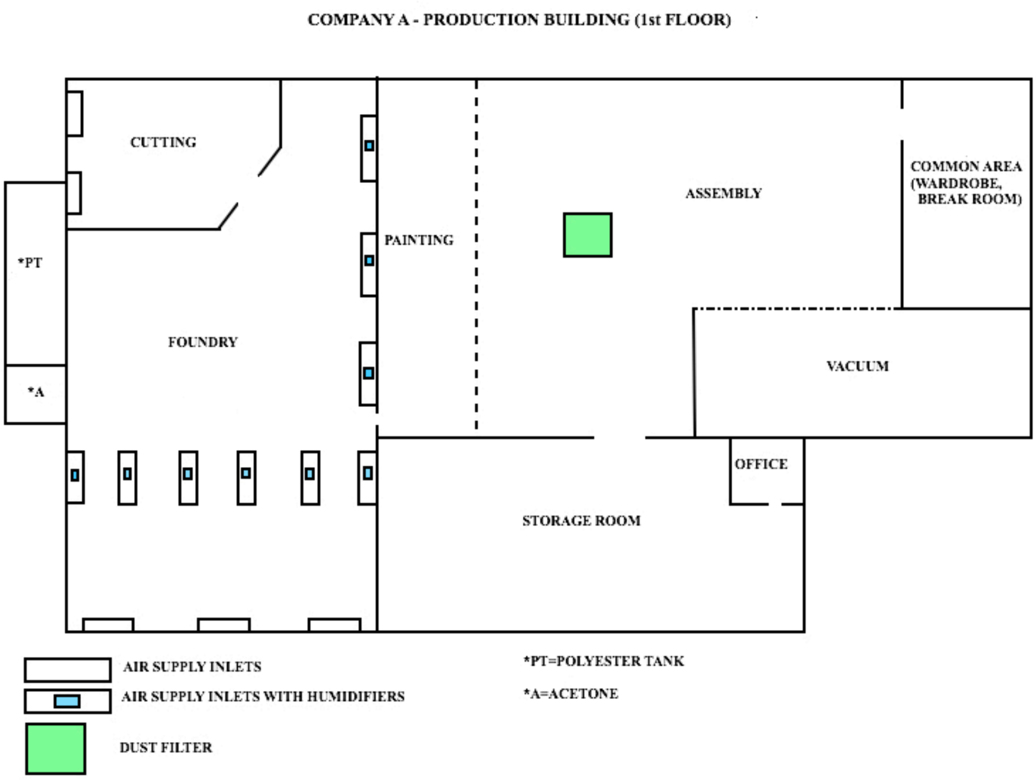


Figure 1. Factory map – Production building (1st floor)

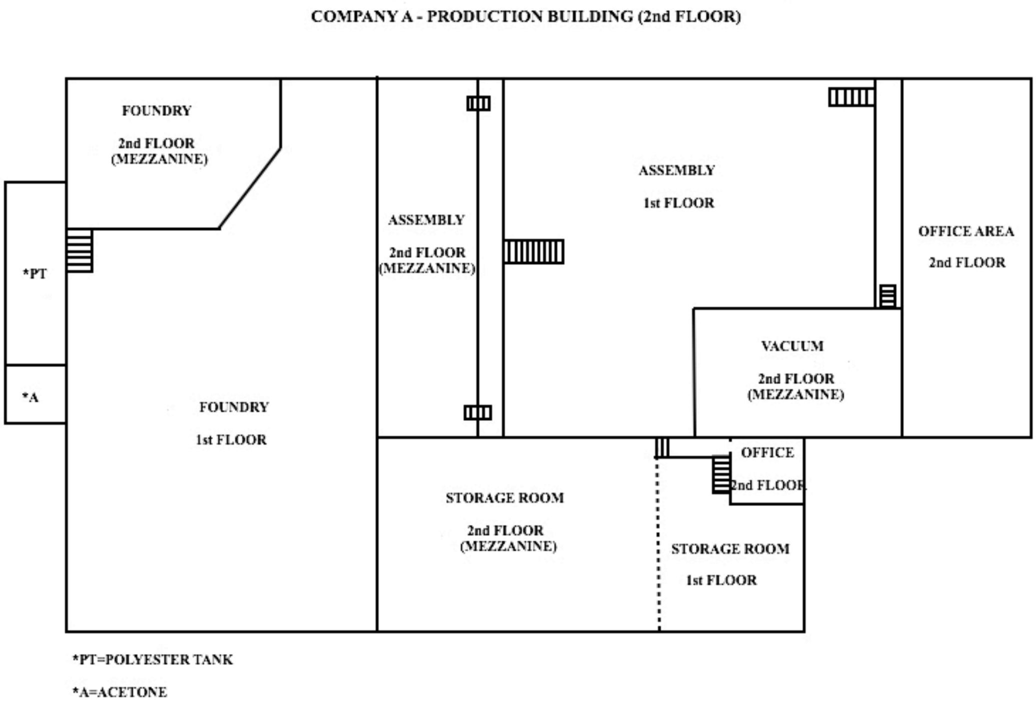


Figure 2. Factory map – Production building (2nd floor)

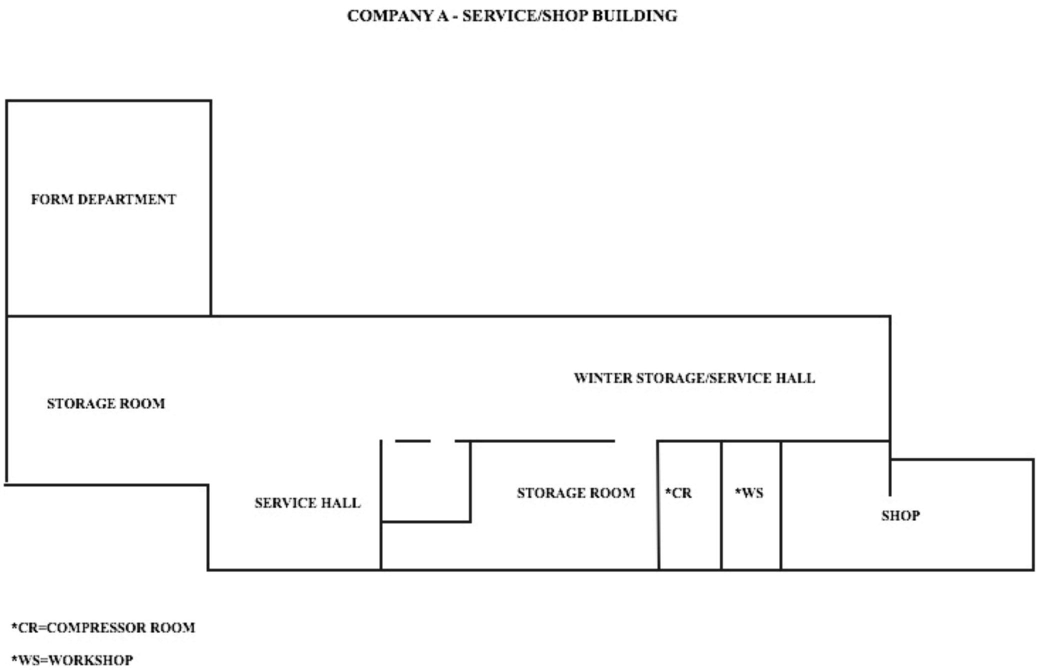


Figure 3. Factory map – Service/shop building

2. <u>Main sections</u>

The factory complex of Company A consists of two large buildings (hangars) that are located close to each other.

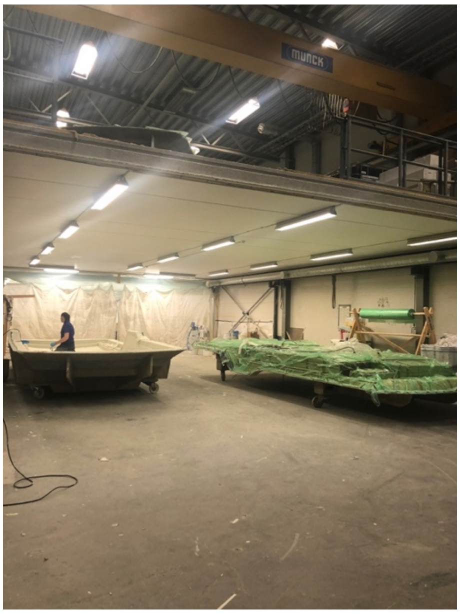
The building where the production is located has approximately 2000m^2 floor area, ceiling height of 8m and a volume of about 16000m^3. The building is divided into 7 areas (Figure 1 and 2):

1) Common area – consists of wardrobe (male and female) and break room.
2) Assembly area - around 1200m^2 and about 10m high. In this area, manual laminating (rolling and spraying) work is performed as well as preparation for the vacuum process (Picture 3 and 4). This space is equipped with dilution ventilation system and one big dust filter hanging from the ceiling in the middle part of the room. Totally 5 workers are employed here.

Picture 3. Assembly department [31]

Picture 4. Assembly department [31]

3) Vacuum area – is where the vacuum process is done. This section is below the mezzanine (Picture 5) and can be closed with curtains and is used for gel coating (Picture 6). Molds are also left here for drying (Picture 7). It measures around 100 m^2 and is about 3.5m high. The vacuum process is performed by 7 workers.

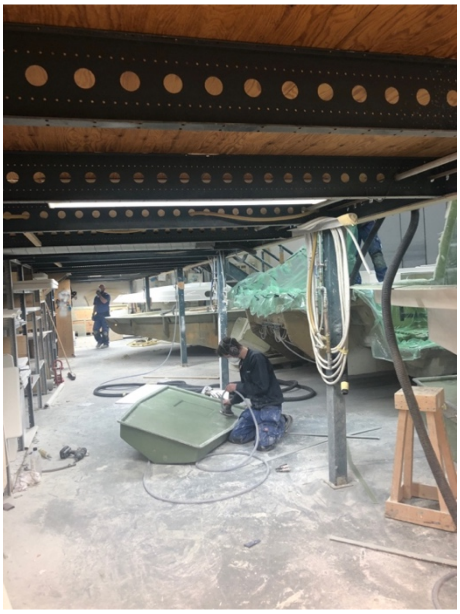


Picture 5. Vacuum department [31]

Picture 6. Preparation for vacuum [31]

Picture 7. Vacuum department [31]

4) Painting area (form department) – is an area located under the mezzanine. It is open toward the assembly area. Painting of small parts is performed here (Picture 8). Painting work was performed by 2 workers.



Picture 8. Form department [31]

5) Storage area – there are in total three storage rooms in the production building (one in the 1st floor and two in the 2nd floor).

6) Foundry area –a 1000m^2 floor area with a height of 8m and a volume of about 8000m^3. This is where manual laminating work is done and where the large boat parts are gel coated (rolling and spraying) (Picture 9, 10 and 11). This area is equipped with general displacement ventilation system (with inlets for air supply at the floor level) and humidifiers. Seven workers are employed in this section.

Picture 9. Foundry department [31]

Picture 10. Foundry department [31]

Picture 11. Gel coating with gun-spray [31]

7) Cutting area (finish-polish department) –In this room of about 40m^2 cutting, polishing and painting is performed (Picture 12). It is equipped with general displacement ventilation system (with inlets for air supply at the floor level) and with local exhaust ventilation on each work unit. In this section one worker usually works.

Picture 12. Finish-polish department

8) Second building – This big hall is between 1500-2000m^2 and 8m high and contains one big and one small storage, Form department, service halls, small workshop and shop (Figure 3). Approximately 6 workers are working in this hall.

3. Chemicals

In Company A, the main polyester based chemicals in the production process were Polylite 505-M880 and Synthopan 281 IPX-17 (Table 2). In the Foundry department, polyester with a styrene content of 30-35% was used for spraying and rolling lamination. The same styrene percentage was used in the assembling section. The vacuum section used polyester containing 35-40% styrene. Monthly use of these polyesters varied from 1-2 tons for spraying and gel coating technique, while around 1.2 tons was used per month in the assembly section. Approximately 10 tons of polyester per month was used in the vacuum area. Acetone (40%) was mostly used during cleaning processes, with monthly use of roughly 450 l/month.

Table 2. Monthly use of polyester and acetone in Company A

Chemical	Monthly use per department/concentration of active substance		
	Foundry	Vacuum	Assembly
Polyester (Polylite 505-M880; Synthopan 281 IPX-17)	1-2 tons 30-35% styrene	10 tons 35-40% styrene	1,2 tons 30-35% styrene
Acetone	450 liters 40%		

4. Personal protective equipment (PPE)

During the walk-through survey, it was observed which type of PPE the workers used.

In Company A, different types of PPE were used dependent on the type of process (Table 3):

- Spraying/vacuum section

  When the spraying and vacuuming processes were conducted, some of the workers used powered mask with combination filter (Scott Safety Pro CF22 A2P3). Disposable coveralls (Worksafe ProTect® 250) were used by some workers during spraying. When it comes to hand protection, employees used disposable gloves (Worksafe Latex Light) and chemical latex gloves (Mapa Jersette 301).

- Rolling section

  Powered mask with combination filter (Scott Safety Pro CF22 A2P3) and light disposable gloves (Worksafe Latex) were used by the workers during the rolling operation.

Assembly section

- In the assembly section, workers used 3M™ 8300 Series Particulate Respirators (equipped with 3M™ Advanced Electret Filter Material and ear protection headset.

Table 3. Use of personal protective equipment in Company A

	Mask	Gloves	Coverall	
Rolling	Powered mask with chemical combination filter (Scott Safety Pro CF22 A2P3)	Light disposable gloves (Worksafe Latex)	-	-
Spraying/vacuum	Powered mask with chemical combination filter (Scott Safety Pro CF22 A2P3)	Disposable gloves (Worksafe Latex Light) Chemical latex gloves (Mapa Jersette 301)	Disposable coverall (Worksafe ProTect® 250)	-
Assembly	Particulate Respirators (3M™ 8300 Series Particulate Respirators	-	-	Ear protection headset

II. Company B:

Company B, established in 1990, manufactures high quality tanks and vessels in fiberglass reinforced unsaturated polyester.

1. Factory layout

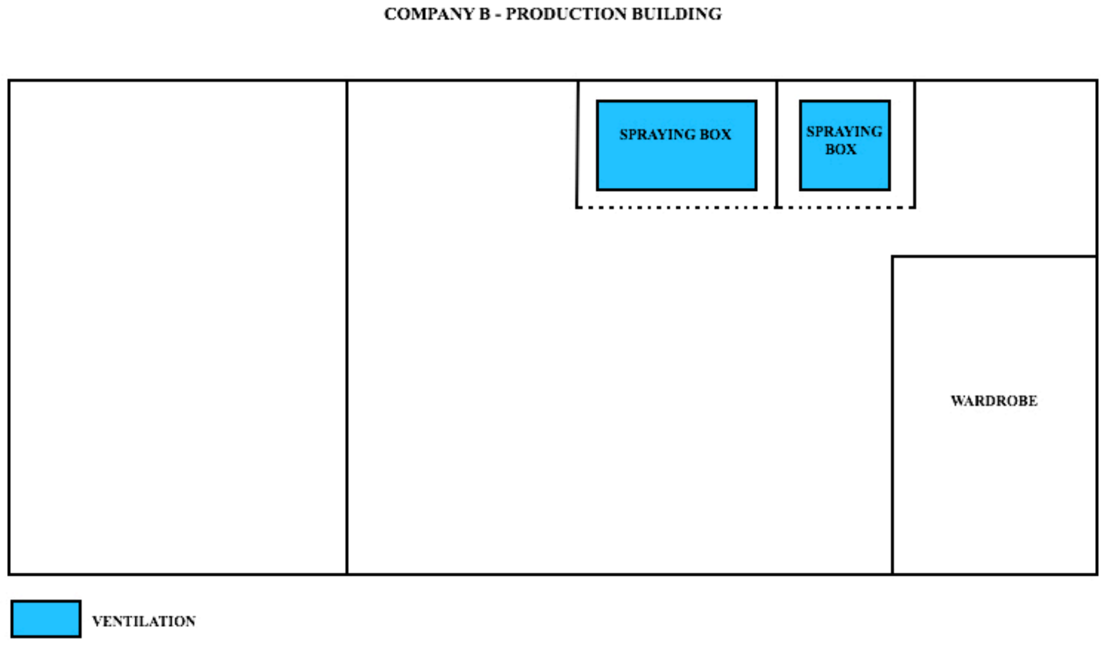


Figure 4. Factory map – Production building

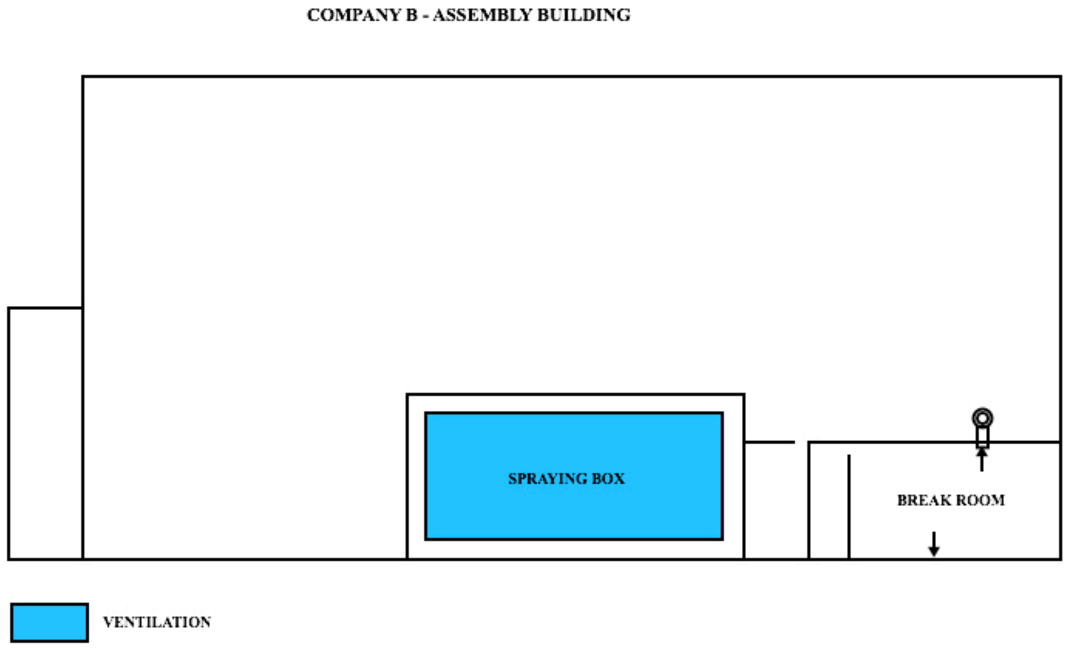


Figure 5. Factory map – Assembly building

2. Main sections

1) Production (foundry) - this big hall of around 1200m^2 and about 10m high has two spraying boxes, each equipped with local ventilation system (Figure 4) (Picture 13 and 14). This is where manual laminating work is done (spraying and rolling) (Picture 15 and 16). In this area 3 workers are employed. This area also contains wardrobe, break and office areas.

Picture 13. Foundry department [31]

Picture 14. Foundry department [31]

Picture 15. Gel coating with spray-gun [31]

Picture 16. Manual rolling [31]

2) Assembly – this building is around 1500m^2 and is 10m high (Figure 5). A big spraying box and one break room are located in this area. Manual laminating (spraying and rolling) is also performed there (Picture 17 and 18). Totally 5 workers are employed in this area.

Picture 17. Rolling (spraying box) [31]

Picture 18. Spraying (spraying box) [31]

3. Chemicals

In Company B, the main polyester based chemical used during the production process was Polylite 440-M950 with styrene content 41-45% (Table 4). Acetone (40%) is used during cleaning process. Monthly use of polyester was approximately 12 tones, while they used around 330 l/month of acetone.

Table 4. Monthly use of polyester and acetone in Company B

Chemical	Monthly use of the chemical
Polyester (Polylite 440-M950)	12 tones 41-45% styrene
Acetone	330 liters 40%

4. <u>Personal protective equipment (PPE)</u>

In Company B, depending of the production processes, the following PPE was used by the workers (Table 5):

- Spraying

  Powered mask with chemical combination filter Scott Safety Pro CF22 A2P3, protective disposable hood and Granberg Premium Latex disposable gloves.
- Rolling

  Powered mask + filter on mask and Granberg Premium Latex disposable gloves

Table 5. Use of PPE in the production in Company B

	Mask	**Gloves**	**Coverall**	**Headset**
Rolling	Powered mask with chemical combination filter (Scott Safety Pro CF22 A2P3)	Disposable gloves (Granberg Premium Latex)	-	-
Spraying		Disposable gloves (Granberg Premium Latex)	-	-

3.3 Data collection

Pre-visits in the two companies were performed in January 2018 to identify types and sources of chemical hazards in the different departments. This survey helped to identify and categorize chemical hazard/s for exposure assessment and provided information on work procedures, ventilation systems and use of PPE.

The actual field work was carried out in March 2018 and the master thesis comprises the results from the walk-through survey, questionnaires, air measurements and urine sampling (Figure 6).

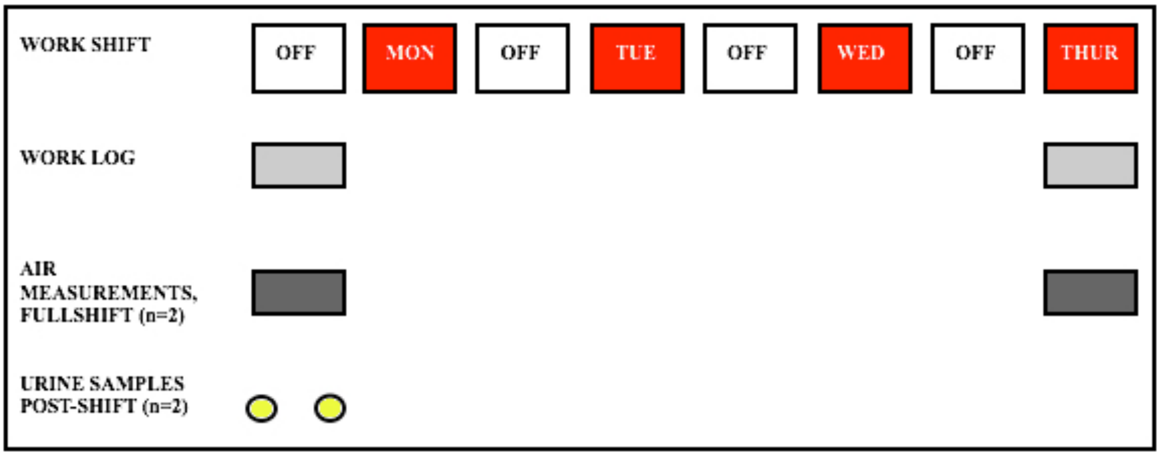


Figure 6. Protocol for styrene air sampling and urine sampling

I. Walk-through survey

On Monday morning during the working hours a new walk-through survey was performed to collect more details about the production processes, use of chemicals and working habits of the employees.

II. Questionnaires

The workers filled in self-administered questionnaires on the two days of sampling. They were asked questions about type of work they were performing during the measuring days and use of personal protective equipment.

III. Air sampling with equipment and sampling form

All participants were monitored for personal exposure to styrene and acetone over two full (8 hours) work shifts on Monday and Thursday (Figure 6). Totally 72 air samples were taken from 37 workers. Air samples were gathered by using organic vapor passive dosimetry badges (3M 3500R) attached to workers collar in the breathing zone according to Norwegian Standard NS-EN 689-2018 [23]. Dosimeters were put into operation pre-shift between 07-09 a.m. on both days and taken out of use at the end of the shift between 2-4 p.m. Blank dosimeters were used as a quality control on both days, one each day.

Personal air sampling was performed in five different work departments in Company A:

1. Foundry
2. Vacuum
3. Assembly
4. Forming
5. Finish-polish
6. Office, shop and service

In Company B, air sampling took place in the following work departments:

1. Foundry
2. Assembly
3. Office

IV. Method of analyses – air measurements

After sampling, the dosimeters were stored in a freezer (-20°C) until they were transported for analyses at the laboratory of Occupational and Environmental Health, University of Milan, Italy. Analyses of styrene and acetone concentrations has been described elsewhere [24, 25], but in brief the analytes were determinated by gas chromatography-mass spectrometry (GC-MS) (HP 5890 Series II equipped with a HP 5972 MS detector, Agilent, Cernusco sul Naviglio, Italy) operating in the electron ionization mode. The limit of quantification of the assay for styrene and acetone were 1 mg/m^3 and 27 mg/m^3, respectively.

V. Method of analyses – urine samples

Urine samples were collected at the beginning and end of the work shift on Monday to determine styrene metabolites in urine (mandelic acid (MA) and phenylglyoxylic acid (PGA)). The samples were then immediately stored at -20^{o}C before they were sent to the laboratory of Occupational and Environmental Health, University of Milan, Italy for analyses. The analysis has been described elsewhere [26], but in brief it was assayed by liquid chromatography with tandem mass spectrometry (LC-MS/MS). The limit of detection was 0.1 mg/ml for both MA and PGA. Concentrations of metabolites in urine samples were expressed as a function of the creatinine concentration, measured by the method of Jaffe [27].

Occupational Exposure Limits (OEL)

For comparison with OELs we have used The Norwegian Occupational Exposure Limits (OEL) in workplace air, available from the Norwegian Labour Inspection Directorate [28]. The OEL for styrene is 25 ppm (106 mg/m^3). However, according to Norwegian regulations the exposure levels for carcinogenic compounds should be reduced as far as possible.

The Norwegian Occupational Exposure Limit (OEL) for acetone is 125 ppm (256 mg/m^3) [28]. For the urine metabolites, the Biological Exposure Index (BEI) from the American Conference of Governmental Industrial Hygienists (ACGIH) for the total concentration of MA and PGA in post-shift urine is 400 mg/g creatinine was used for comparison [29].

4. Ethical considerations

The study was approved by the Regional Committee for Medical Research Ethics. All the participants were asked and gave their informed written consent according to the Declaration of Helsinki on Ethical principles for medical research involving human subjects. Only the involved researchers from the Research group of Occupational and Environmental Medicine, University of Bergen and the Department of Occupational Medicine, Haukeland University Hospital had access to confidential information. Employers would get access to reports that contain aggregated information on a group level only, not on individual level, while the participants will get cumulated results in written reports and in oral presentation at their work site.

5. Statistical analyses

Results from measurements of air and urine levels are presented as arithmetic mean (AM), standard deviation (SD), geometrical mean (GM), median, minimum and maximum values. The frequency distributions of styrene, acetone and MA+PGA were skewed. Thus, these data were $\log_e$(ln) transformed before the statistical analyses. The relationships between airborne styrene and acetone in air samples, and between styrene in air and MA+PGA concentration in urine were assessed by using Pearson`s correlation coefficient (*r*). Differences in exposure levels between groups were tested statistically using independent t-test. A p-value <0.05 was considered significant.

The statistical analyses were carried out by using the IBM SPSS Version 23.0 statistical package for Mac.

6. Results

6.1 Study population

A total of 37 workers participated in this study, 26 from Company A and 11 from Company B. Most participants were male, apart from 3 females in Company A. The workers were assigned to six departments. The age of the workers varied between 27 and 68 years with a mean age of 46 years for both companies.

All included workers in Company B were engaged in air measurements, gave urine samples and answered questionnaires on both measurement days (Monday and Thursday), while in Company A two of the included workers participated only one day (Monday), 24 workers were active in the study on both days.

6.2 Personal exposure level of styrene and acetone

A total of 72 full shift exposure measurements were collected among the 37 workers. The overall sampling time for measurements of exposure styrene and acetone exposure varied from 270 to 482 minutes, with an arithmetic mean (AM) of 417 minutes (Table 6).

6.2.1 Styrene

The overall (AM) of exposure to styrene among all production workers in the two companies was 11.8 ppm (range 0.35-61.9). The mean exposure to styrene among the production workers did not differ significantly (p=0.39) between Company A (11.0 ppm) and Company B (13.7 ppm).

In Company A, the highest mean exposures to styrene were found in the Foundry (15.6 ppm) and in Vacuum (11.4 ppm) (Table 6). The highest individual measurements were also found in these two departments (60.7 ppm and 61.9 ppm, respectively). Office workers were exposed to low concentrations of styrene with an AM of 0.14 ppm. Out of 50 measurements in Company A, 4.8% had mean exposure above OEL for styrene (25 ppm) and 59.5% was above ¼OEL (6.25 ppm) (Table 7). The highest percentage of styrene exposure levels exceeding the OEL in Company A was in the Foundry department (8.3%) and in Vacuum (7.1%).

In Company B, the highest styrene exposure was measured in the Foundry (25.2 ppm) and Assembly (30.7 ppm). Office workers were exposed to low concentrations of styrene with an AM of 3.1 ppm. Out of totally 22 measurements in Company B, 11.1 % had values above OEL for styrene and 88.9% were above ¼OEL. The Foundry department had the highest percentage of measurements of styrene above OEL (14.3%). Mean exposure to styrene did not differ significantly between the foundry departments in the two companies (p=0.87).

6.2.2 Acetone

The overall mean exposure to acetone among all production workers in the two companies was 69.7 ppm (range 5.7-355 ppm). The AM exposure to acetone in Company A (70.9 ppm) was statistically significantly higher than in Company B (33.4 ppm) (p=0.006).

In Company A, the highest mean exposures to acetone was in the Form department (202.34 ppm) and in the Finish-polish department (170 ppm), but the number of samples in these departments was small (Table 6). In the Foundry, Joining and Vacuum the exposure was lower (47.5 ppm, 83.8 ppm and 66.5 ppm, respectively). Office workers were exposed to low concentrations of acetone with an AM of 6.8 ppm. Overall for acetone in Company A, 21.4% of the measurements were above OEL (125 ppm) and 69% were above ¼OEL (31.25 ppm) (Table 7). In the Finish-polish department all measurements were 100 % above both OEL and ¼OEL, while in the Form department 75% of the measurements were above OEL and 100% were above ¼OEL.

In Company B, there were no values above OEL. The highest mean exposure was measured in Assembly (46.8 ppm). Office workers were exposed to low concentrations of acetone with an AM of 9.7 ppm. Out of totally 22 measurements in Company B, none of them were above OEL for acetone, while 50% of the measurements were above ¼OEL. Mean exposure to acetone in the foundry departments did not differed significantly between these two companies (p=0.52).

There was a statistically significant, but weak correlation between exposure to styrene and acetone (r=0.375, p=0.001, n=72).

Table 6. Exposure values for styrene and acetone for full 8-hour shift

	Department	N	m	Sampling time (min)			Styrene (ppm)					Acetone (ppm)				
				AM	Min	Max	AM	SD	Median	Min	Max	AM	SD	Median	Min	Max
Company A	Foundry	7	12	409	303	463	15.6	16.2	11.4	.4	60.7	47.5	84.2	22.9	5.7	311
	Assembly	5	10	428	373	468	8.4	4.1	7.3	2.4	14.7	83.8	83.3	60.1	12.0	257
	Vacuum	7	14	407	270	437	11.4	16.3	6.9	.5	61.9	66.5	40.7	64.3	5.7	153
	Form	2	4	335	299	373	7.6	4.5	6.5	3.9	13.7	202.3	135.3	207.0	40.1	355
	Finish-polish	1	2	448	434	463	.56	.30	.56	.35	.77	170.4	56.1	170.4	130.8	210
	All produc.	22	42	408	270	468	11.0	13.2	7.6	.35	61.9	83.1	87.1	45.9	5.7	355
	Office	4	8	436	417	467	.14	.07	.12	.12	.33	6.8	3.2	5.7	5.7	15
Total A		26	50	412	270	468	9.3	12.7	6.1	.12	61.9	70.9	84.6	38.1	5.7	355
Company B	Foundry	3	7	426	380	464	14.5	7.6	14.1	1.7	25.2	25.8	23.5	23.2	5.7	61
	Assembly	6	11	427	391	482	13.2	7.0	11.5	4.7	30.7	46.8	23.3	50.4	12.4	91
	All produc.	9	18	427	380	482	13.7	7.0	12.4	1.7	30.7	38.6	25.0	35.5	5.7	91
	Office	2	4	434	387	460	3.1	1.2	3.0	1.9	4.5	9.7	8.0	5.7	5.7	22
Total B		11	22	428	380	482	11.8	7.6	11.4	1.7	30.7	33.4	25.4	24.8	5.7	91
Total production A, B		31	60	414	270	482	11.8	11.7	9.8	.35	61.9	69.7	76.7	44.2	5.7	355
Total A, B		37	72	417	270	482	10.0	11.4	7.6	.12	61.9	59.4	73.7	34.4	5.7	355

N=number of workers; **m**=number of samples; **AM**=arithmetic mean; **SD**=standard deviation; **Median**=median value; **Min**= minimum; **Max**=maximum

Table 7. Percentage of the measurements for styrene and acetone exceeding the OEL and ¼ OEL

	Department	N	m	Styrene >OEL (%)	Styrene >OEL25% (%)	Acetone >OEL (%)	Acetone >OEL25% (%)
Company A	Foundry	7	12	8.3	66.7	8.3	41.7
	Assembly	5	10	0	70	20	70
	Vacuum	7	14	7.1	57.1	7.1	78.6
	Form	2	4	0	50	75	100
	Finish-polish	1	2	0	0	100	100
	All produc.	22	42				
	Office	4	8	-	-	-	-
Total A		26	50	4.8	59.5	21.4	69
Company B	Foundry	3	7	14.3	85.7	0	28.6
	Assembly	6	11	9.1	90.9	0	63.6
	All produc.	9	18				
	Office	2	4	-	-	-	-
Total B		11	22	11.1	88.9	0	50
Total production A, B		31	60	-	-	-	-
Total A, B		37	72	-	.	.	.

N=number of workers; **m**=number of samples; **>OEL (%)**=percentage of measurements exceeding the OEL; **>OEL25% (%)**=percentage of measurements exceeding ¼ OEL

6.2.3 Biological monitoring of styrene

The arithmetic means for the post-shift MA+PGA for production workers in both Company A and Company B (154.1 mg/g creatinine and 197 mg/g creatinine, respectively) were under the Biological Exposure Index (BEI) of ACGIH (Table 8). The concentrations of post-shift MA+PGA were not significantly different between the companies (p=0.32).
In Company A, the maximum, individual concentration of metabolites post-shift was measured in the foundry department (406.4 mg/g creatinine), while in Company B it was in the assembly department (461.8 mg/g creatinine), which are both above the BEI value.

The AM of the difference in concentrations of these metabolites in urine between pre- and post-shift (ΔMA+ΔPGA) among all production workers was 120.7 mg/g creatinine for Company A and 171.7 mg/g creatinine for Company B, respectively (Table 8). The difference between the companies in ΔMA+ΔPGA for these metabolites was not significant (p=0.20).
Looking at all departments in Company A, the highest increase in concentration of MA+PGA cross-shift was in the Foundry department (158.8 mg/g creatinine), while in Company B the highest increase was measured among workers in the Assembly department (197.7 mg/g creatinine).

Table 8. Mean values of mandelic acid and phenylglyoxylic acid in urine pre- (MAo; PGAo) and post-shift (MA; PGA)

		N	**MAo mg/g creatinine**		**MA mg/g creatinine**		**PGAo mg/g creatinine**		**PGA mg/g creatinine**		**MAo+PGAo mg/g creatinine**		**ΔMA+ΔPGA mg/g creatinine**		**MA+PGA mg/g creatinine**				
			AM	SD	AM	SD	AM	SD	AM	SD	AM	SD	AM	SD	AM	SD	Median	Min	Max
Company A	Office	4	.6	.4	5.2	2.2	.8	.8	2.8	1.7	1.4	1.1	**6.6**	3.1	**7.9**	3.6	7.8	4.4	11.6
	Foundry	6	12.8	7.9	142.7	121.3	11.6	5.6	48.6	30.5	24.4	11.0	**158.8**	151.1	**191.3**	146.1	150.8	31.3	406.4
	Assembly	5	12.4	7.2	105.5	23.6	14.0	12.4	39.6	15.7	26.4	18.8	**118.7**	31.4	**145.1**	30.9	160.5	101.8	170.1
	Vacuum	7	13.8	5.7	84.0	48.2	17.9	8.2	39.5	16.6	31.8	12.5	**94.6**	54.6	**123.5**	62.9	116.0	58.4	239.6
	Form	2	30.5	30.5	140.8	114.7	23.2	13.2	63.1	54.7	53.7	43.8	**150.2**	125.6	**203.9**	169.4	203.85	84.1	323.6
	Finish-polish	1	7.8	.	10.1	.	16.6	.	13.7	.	24.4	.	**-.60**	.	**23.8**	.	23.8	23.8	23.8
	All production	21	14.5	10.6	110.6	83.3	15.6	9.0	43.6	25.4	30.1	17.8	**120.7**	96.8	**154.1**	104.4	123.2	23.8	406.4
Total A		25	12.3	11.0	93.7	85.7	13.2	9.9	37.0	27.8	25.5	19.5	**101.7**	98.1	**130.7**	109.9	111.4	4.4	406.4
Company B	Office	2	2.2	.3	38.9	8.0	2.1	.3	17.5	3.8	4.3	.6	**52.1**	12.4	**56.4**	11.8	56.4	48.0	64.7
	Foundry	3	10.9	4.1	101.1	46.3	14.8	3.8	44.3	9.9	25.7	6.4	**119.7**	49.4	**145.4**	55.8	129.2	99.4	207.5
	Assembly	6	12.0	5.8	154.8	93.3	12.9	4.9	67.8	35.1	24.9	9.9	**197.7**	119.8	**222.6**	127.6	206.3	96.9	461.8
	All production	9	11.6	5.1	136.9	81.9	13.5	4.4	60.0	30.5	25.1	8.4	**171.7**	105.4	**197**	111.5	189.7	96.9	461.8
Total B		11	9.9	5.9	119.1	83.3	11.4	6.1	52.2	32.3	21.4	11.3	**150.0**	106.0	**171.3**	114.9	137.6	48.0	461.8
Total		36	11.6	9.7	101.5	84.6	12.7	8.9	41.7	29.6	24.3	17.3	**116.8**	101.7	**143.1**	111.4	123.2	4.4	461.8

N=number of workers; **AM**=arithmetic mean; **SD**=standard deviation; **MA_o**=MA in pre-shift urine; **MA**= MA in post-shift urine; **PGA_o**=PGA in pre-shift urine; **PGA**=PGA in post-shift urine; **MAo+PGAo**=sum in pre-shift urine; **ΔMA+ΔPGA**=difference between pre- and post-shift urine; **MA+PGA**=sum in post-shift urin

<u>Association between styrene in air and cross-shift increase in urinary concentration of styrene metabolites</u>

The correlations between exposure to styrene and ΔMA+ΔPGA was strong and statistically significant (r=0.844, p=<0.001, n=34) (Table 9 and Figure 7). Also, there was a statistically significant, but moderate correlation between acetone and ΔMA+ΔPGA (r=0.442, p=0.009, n=34) (Table 9).

Table 9. Pearson correlation test for LNStyrene, LNAcetone and LN(ΔMA+ΔPGA)

		lnStyrene (ppm)	lnAcetone (ppm)	ln(ΔMA+ΔPGA) (mg/g creatinine)
lnStyrene (ppm)	*r	1	.375	.844
	Sig. (2-tailed)		.001	<0.001
	N		72	34
lnAcetone (ppm)	r		1	.442
	Sig. (2-tailed)			.009
	N			34

***r**=Correlation coefficient; **ln**=log-value; **N**=number of workers

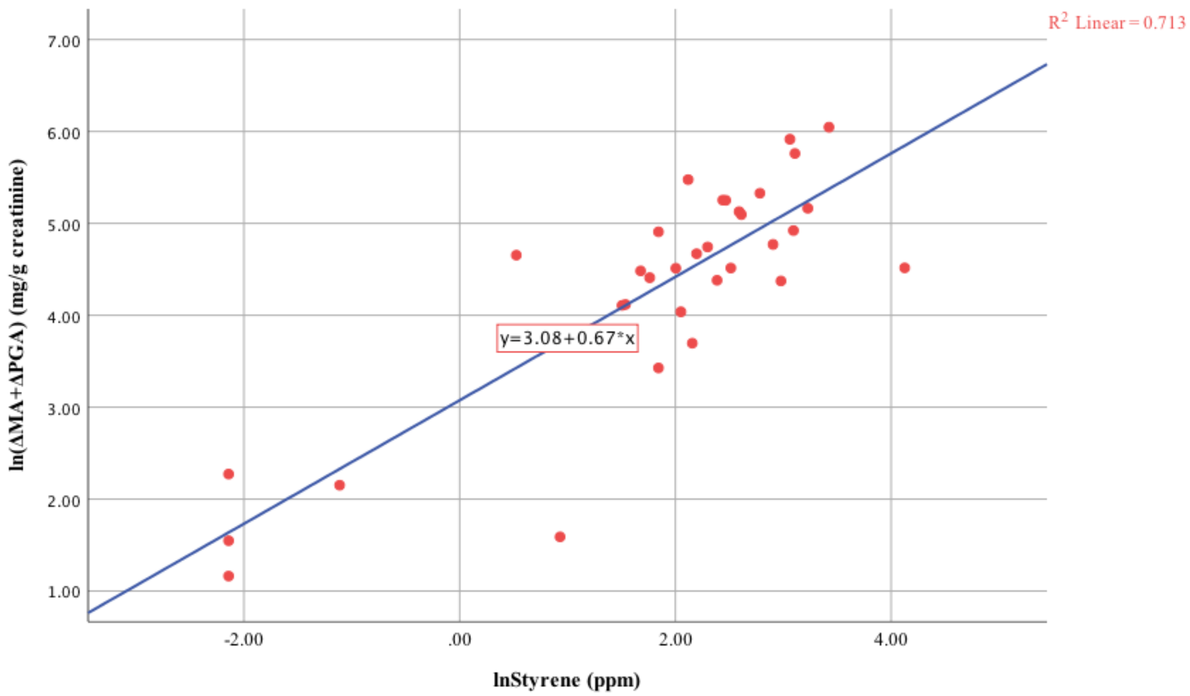


Figure 7. Correlation between exposure to styrene and difference in concentration of mandelic acid and phenylglyoxylic acid in urine post-shift (ΔMA+ΔPGA)

6.2.4 Personal protective equipment

In Company A 62% of the workers in the production departments reported that they used protective masks and 95% used protective gloves when they carried out work tasks associated with exposure to styrene and/or acetone. In Company B, the usage of protective masks was 83% and for protective gloves 94% (Table 10). This information was gathered by questionnaires.

Table 10. Use of PPE for both measurement days

	Department	**Mask**				**Gloves**			
		Yes		**No**		**Yes**		**No**	
		m	**(%)**	**m**	**(%)**	**m**	**(%)**	**m**	**(%)**
Company A	Foundry	12	100	0	0	12	100	0	0
	Assembly	9	90	1	10	9	90	1	10
	Vacuum	3	21	11	79	14	100	0	0
	Form department	2	50	2	50	3	75	1	35
	Finish-polish	0	0	2	100	2	100	0	0
	All production	26	62	16	38	40	95	2	5
Company B	Foundry	7	100	0	0	7	100	0	0
	Assembly	8	73	3	27	10	91	1	9
	All production	15	83	3	17	17	94	1	6
Company A+B		41	57	31	43	57	79	15	21

m=number of samples

7. Discussion

7.1 Exposure to airborne styrene

Workers in the production, especially those engaged in open molding tasks, were exposed to relatively high levels of airborne styrene when compared to OEL values. In the Foundry, this is most likely due to the method of styrene application i.e. by using a spray gun on large, open surfaces. In the Vacuum department, the molds are covered with plastic film that should reduce the styrene emissions (close mold technique). Nevertheless, styrene exposure seems to occur due to emissions from openings in the plastic cover and from open styrene containers. Still, the exposure levels were higher during the use of open mold technique when compared to closed mold technique. The same conclusion was made in the study by Tranfo *et al.,* [18] who compared the exposure levels of airborne styrene between open- and close mold techniques in two different FRP industries in Italy. The median values in their study (open mold 7.3 ppm and closed mold 5.6 ppm) where lower than the median values in the present study; 11.4 ppm in open mold Foundry and 6.9 ppm in closed mold Vacuum.

In Company A, the styrene exposure was higher in the Foundry and Vacuum departments than in the Form and Finish-polish departments. In the Foundry department, styrene was applied mainly by spraying, which causes the higher exposure to airborne styrene. The workers in the Form and Finish-polish departments are not engaged in laminating processes as their working tasks are focused on painting (Form department) and, cutting, polishing and painting (Finish-polish department) of the boat parts that have already been through the laminating and drying stage. The fact that the Form department is located in the same space as the Assembly and Vacuum department, with no physical barrier between them, might be the reason why styrene exposure was still detected at about 1/3 of the OEL (AM=7.6 ppm). The Finish-polish department is located close to the Foundry, but it is enclosed in separate room with only one side open as a room entry. Furthermore, all workstations in this department is equipped with local exhaust ventilation (LEV). These measures seem to provide good protection against exposure to airborne styrene, as the measured styrene exposure was very low (AM=0.56 ppm). However, care should be taken when interpreting the results from the Form and Finish-polish departments as only few samples were taken in these departments.

In Company B, the exposure levels to styrene did not differ much between the Foundry and Assembly departments. This may not be surprising since, although located in two different buildings, the workers in both departments were engaged in laminating processes that was performed in spraying boxes equipped with LEV.

The difference between the maximum concentrations between the companies was large, with Company A having maximum concentrations twice as large as those in Company B. This can be explained by the fact that production in Company A is larger, the parts that they produce are much more complex i.e. many different forms, shapes and sizes of the molds and it might take longer time to achieve the wanted quality. Furthermore, some of the departments in Company A are placed closely together, in the same hall and spraying process is not enclosed in spraying boxes like in Company B.

Despite these differences, when including all production workers, the mean exposure to styrene was below the OEL, and did not differ significantly between the two companies.

7.2 Exposure to acetone

Company A workers performing finishing tasks were exposed to much higher concentrations of acetone than those employed in molding tasks. This might be the case because in these departments the amount of acetone used for washing is higher or/and the use is more frequent than in the other departments. It is, however, important to notice that although the mean values were elevated only in the Form and Finish-polish departments, the maximum values in all departments were above the OEL for acetone.

Contrary to this, in Company B levels of exposure to acetone were relatively low compared to the OEL in all departments. One possible reason to this is that in Company B, almost all tasks are performed in spraying boxes which are equipped with LEV. Also, it is important to point out that departments are spread out in two different buildings with a lot of space between the working stations.

The mean exposure to acetone in Company A was significantly higher than in Company B, and this could be due to the larger production in Company A that the departments are placed more tightly together.

7.3 Concentrations of post-shift styrene metabolites in urine

Our data shows that the mean concentrations of styrene metabolites in post-shift urine (MA+PGA) among production workers for both companies were below the BEI, although the maximum values in the Foundry department in Company A and the Assembly department in Company B were above the BEI.

The measured post-shift values of mandelic acid among the production workers in Company A 110.6 mg/g creatinine and Company B 136.9 mg/g creatinine in the present study were much lower compared to the measurements for hand and spray laminators found in the Italian study by Galassi *et al*., [16] in 1993. They reported mean values of post-shift MA 682 mg/g creatinine for hand and 404 mg/g creatinine for spray laminators. This is not so unexpected since the exposure levels for airborne styrene were also much higher (mean 53.4 ppm for hand and 31.5 ppm for spray laminators) than found in the present study.

The change in pre- to post-shift concentrations of the measured metabolites (ΔMA+ΔPGA) did not differ significantly between the companies. This result seems logical since there was no difference in styrene exposure between the companies. In addition, this result indicates that the companies are similar with respect to the efficiency of the PPE to reduce uptake of styrene. The correlation between exposure to styrene and urinary concentration of the biomarker of styrene (MA+PGA) was strong and significant. This might be due to a low efficiency of the personal protective equipment. This finding might be caused by a several factors such as use of masks that do not fit the worker resulting in leakage of styrene into the mask, workers who did not use PPE continuously, and poor maintenance of the masks like infrequent filter change, inadequate inside cleaning of the mask and storage of the masks in polluted atmosphere. Also, uptake of styrene through the skin can contribute to these results since some of the workers did not use protective suite and/or gloves, or did not use it properly like folding the sleeves if they feel hot or do not close the protective suit completely, etc.

7.4 General strengths and limitations

One of the strengths of this study is that measuring of exposure to airborne styrene and acetone was performed by taking full-shift samples during the working days that represent normal daily activity according to Norwegian Standard NS-EN 689-2018. By using this method, we can get an overview of the workers exposure to airborne styrene and acetone. Similar method for measuring of exposure to airborne styrene was used in the previous studies [9, 14].

Another strength of this study is that the all air samples were analyzed in the high-quality laboratory where the analytes were determinated by gas chromatography-mass spectrometry (GC-MS) (HP 5890 Series II equipped with a HP 5972 MS detector, Agilent, Cernusco sul Naviglio, Italy) operating in the electron ionization mode. The same type of analyses was used by other authors [25, 30]. It is also a strength that we included all workers in the factories, instead of selecting a subgroup of workers that might not have been representative for the whole workforce.

Biological monitoring of workers exposed to styrene by measuring the pre- and post-shift concentrations of mandelic acid (MA) and phenylglyoxylic acid (PGA) is a valid method that shows the uptake of the styrene in the body. This method indicates the effectiveness of preventive measures that are used in order to minimalize the exposure to airborne styrene.

The companies produce different types of products, but they use the production methods which is representative for companies in the FRP industry. With this said, the results of this study could be relevant for all types of products manufactured in this type of industry.

A limitation of the study was that the number of workers employed, especially in the Form (n=2) and Finish-polish (n=1) departments in Company A and in Foundry departments in Company B (n=3) was low. However, since the production rate was reported to be normal during the sampling days, larger sample size might not have changed the main results for exposure to styrene significantly. Although the mean sampling time in our study was seven hours, we consider the sampled time periods to be representative for the whole work shift.

8. Conclusion

This study shows that workers employed in FRP industry are potentially exposed to relatively high levels of airborne styrene and acetone compared to the occupational exposure levels. Furthermore, for some of the workers post-shift urinary concentrations of the styrene metabolites MA+PGA were above the BEI. There was a strong correlation between exposure to styrene and concentrations of the urinary metabolites, indicating that the personal protective equipment did not effectively prevent biological uptake of styrene.

Both companies should consider additional preventive measures in order to minimalize workers exposure to airborne styrene and acetone.

9. References

1. Marsh, G. *50 Years of reinforced plastic boats.* Reinforced Plastics, 2006. 50. 16-19. 10.1016/S0034-3617(06)71125-0.
2. Aurer, J.H., Kasper, A.B. *Unsaturated Polyester Resins: Polymers with unlimited possibilities*. Verlag Moderne Industrie, 2003. P. 32-38.
3. International Agency for Research on Cancer (IARC), *IARC Monographs on the evaluation of carcinogenic risks to humans. Styrene, styrene-7-8-oxide, and quinolone.* IARC, 2019. **Volume 121**.
4. Rueff, J., Teixeira, J.P., Santos, L.S., et al., *Genetic effects and biotoxicity monitoring of occupational styrene exposure.* Clin Chim Acta, 2009. **399**: 8-23.
5. Paci, E., Pigini, D., Caporossi, L., et al., *Matrix effect in the Quantitative Determination of Mandelic and Phenylglyoxylic Acid in urine samples by HPLC-MS/MS with Isotopic Dilution*. Curr Anal Chem, 2013. **9**: 439-46.
6. Miller, R.R., Newhook, R., Poole, A., *Styrene production, use, and human exposure.* Crit Rev toxicol, 1994. **24 (Suppl.)**: S1-10.
7. Costa, C., Costa, S., Silva, S., et al., *DNA damage and susceptibility assessment in industrial workers exposed to styrene*. J Toxical Environ Health A, 2012. **75**: 735-46.
8. The American Conference of Governmental Industrial Hygienists (ACGIH), *Documentation of the biological exposure indices*. OH: ACGIH Signature Publication Series, 2001. 7th edn.
9. Prieto, M.J., Marhuenda, D., Cordona, A., *Analysis of Styrene and its Metabolites in Blood and Urine of Workers Exposed to both Styrene and Acetone.* Journal of Analytical Toxicology, 2002. **Vol. 26**, 23-28.
10. Government of Western Australia, *Code of Practice: Styrene.* WorkSafe Western Australia Commission, 1996. p. 14, [Homepage Government of Western Australia] 2019 [cited 4. March 2019] Available from: https://www.commerce.wa.gov.au/sites/default/files/atoms/files/code_styrene.pdf
11. European Chemical Agency (ECHA), *Acetone*. [Homepage ECHA] 2020 [cited 17. June 2020] Available from: https://echa.europa.eu/registration-dossier/-/registered-dossier/15460/7/2/1
12. Canadian Centre for Occupational Health and Safety (CCOHS), *Chemical Profiles: Acetone*. Canadian Centre for Occupational Health and Safety (CCOHS), 2017. [Homepage ECHA] 2019 [cited 17. November 2019] Available from https://www.ccohs.ca/oshanswers/chemicals/chem_profiles/acetone.html
13. Van Rooij, J.G., Kasper, A., Triebig, G., et al., *Trends in Occupational Exposure to Styrene in the European glass Fiber-Reinforced Plastic Industry.* Ann Occup Hyg, 2008. **52**: 337-349.

14. Geuskens, R.B.M., van der Klaauw, M.M., van der Tuin, J., van Hemmen, J.J., *Exposure to styrene and health complaints in the Dutch glass-reinforced plastic industry.* Aim. occup. Hyg, 1992. **Vol. 36, No. 1**, pp. 47-57.

15. Lenvik, K., *Occupational exposure to styrene in Norway, 1972-1996.* Applied Occupational and Environmental Hygiene, 1999. **Volume14-Issue 3**: 165-170.

16. Galassi, C., Kogevinas, M., Terro, G., et al., *Biological monitoring of styrene in the reinforced plastic industry in Emilia Romagna, Italy.* Int Arch Occup Eviron Health, 1993. **65**: 89-95.

17. Carlo, R.V., Hammond, D., Feng, H.A., et al., *In-Depth Survey Report: Styrene Exposures During Fiber Reinforced Plastic Boat Manufacturing at U.S. Marine Incorporated Arlington, Washington.* US Department of Health and Human Services, 2007. Report No: EPHB 306-17a.

18. Tranfo, G., Gherardi, M., Paci, E., et al., *Occupational Exposure to Styrene in the Fiberglass Reinforced Plastic Industry: Comparison Between Two Different Manufacturing Processes.* Med Lav, 2012. **103(5)**: 402-12.

19. Polakova, M., Krajcovicova, Z., Melus, V., Stefkovicova, M., Sulcova, M., *Study of urinary concentrations of mandelic acid in employees exposed to styrene.* Cent Eur J Public Health, 2012. **20 (3)**: 226-232.

20. Bonanni, R.C., Gatto, M.P., Paci, E., Gordiani, A., Gherardi, M., Tranfo, G., *Biomonitoring for Exposure assessment to Styrene in the Fiberglass Reinforced Plastic Industry: Determinants and Interferents.* Ann. Occup. Hyg., 2015. **Vol. 59**, No. 8, 1000–1011 doi:10.1093/annhyg/mev047

21. Høgstedt, C., *Has the Scandinavian solvent syndrome controversy been solved?.* Scand j Work Environ Health, 1994. 20 Spec No:59-64.

22. Statistics Norway (Statistisk sentralbyrå) [Homepage SSB] [cited 17. November 2019] Available from: https://www.ssb.no

23. Standard_Norge, *NS-EN 689-2018 Workplace exposure - Measurement of exposure by inhalation to chemical agents - Strategy for testing compliance with occupational exposure limit values.* 2018, Standard Norge: Norway.

24. Tornero-Velez, R., Rapparot, S.M., *Physiological modeling of the relative contributions of styrene7,8oxide derived from direct inhalation and from styrene metabolism to the systematic dose in humans.* Toxicological Sciences, 2001. **64**: 151-161.

25. Fustinoni, S., Campo, L., Manini, P., Buratti, M., Waidyanatha, S., de Palma, G., Mutti, A., Foa, V., Colombi, A., Rappart, S.M., *An integrated approach to biomonitoring exposure to styrene and styrene(7,8)-oxide using a repeated measurements sampling design.* Biomarkers, 2008. **13 (6)**: 560-578.

26. Manini, P., Andreoli, R., Poli, D., De Palma, G., Mutti, A., Niessen, W.M.A., *Liquid chromatography/electrospray tandem mass spectrometry characterization of styrene metabolism in man and rat.* Rapid Commun. Mass Spectrom, 2002. **16,**2239–2248.

27. Kroll, M.H., Chesler, R., Hagengruber, C., Blank, D.W., Kestner, J., Rawe, M., *Automated determination of urinary creatinine without sample dilution: theory and practice.* Clin Chem, 1986. **32(3)**:446-452.

28. Arbeidstilsynet, *Forskrift om tiltaksverdier og grenseverdier for fysiske og kjemiske faktorer I arbeidsmiljøet samt smitterisikogrupper for biologiske faktorer (forskrift om tiltaks- og grenseverdier).* Arbeidstilsynet*,* 2011. Hefte 14: Norway [Homepage Arbeidstilsynet] 2020 [cited 18. July 2020] Available from https://www.arbeidstilsynet.no/regelverk/forskrifter/forskrift-om-tiltaks--og-grenseverdier/8/1/
29. The American Conference of Governmental Industrial Hygienists (ACGIH), *TLVs and BEIs Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*. OH: ACGIH Signature Publication Series, 2020.
30. Fustinoni, S., Manini, P., Campo, L., De Palma, G., Anderoli, R., Mutti, A., Bertazzi, P.A., Rappaport, S.M., *Assessing variability and comparing short-term biomarkers of styrene exposure using a repeated measurements approach*. Toxicology Letters, 2010. Vol. 192, 40-44 doi:10.1016/j.toxlet.2009.02.004
31. Photo: Snezana Nedeljkovic, 2018.

10. Annexes

10.1. Air sampling Worksheet – dosimeter

Date	Sample ID	Employee	Job tasks	Time 1 start	Time 2 stop	Sampling Time (min)	Analysed amount (µg)	Air conc. (mg/m^3)	Air conc. (ppm)

10.2 Work report form

ARBEIDSLOGG

BEDRIFT: ______________

DATO: ______________

PERSON ID: ______________

DOSIMETER ID: ______________

AVDELING: **Støping☐** **Montering☐** **Vakuum☐** **Kontor☐**

Annen☐ ....

Hvor stor del av dagen har du vært:

1. I produksjonslokalet ______ timer
2. Andre steder (pauserom, kontor, o.l.) ______ timer

Hvilke arbeidsoppgaver har du hatt i løpet av dagen?

(kryss av for utført prosess (X) og evt. bruk av maske (M) og hansker (H)

	07-11		11-15	
	Utført (X)	PPE(M/H)	Utført (x)	PPE(M/H)
Gel coating				
Manuell pålegging matter				
Rulling				
Sprøyting				
Vasking				
Voksing				
Pålegging av plastfilm				
Vakuum-tilsetting polyester				
Montering				
Kontor				

Var du i går ettermiddag/kveld eksponert for kjemikalier i forbindelse med ekstrajobb eller hobby?