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Management of health hazards during shale oil handling

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Abstract. The current paper describes the investigations in Tallinn University of Technology of the hazardous gaseous phase during handling of shale fuel oil. The combined-method gas chromatography-mass spectrometry (GC-MS) was used for determination of the gaseous components evaporating from the shale fuel oil during handling. Parallel measurements were made using Dräger tubes. The model for determination of risk levels to the workers' health is compiled. The occupational illness stages are developed using statistical data of diagnoses made by the occupational health doctors. In the case of benzene, xylene, toluene and phenol, the main health impairments are divided into two different groups – irritating and neurotoxic effects. According to the proposed model, the exposure to toluene and xylene poses a justified risk (risk level II), benzene and phenol an unjustified risk (risk level III). Without any additional control measures applied, the risk for occupational diseases caused by these chemicals is significant.

Key words: shale fuel oil, gaseous phase hazardousness, occupational health.

INTRODUCTION

Based on the WEC 2007 report, Estonia was the world's largest producer of shale oil, producing 345,000 ton of shale oil per year. Approximately 8,000 ton of shale oil was utilised for domestic electricity generation; 98,000 ton of oil for heat generation and the remaining 222,000 ton was exported (WEC, 2007).

Investigations of oil shale for energetic use started in Tallinn University of Technical (TUT) at the beginning of the 1920s. At the present time the Estonian government invests in the use of oil shale in the form of oil. It is used as boiler fuel in houses, might also be used in cars, vessels and other applications are possible.

The current paper describes the investigations in Tallinn University of Technology of the hazardous gaseous phase during handling of shale fuel oil. The gaseous phase of shale fuel oil is investigated at different temperatures. In the local boiler enterprise, the temperature in the storage tanks room is approximately 27 °C; during the loading the temperature is ~50 °C; in the boiler systems room where the workers deal with shale fuel oil the temperature is 70 °C (Al-Sharrad et al 2010).

The aim of the study is the qualitative valuation of the hazardous gaseous components evaporating from the shale fuel oil at handling temperatures (20–70 °C) with chemical methods and the determination of their concentration in the air of the work environment with Dräger-tubes express method.

The hazardousness of the gaseous components has to be determined as these gases are important components in the risk assessment model (Fig. 2).

Rarely in the industrial situations, only one substance is used and therefore a decision must be made as to which, of potentially many substances, should be measured (Aw et al 2007). A useful means of combining both the WEL (working exposure limits, ppm) and the volatility of a substance (which is temperature dependent) is the vapour hazard index or ratio (VHR):

$$VHR = \frac{concentration\ of\ saturated\ vapour\ (SC)}{WEL}, \tag{1}$$

where WEL is the relevant workplace exposure limit for the material in question (in parts per million by volume, ppm) and SC is the saturation concentration (also ppm), given by:

$$SC = \frac{VP_{STP}}{BP} \text{ x } 10^6 \tag{2}$$

in which the barometric pressure (BP) is 760 mm Hg and VP_{STP} is the vapour pressure in millimetres of mercury at standard temperature (20 °C) and pressure (760 mm Hg).

The breathing zone is defined as approximately 20–30 cm from the nose/mouth.

Epidemiological evaluation poses greater problems because it is necessary to have some knowledge of the rate at which the contaminant causes a biological effect. If the substances have an acute effect (seconds to hours), the duration of sampling must be able to reflect this variability within a shift. When the effect is chronic, a more appropriate duration may be a weekly, monthly, annual, average or lifetime dose. For substances known to cause an immediate effect on, e.g. mucous membranes, ceiling values are quoted in some countries.

Periods of work greater than 8 hours: the longer the day over which the contaminant is absorbed, the shorter the period of recovery before the next insult. For substances with very short half-lives, this may not be a problem, but for those whose half-lives approach or exceed 16 h (the period of recovery for an 8 h working day), the body burden may rise over the week/shift period. The model has been postulated by Brief and Scala for longer periods:

$$\text{WEL multiplication factor} = \frac{8}{H} \text{ x } (24\text{-}H/16), \tag{3}$$

where H is the number of hours worked per day (Aw et al 2007).

MATERIAL AND METHOD

Chromatography of gases (GC) is used in the current study to distract the complex organic compounds created in the production and handling processes of shale fuel oil. Besides the GC, mass spectrometry (MS) is used. The combined method is called gas chromatography-mass spectrometry (GC-MS) (Eiceman, 2000).

For determination of gases concentrations in the workplace air, the express method using Dräger indicator tubes was used. Benzene (C_6H_6), phenols (C_6H_5OH), toluene ($C_6H_5CH_3$) and o-xylene (C_8H_{10}) were the main determined gases (Table 1).

The toxicity of the substances was determined using toxicology databases (TOXNET, ECOTOX, TOXSEEK, etc.).

Table 1. Determination principles of chemicals, the Dräger tubes determination ranges

Reaction principle	Dräger tubes	Determination range	Colour change of adsorbent
$2\ C_6H_6 + HCHO = C_6H_6\text{-}CH_2\text{-}\text{-}C_6H_6 + H_2O$ $C_6H_5\text{-}CH_2\text{-}C_6H_5 + H_2SO_4 \rightarrow$ p-chinoic compound	Benzene 0.5/c	0.5 to 10 ppm	from white to brownish-yellow
$C_6H_5OH + Ce(SO_4)_2 + H_2SO_4 \rightarrow$ brown grey reaction product	Phenol tubes 1/b	1 to 20 ppm	from yellow to brown grey
$C_6H_5CH_3 + I_2O_5 + H_2SO_4 \rightarrow I_2$	Toluene tubes 5/b	50 to 300 ppm; 5 to 80 ppm	from white to pale brown
$C_6H_4(CH_3)_2 + HCHO + H_2SO_4 \rightarrow$ quinoid reaction product	Xylene tubes 10/a	10 to 400 ppm	from white to red brown

Boiler fuel oil was collected from a local boiler enterprise. Description and mark of material is shale oil VKG D EE 10528765 TS 34:2011, Batch no. 8 (the properties given in Table 2). Petroleum-based fuel (Conoco Phillips, 2007) used as a comparison in the current study was gained from a petrol station in Tallinn.

Table 2. Properties of the shale fuel oil (VKG, 2012)

Quality characteristics of goods	Facts	Norms
Flash point (°C)	Min. 61	68
Freezing point (°C)	Max. -15	-17
Sulphur (%)	Max. 0.8	0.61
Density at 15 °C kg $(m^3)^{-1}$	Not measured	1,005.4
Moving viscosity at 80 °C	Max. 2.8	2.49
Ash (%)	Max. 0.1	0.03
Water (%)	Max. 1.0	0.1

RESULTS OF MEASUREMENTS

Fig. 1 shows that hydrocarbon GC retention time was essentially determined by ions peaks.

The GC of a mixture of hexane, benzene, toluene, n-decane, o-xylene and phenol gave the expected elution order based on ion peaks. The response of the flame ionisation detector is proportional to the number of ions. Only phenol determination did not give the expected results because the ions peak is very low in the mass chromatogram. There is reason to believe that phenol leaves with decane because they are essentially the same ions. The results of reagents on different temperatures are given in Table 3. The results of measurements with Dräger tubes are shown in Table 4.

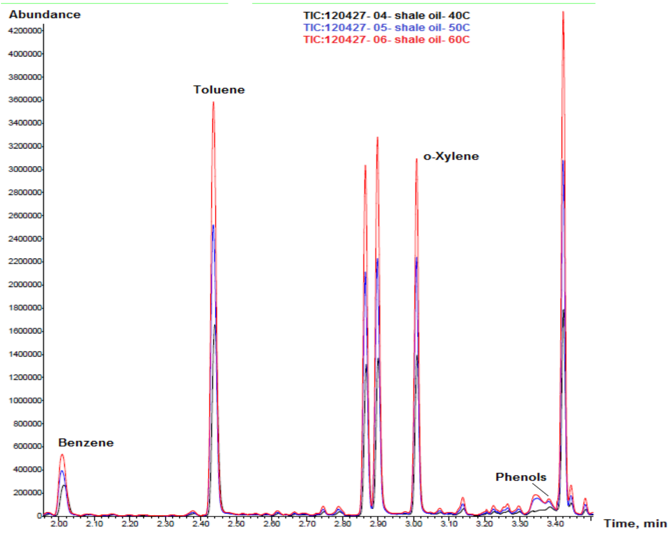


Figure 1. The retention time of hydrocarbons determined by GC (Traumann et al., 2012).

Table 3. GC retention times and vapour pressures for investigated chemicals

Hydro-carbon	CAS. No.	Vapour pressure, kPa (40 °C)	Boiling temperature, °C	Retention time, s
Benzene	71-43-2	10.0	80.1	2.0
Toluene	108-88-3	3.8	110.6	2.44
o-Xylene	95-47-6	0.9	144.4	3.0
Phenol	124-18-5	3,9	174.1	3.34

Table 4. Determined chemicals concentrations and exposure limits

Used fuel in the boilerhouse	Concentration (C_1) of the chemicals (measured), ppm U^1 = 10…30%	Concentration (C_1) of the chemicals (calculated), mg $(m^3)^{-1}$	C_2 (after 5 months storage), ppm	Exposure limits for chemicals, ppm / mg $(m^3)^{-1}$ (Resolution, 2007)
Shale fuel oil	benzene – 1.0	3.2	0.7	0.5 / 1.5
	toluene – 6.0	23.0	4.0	50 / 192.0
	xylene – 8.0	35.0	n.m.*	50 / 200.0
	phenol – 9.0	34.0	1.5	2.0 / 8.0
Petroleum-based fuel oil	benzene – 1.0	3.2	0.5	0.5 / 1.5
	toluene – 300.0	128.0	100	50 / 192.0
	xylene – 60.0	260.4	60.0	50 / 200.0
	phenol – 20.0	76.0	0	2.0 / 8.0

*n.m. – not measured
U^1 – uncertainty of measurements

The most hazardous component in the work area is benzene, the concentration in the worker's breathing zone was 3.2 mg $(m^3)^{-1}$ (exposure limit = 1.5 mg $(m^3)^{-1}$).

Benzene is carcinogenic and it has to be removed from the work environment. The other chemical found in the work environment over the limits was phenol.

During the inhalation, the solvents enter the arterial bloodstream, and their concentration in blood increases gradually toward the plateau that is the level determined by the ambient air concentration and solvent solubility in blood, expressed by air/blood ratio. Arterial blood is not suitable for routine sampling. Therefore, venous blood is obtained to determine the concentration of solvents in the blood.

Benzene is a clear, colourless, volatile liquid (boiling point (B.P.): 80.10 °C) widely used in the past as the industrial solvent. Its use is restricted because of its recognised toxicity to man. Absorption of benzene in humans takes place mainly by inhalation (Heiselmann, 1990).

Toluene is a colourless liquid with an aromatic odour (B.P.: 110.4 °C), insoluble in water, soluble in acetone. Toluene is mainly absorbed in the human body by inhalation. Dermal absorption is also possible. 20% of absorbed toluene dose is eliminated unchanged with expired air, and less than 1% is excreted unchanged in urine. About 80% of toluene in the body is oxidised to benzoic acid, which is then conjugated with glycine and excreted in urine as hippuric acid. Acute effects with toluene include: 50–200 ppm: fatigue and headache; 200–400 ppm: headache, slight incoordination, and slightly reduced reaction time; between 400–800 ppm: headache, dizziness, hilarity, incoordination, reduced time, weakness and confusion; at 800 ppm the symptoms are more severe, and as the level increases, loss of consciousness occurs (OSHA, 2008).

Xylene is a clear, moderately volatile liquid (B.P.: 138.5 °C). Xylene is absorbed by inhalation, but can also penetrate the skin. Pulmonary retention averages 60–65% of the inhaled dose. About 95% of the absorbed amount is biotransformed by oxidation to methyl benzoic acids. In man, the latter is excreted with urine (96%) (OSHA, 2008).

Phenol is toxic (Hanscha et al 2000): inhalation, ingestion or skin contact with material may cause severe injury or death. Colourless to light-pink, crystalline solid with a sweet, acrid odour. Phenol liquefies by mixing with about 8% water. Upon heating, toxic fumes are formed. The substance can be absorbed into the body rapidly by inhalation of its vapour, through the skin and by ingestion.

Modelling the connections between the hazards and health disturbances

Table 5 presents the essential data of investigated four chemicals (such as odour threshold, exposure limit and IDLH value) to determine the risk levels. (Heiselman, 1990). Odour threshold is used as the '**optimal limit**' in the current scheme (Bleecker 1994; Reinhold et al 2009).

Workers' exposure concentration is an estimate of the chemical concentration that is potentially inhaled by the workers in the workplace. Occupational exposure limits (Resolution, 2007) are specifications for the maximum airborne concentration of substances, averaged over a reference time period (in our case 8-h shift) in workplace air and are used as the '**norm**' in the current scheme.

The '**conditional limit**' is determined using the highest exposure value which is not is not associated with any adverse symptom, yet, derived from the toxicological profiles.

For the '**critical limit**', half of the IDLH (immediately dangerous to life or health concentration) values are used (Sax, 1989; OSHA, 2008).

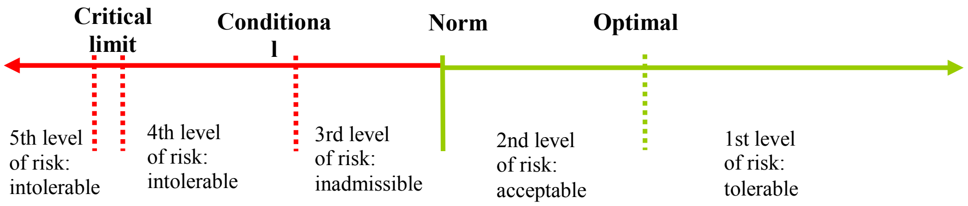
Table 5. Odour thresholds, exposure limits, and lethal concentrations of investigated solvents

Hydrocarbon	Odour threshold, mg $(m^3)^{-1}$	Exposure limit, mg $(m^3)^{-1}$	IDLH, mg $(m^3)^{-1}$
Benzene	5	1.5	1,600
Toluene	11.1	192	1,880
o-Xylene	4.9	200	3,906
Phenol	19	8.0	950

The risk assessment model is given in Fig. 2. Four risk levels are determined.

The methodology is based on EVS EN 151251 standard. Other methods for use are presented by Reinhold et al 2009; Hassim & Edwards, 2006.

650	200	90	19.0	**Phenol**, mg $(m^3)^{-1}$
940	300	150	5.0	**Benzene**, mg $(m^3)^{-1}$
1,382	300	221	221	**Xylene**, mg $(m^3)^{-1}$
530	375	192	11.1	**Toluene**, mg $(m^3)^{-1}$



Irritating effects

H*340, 350, 360, 362	H340, 360	H333, 334, 335	Eye, skin and nasal irritation	Eye, skin and nasal irritation

Neurotoxiceffects

3rd stage of illness: Hyperstenic syndrome (mild level of asthenia, irregular speed of mental activity)	**2nd stage of illness: Hypostenic syndrome** (moderate asthenia, decreased speed of mental activity)	**1st stage of illness: Organic psycho-syndrome** (expressed asthenia, memory disorders)	**1st stage of illness** (for hypersensitive persons): expressed asthenia, memory disorders of organic type)	**1st stage of illness** (for hypersensitive persons): expressed asthenia, memory disorders of organic type)

*H333 – Hazard statements (GHS, 2012)

Figure 2. The levels of risk for investigated chemicals.

CONCLUSIONS

The occupational illness stages are developed using the statistical data of diagnoses of occupational diseases by occupational health doctors. In the case of benzene, xylene, toluene and phenol, the main health impairments are divided into two different groups – irritating and neurotoxic effects.

According to the proposed model, the exposure to toluene and xylene poses justified risk (risk level II), benzene and phenol unjustified risk (risk level III). Without any additional control measures applied, the risk for occupational diseases caused by these chemicals is significant.

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