Solvents Measurement and Influence on Health in the Work Environment in Manufacturing

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The composition of chemical mixtures in the work environment depends mostly on the temperature of the air or the processing temperature of the raw material or the intermediate products. To determine the chemicals in the air FTIR/FT-NIR spectrometer Interspec 301-X with open optical path and Dräger tubes were used. The toxicology of the gaseous components was determined on the basis of the scientific literature. Resulting from these investigations and the legislation on the chemicals safety (exposure limits) the health risk assessment model (HRA) was worked out. This model connects the hazards in the work environment and the health risk to the workers and enables the possibility to the medical personnel to determine the frequency of the medical examinations and biomonitoring for the workers continuously working in the hazardous conditions. The novelty of the study lies in the possibility to keep the chemicals concentration in the work environment air under control through the use of the HRA model and the measurement with modern measurement equipment (FTIR/FT-NIR).

Keywords: indoor air, risk assessment chemicals in the air.

1. INTRODUCTION

Focus is on the development of a health risk assessment (HRA) model and the compatibility check of this model in the work environment (WE) polluted mainly with neurotoxic solvents in the different (small) concentrations. The topical problem in the Estonian manufacturing industry connected with the chemicals' pollution is the strong unpleasant odor of the nonidentified chemicals (often mixtures). Frequently, the employers lack exact knowledge of the solvents present in the WE. Moreover, there is inconsistency in the content of the mixture of them (based on the results of the measurements) with the data of safety data sheets. If the occupational exposure limit (OEL) is much higher than the odor threshold, then the complaints from the side of workers occur. The investigated industries were: wood processing, shale fuel oil handling, metal processing industry (welding) (Fig.3) and plastics manufacturing (plastic and rubber based industrial activities). Metal processing and manufacturing is part of different industrial activities (welding, painting of large metal ships etc.) (Fig. 1) where chemicals are present. The same processes are present in the production of plastic boats or wood processing (painting) (Fig. 2) or fuel oil or gasoline handling. During preparation and painting of metal surfaces with different oil products, the volatile organic components are released into the workplace air. All these hazardous components can significantly impact the workers health by inhalation or direct skin contact [1 - 8]. To provide recommendations to the employers and the medical personnel who are conducting medical health examinations (MHE) of the workers engaged in hazardous conditions, the health risk assessment (HRA) model is very

useful. The model connects the health risks, exposure time and possible health damages and determines the frequency of MHE. Our previous model [3] is improved here and the results of the experiments in different industries are presented. The polluting substances in the air of the work environment have a summation impact on humans' health and should not exceed the value "one", that is [9]:

$$C_1/OEL_1 + C_2/OEL_2 + ... + C_n/OEL_n \le 1,$$
 (1)

where $C_1...C_n$ – the values of concentrations of polluting substances identified in the air of the work environment; $OEL_1...OEL_n$ – exposure limit values for corresponding substances.

This formula does not take into account the specific hazardous properties of the chemical substances and dust (carcinogenicity) and the resulting health disturbances (irritation and dermatitis of skin, asthma and other diseases of pulmonary organs, headaches, and neurological problems).

Workplace exposure limits for volatile substances are expressed or in ppm (parts per million by volume) or in milligrams per cubic metre (mg/m^3) of (in) air.

To convert the OEL expressed in ppm to mg/m^3 , the following equation [9] could be used:

OEL in mg/m³ =
$$\frac{OEL(ppm)xMWt}{24.05526}$$
, (2)

where *MWt* is the molecular weight (molar mass in g/mol) of the substance; 24.05526 l/mol is the molar volume of an ideal gas at 20 °C and at atmosphere pressure equal to 1 atmosphere (760 mm mercury, 101325 Pa).

Organic solvents (toluene, styrene etc.) have usually neurotoxic effect on the humans. The prevention of chronic neurological occupational diseases is possible in their early detection and exact diagnoses in the early stage of the functional disorders. On that condition only, it is feasible

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to rehabilitate the workers' health and work ability at large. The nervous system is one of the most sensitive systems of the organism that dynamically reacts to various exogenous factors [10, 11]. The experimental data of exposureresponse relationship have to be determined individually for every single chemical. For example, the literature data for gasoline show that the methyl tert-butyl ether (MTBE) is the most widely used oxygenate added to gasoline at concentrations up to 15 % by volume. The human toxicology tests are possible with volunteers. In Sweden, a study of acute MTBE vapor on the health of male volunteers, exposure occasions showed minimal effects such as tendency to slight nasal swelling [12]. In a Finnish study focused on changes in neuropsychological symptoms and moods among tanker drivers from three oil companies in various parts of Finland exposed to MTBE, acute symptoms of headache, dizziness, nausea, dyspnoea, irritation of saliva excretion at the end of workweek were reported [13].

Recently developed by Marquart et al. "Stoffenmanager model" [14] is an internet-based tool containing risk banding scheme, but it is too difficult to understand for the managers of small and medium-size enterprises in previous social countries (Estonia) and it is expensive.

2. EXPERIMEMTAL DETAILS

The portable FTIR/FT-NIR spectrometer Interspec 301-X with open optical path was used for the determination of chemical vapors in the air. Thermo Scientific Nicolet IR100 is the real-time process analyser that enables quantitative determination of 435 different chemicals in the air of the work environment. The overall wavelength range is 7000 to 400 cm^{-1} (IR). Infrared spectrometers measure the spectrum of light (colors) which is absorbed, emitted or reflected from the test material. The shale fuel oil vaporization properties depend on fuel oil

characteristics, like phenolic OH content, number of average molecular weight and molecular weight distribution. An infrared spectroscope (FT-IR) with an attenuated total reflection (ATR, ZnSe crystal) system was used to characterize fuel oil functional groups and specifically to evaluate qualitatively the phenolic OH content. For quantification, a correlation was used that relates to the area of the 3600 - 3100 cm⁻¹ region to the phenolic OH group content of shale oil fractions. Unpleasant odor of shale fuel oil might also be caused from phenols. Unfortunately, we were unable to determine the number of phenol quantitatively, because it is not included in the analyzers database of substances.

Dräger-Accuro Gas Detection Pump is the device of the express method to determine the gaseous components in the work environment air. We can use different indicator tubes for the parallel determination of chemicals that have been detected by FTIR. Comparison of the results improves the accuracy of the results obtained by the spectrometer. The express method helps to determine substances in the air qualitatively.

3. RESULTS

3.1. Development of the health risk assessment (HRA) model for industrial rooms

The suggested criteria for risk levels of occupational hazards as chemicals and possible health complaints were obtained from the scientific literature and relative legislation. The focal points in the model are the boundary lines between the four health risk levels (Table 1). The model proposed takes into account the interrelationships between exposure to occupational hazards (based on the literature data) [15 - 19], the measurements in the WE, analysis on the basis of the relevant legislation requirements

Table 1. Determination of ne	and this levels of chemic				
Operative temperature, ⁰ C	more	19-27	20-26	21-23.5	
Relative Humidity (RH), %	RH<70 or RH>70	20 <rh<70< td=""><td>25<rh<60< td=""><td>30<rh<50< td=""></rh<50<></td></rh<60<></td></rh<70<>	25 <rh<60< td=""><td>30<rh<50< td=""></rh<50<></td></rh<60<>	30 <rh<50< td=""></rh<50<>	
Methyl methacrylate, ppm	110	100	50	0.08	
Thiols (mercaptane), ppm	-	-	1.0	0.5	
Ethyl acetate, ppm	320	300	150	75	
Toluene, ppm	110	100	50	25	
Benzene, ppm	3.3	3-0	0.5	0.05	
Styrene, ppm	55	50	20	1.0	
Phenol, ppm	4.4.	4.0	2.0	1.0	
Xylene, ppm	110	100	50	25	
Butanol, ppm	83	75	50	25	
			OEL		
	◀				
	B4	B3	B2	B1	
Variables	4th health risk level	3rd health risk level	2nd health risk level	1st health risk level	
	B4*;	B3*;	B2*;	B1 *; c=10-50% of	
	c=!00% over STL	c=STL	c=OEL;	OEL or Odor	
	Exposure time: less	Exposure time: 15 min.	Exposure time: 8 hours	Threshold;	
	than 15 min.		_	Exposure time: 8	
				hours	
	ME** twice a year	ME** once a year	ME** once in 3 years	ME**once in 3	
				years	

Table 1. Determination of health risk levels of chemicals in manufacturi	ng
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B1*, B2*, B3*, B4' are the borders between the health risk levels (1-4); ME- medical examinations

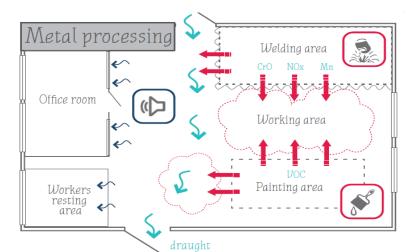


Fig. 1. Hazards profile in industrial and office areas in the metal processing industry

and occupational exposure limits [20 - 24], determination of risk levels and connecting them with possible health complaints.

To connect the risk levels and the health complaints, we used appropriate questionnaires in the Estonian enterprises to receive the opinions of a large number of workers concerning chemical exposure at work.

Occupational exposure limits (OEL) are set in order to protect the health of the workers in the working environment. The limits are the concentrations of hazardous substances in the air, averaged over a specified period of time, referred to as a time-weighted average (8 hour workdays and 40 hours per week). The limits are given in two types: as a long-term exposure limit (OEL) for 8 hours' exposure and the short-term exposure limit (STL) for 15 minutes. The latter is set for substances having a strong smell (like NH₃ or ethyl acetate etc.). During a long-term period, it is assumed, that a variety of substances cannot cause any health disorders during 8 hour workdays and 40 hours per week. The STLs are set to help prevent effects such as eye or throat irritation, which may occur caused by the exposure to the chemical during a few minutes [9].

The boundary lines in the model (Table 1) are as follows:

B1 – the hazardous exposure to the worker begins: the boundary concentration value for chemicals is 10-50 % of OEL or odors threshold; the exposure time is 8 hours for those who are not allergic to the substances present in the work environment. The latter have to undergo the consultation with medical specialists on the possibilities of continuing the work in this environment.

B2 – the boundary line for the 2nd health risk level. The concentration of substances is equal to OEL [9]. The summation in the case of mixture has to be taken into account. The exposure time is 8 hours per day with compulsory use of personal protective equipment (PPE).

B3 – the boundary line for the 3rd health risk level. The concentration of a substance is equal to the short-time level (STL). The PPE is compulsory and the exposure time is 15 minutes per day.

B4 – the boundary line for the 4th health risk level. The concentration of the chemical is 10 % over the short-time level (STL), exposure time under 15 minutes and PPE

(totally separating gas masks) is compulsory. The 4th health risk level is allowed only during changes like during the introduction of new technology etc. These actions will hopefully manage to keep the workers' health. The hazard statements are available on the labels of chemical packages and on the safety card of chemicals.

Awareness of the hazard statements and the HRA levels in the work environment would enable the occupational health personnel to foresee the possible negative health effects on the workers.

Simultaneously to the HRA model, the hazard statements have to be followed for each health risk level (Regulation, 2007):

1nd HRL: H313, H335, H336

2nd HRL: H303, H305, H313, H316, H317, H333, H334, H 335, H336

3rd HRL: H302, H311, H312, H315, H320, H331, H332, H371, H372, H373

4th HRL: H 300, H 301, H304, H310, H314, H318, H319, H330, H340, H341, H342, H350, H351, H360, H362, H370.

A hazard statement is a phrase that describes the nature of the hazard in the substance or mixture. A hazard statement will be determined by the application of the classification criteria [20].

The model also proposes to link the health risk levels (HRLs) with the frequency of health medical examinations (HME) for workers in hazardous conditions. The Estonian regulation of the Ministry of Social Affairs "Procedure for health examination of workers" [23] defines the health surveillance as follows: employee's health begins with the initial ME within the first month of the work activities and thereafter by the intervals indicated by the occupational physician, but not less than once every three years and for workers under 18 not less than once every two years. These demands are taken into account in the proposed HRA model (see Fig. 1, noted bold).

3.2. Use of the health risk assessment (HRA model)

Table 2 presents the results of the measurement of chemicals, the developed risk criteria and the health risk levels according to the HRA model. The harmful effect of some chemicals or dust begins at the concentration which the person (worker) feels as smell (the odor threshold, B1), or if the chemical has no smell, then at 50 % of the concentration which is established as OEL for 8 working hours per day by the regulations of the Estonian Republic, allowed in production space.



Fig. 2. Painting in the furniture industry

For some (carcinogenic) substances, like benzene, 50 % of OEL is too high (dangerous), then B1 in the model (Table 1) is taken lower: 10% of OEL. In the HRA model (Table 1) the occupational limit value B2 is marked as OEL (operation permitted for 8 hours per day). In this case, the 2nd risk level begins. As said above, the working time with this concentration of the chemical in the air is 8 hours. The 3rd risk level begins with the chemical's concentration B3 which is equal to the Estonian legislation's 15-minute limit. Operation with this concentration is allowed for 15 minutes. The 4th risk level begins with the chemical concentration of 10 % over the 15 minute limit (B4). Run time in these conditions is less than 15 minutes (4th level of risk). Higher chemical concentration in the work environment is not allowed. Longer work with the concentration B4 is allowed if the collective protective means (firstly) and separating from the polluted environment PPE are used. The tendency is to the protective solutions towards lower concentrations of chemicals in the work environment (more closed equipment).

The HRA model (Table 1) sets very clear limits of chemicals that employers can allow in the workrooms during the workday and during short use (15 minutes). If the chemical is carcinogenic, then the limits are very strict.

The spectrograms of the air mixture from plastic boat industry are shown in Fig. 4. The analysis of the air phase from the WE during shale fuel oil handling is presented in Fig. 5.

4. DISCUSSION

From the investigated vapors, benzene is carcinogenic, toluene influences the central nervous system, benzene and toluene have also influence on unborn babies and may cause mutagenic effects. Xylene and phenols have effect on skin and if swallowed. Methyl mercaptan found in the work environment air in rubber (old car tires re-cycling) manufacturing is a central nervous system depressant that acts on the respiratory centre to produce death by respiratory paralysis. Therefore the OEL is so low (1.0 ppm, Table 2). Formaldehyde and benzene both are carcinogenic. Styrene is irritating to eyes and skin, harmful by inhalation, also influencing the nervous system. Methyl methacrylate is irritating on skin and the central nervous system. Thus, all the investigated solvents are neurotoxic and can cause occupational diseases developing in 3 stages: hyperstenic (I) and hypostenic syndrome (II), and organic psychosyndrome (III).

The training for use the new model presented in the current work has to be carried out in the co-operation with the National Inspectorate of Estonia.



Fig. 3. Welding in the metal processing industry

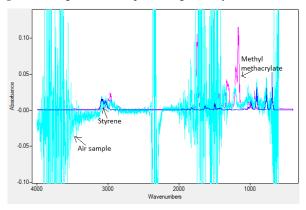


Fig. 4. Spectrogram in the plastic boats industry

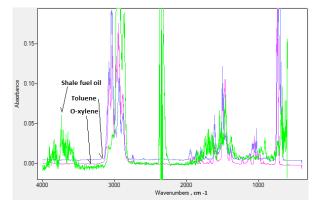


Fig. 5. Spectrogram in the shale fuel oil handling

The questioning of workers about health risks connected with chemicals gave the result that 80% of people do not know how the chemicals influence on their health, or they assess the influence not-correctly. The chemical safety cards are often kept in the computer of the manager and not distributed to the workers. The training on chemicals handling is insufficient. It has be carried out in both languages: in Estonian and in Russian.

Table 2. Measurement results, odor thresholds	, exposure limits, lethal concentrations and	hazard statements of investigated chemicals

Measuring point, measured chemical	Hazard statements [20]	Odor Threshold, ppm [21]	The measured result (Dräger/ FTIR), ppm	Exposure limit, ppm [9]	Health Risk Level
Shale fuel oil handling Benzene	H225, H304, H315, H319, H340, H350	4.68	1.0/n.i.	0.5	IV
Toluene	H225, H315, H304, H373, H361d; H336	1.60	6.0/10.0	50	II
o-Xylene (Fig.6)	H332, H315	0.05	40.0/2.7	50	III
Phenol	H311, H301	0.04	20.0/n.i.	2.0	IV
Rubber manufacturing Methyl mercaptan	H220, H280, H331, H401	0.00007	4.5/5.0	1.0	IV
Wood processing industry Formaldehyde	H227, H301, H311, H315, H317, H318	0.5	0.5/0.42	0.5	II
Metal ship painting Xylene	H331, H334, H351, H370, H402	0.05	20/11.8	50	III
Ethyl Acetate	H225, H319, H333, H336	0.87	40/17.6	150	II
Plastic industry Styrene	H226, H332, H315, H319	0.035	18/20	20	IV
Methyl methacrylate (Fig. 5)	H225, H315, H317, H335, H402	0.21	8/10	1.0-10	IV

5. CONCLUSIONS

Analysis and evaluation of work-related factors have potential use in manufacturing enterprises for a better harmonization of work content, health, occupational hygiene and safety. The paper provides recommendations how to change or modify workplace situations, and to implement a correct (locally adjustable) safety measure to improve working conditions and to reduce work-related diseases.

The study proposed a model of health risk assessment as an effective tool to determine health risk levels in the case of chemicals in industrial rooms, to evaluate the employees' health and to diagnose the occupational diseases as well as the frequency of medical examinations.

The HRA model can be used by senior managers, particularly in manufacturing (small and medium-sized enterprises), safety managers and occupational health professionals.

The main method for cleaning the indoor air from the pollutants (liquid vapors) is ventilation. Dilution ("general") ventilation is forbidden in the case of highly toxic chemicals, only (local) exhaust ventilation is permitted [24, 25]. The exhaust ventilation multiplicity in each particular case can be calculated by the equations given in "Basis of ventilation" [26].

The ventilation rates and operational parameters are determined by the relevant legislations and standards. Nevertheless, there were complex liquid vapors in the air of the work environment, which are constituted during manufacturing or handling of chemicals containing primary products (for instance, in shale fuel oil or rubber handling), where unpleasant and troublesome smell will not disappear even with the adequate ventilation. Thus, future research is needed to evaluate whether possible interventions, such as additional ventilation or air filtration, new technologies, air pollution control systems (like, fume extraction system, gas scrubbing system or dust extraction and collection system) and new more closed equipment for handling the chemicals, is necessary, effective and useful.

Based on the thesis study, the authors emphasize that air pollution needs to be eliminated and reduced, indoor air quality and health indicators need to be monitored; this will enable employers and the relevant authorities to be aware of the trends and consequences of indoor air pollution, so they can determine how to ameliorate the situation.

Thus, the authors suggest that the proposed HRA model can be used as a tool for assessment and evalution the health risk levels and for the preventive measures (risk management), for instance, as a basis for choosing the appropriate personal protective equipment as well as the frequencies of workers' health examination.

The best tool for workers' health protection would be the biomonitoring of workers during their total time working in the hazardous conditions. Countries successful in terms of occupational health and safety countries (like Finland) have introduced this method. This is the goal for Estonia in the future.

It is necessary to reduce emissions of the air pollutants at workstations by improving technological processes and proper operation of general and local ventilation systems. During the handling of shale fuel oil, painting of cars and other activities, the PPE for the specific purpose has to be used (e.g., Organic & Inorganic Gases & Particulates -Painters Masks / Disposable & Re Usable Masks (BS EN 405:2001+A1:2009)).

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