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Case Report

Benzene exposure assessment of printing workers treating petroleum-based cleaner in South Korea

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Abstract: This study was conducted to check whether benzene is contained inside the petroleum-based cleaning agent used in the printing industry and measure whether it is actually exposed to the air. Benzene was analyzed inside the cleaning agent and air exposure evaluation was done by area sampling. Risk assessment was performed using the Chemical Hazard Risk Management (CHARM) technique. Most products contained benzene based on the results obtained from this study. As a result of collecting air samples and checking whether the workers were exposed to benzene actually, benzene was detected in three samples. As a result of the risk assessment, most of printing businesses scored more than four points. Benzene was detected in all petroleum-based cleaning products. In addition, benzene was detected in some of air samples. Considering the fact that even small exposure level of benzene is dangerous to worker health and most of the printing businesses in South Korea operate on a small scale with fewer than five employees so the health management system is poor, it is necessary to prepare appropriate measures to prevent work diseases provoked by benzene exposure.

Key words: Benzene, Petroleum-based cleanser, Exposure evaluation, Risk assessment, Printing business

Introduction

Currently, most chemical management in South Korea relies on Material Safety Data Sheet (MSDS). Therefore, safety and health management are insufficient if even hazard chemicals contained in product are not indicated on the MSDS. The chemicals with a content of less than 1% and carcinogenic substances with a content of less than 0.1% are not obligated to be marked on MSDS. In particular, in the case of cleaning agents, new cleaning agents that are not managed by the Occupational Safety and Health Act have been developed and supplied, but their hazard effects are not properly identified.

A previous study conducted by the Korea Occupational Safety and Health Agency (KOSHA) showed that five petroleum-based products (solvent naphtha, hard naphtha, liquefied petroleum gas, hydrogenated Light Straight Run Naptha (LSR), and Heavy Straight Run Naptha (HSR)) among the 15 chemicals contained in the cleaning agent were at high risk. As a result of analyzing the components of the products, benzene (0.07%–0.93%) was detected in four of the hard naphtha products, although benzene was not indicated on the MSDS[1)].

In addition, in previous studies, it was found that ben-

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zene was included in many products used in daily life such as industrial sites and homes. Shoji *et al.*[2] confirmed that toluene, xylene, benzene, trichloroethylene, butyl alcohol, etc. were detected in diluents and organic solvents, and reported that some products contained up to 48% benzene. Fishbein[3] stated that consumers can be exposed to benzene at home through commercial products, and products such as rubber cement, brush cleaners, paint strippers, and bicycle tire patch compounds are likely to contain benzene at a concentration of 10–100%. Pearce *et al.*[4] studied benzene exposure in industries using paint in China from 1956 to 2005, and the exposure of benzene was 43.9 mg/m^3 (up to 3,212 mg/m^3), in spray painting and 58.2 mg/m^3 (up to 3,374 mg/m^3) in brush painting. According to the International Agency for Research on Cancer (IARC), benzene concentrations detected in individual color samples during traction motor cleaning were between 0.002–0.006 ppm[5] which is likely to be exposed through the respiratory tract. According to a study by Williams[6], benzene was also detected in air in products containing less than 0.1% (v/v), and Lan *et al.*[7] reported that exposure to benzene concentrations below 1 ppm, the exposure standard of Occupational Safety and Health Administration (OSHA), could lead to risks such as leukemia.

Benzene is a representative hematopoietic carcinogen that causes leukemia and bone marrow dysplasia syndrome, and is known to be very hazard to the human body[8]. In addition, benzene is a substance that requires careful safety and health management, and research is needed to analyze the ingredients of products that may contain benzene even if they are not indicated on MSDS.

The aforementioned five types of petroleum products are commonly used as cleaners in workplaces. Among industries that use cleaning agents, most of the printing industry is operated as a small business, so the protection of the working environment and chemical exposure is relatively weaker than that of a large business[9]. Therefore, the purpose of this study is to investigate the benzene content of petroleum cleaning agents used in printing businesses and to identify the health risk level of printing workers through actual exposure evaluation and risk assessment.

Materials and Methods

Subjects

The cleaning agents to be investigated were first selected as petroleum cleaning agents containing benzene, which are mainly used in the printing industry reported in previous studies[1, 10]. In addition, the previous study[1] confirmed that benzene was detected as a result of qualitative analysis of hard naphtha products with a content of 50% or more. Based on this, a product containing 100% n-hexane, a product containing 100% toluene, and a printing business using a mixture of the above three substances regardless of content were evaluated. The field investigation was conducted on a total of 25 sites in the metropolitan area, where the printing industry is the most located in South Korea.

Workplace status investigation

The survey items on the actual condition of the workplace are the composition of cleaning agents, the content of individual components for the mixture of chemical abstract service (CAS No.), and the usage thereof. Based on the monthly usage, the actual worker's use of cleaning agents on the day of measurement was investigated. In the case of 'no response' or 'not knowing' about the usage amount on the same day, it was calculated by dividing the monthly usage amount into the number of working days. Additionally, the temperature, number of workers, whether local exhaust devices are installed, and whether personal protective equipment is worn were investigated.

Analysis of benzene concentration in the product

After collecting about 20 ml of cleaning agent used in the actual workplace in the vial, it was sealed with a stopper and para film and transported to the analysis room, and stored frozen. After 100 times dilution using methanol, 1 µl of the sample was injected into GC-MS for analysis. The conditions of the analysis device are represented in Table 1.

Analysis of benzene exposure level in the air

Measurement of benzene concentration in the air was conducted under the Technical Guidelines for Measurement and Analysis of Work Environment (NIOSH Method 1501) for benzene in the National Institute for Occupational Safety & Health (USA). Air samples were collected using activated carbon tubes (100 mg/50 mg, SKC, USA), and flow correction of low volume pumps (LES-113, Gillian, USA) set at 0.05 m/s flow rate was performed before and after sampling using a dry flow meter (Bio Drycal Defender 510-H, Mesa Labs, USA). The air sample was measured as an area sample for reasons such as pandemic of COVID-19, reduction in workload, and non-cooperation of workers. The measurement location was the operator's main working space. The sample collection time was set to 8 h according to the TLV-TWA, Threshold Limit Value-

Table 1. Instrument conditions for analyzing benzene concentrations in petroleum products

GC (Agilent 7890B, U.S.A)		MS (Agilent G7081B, U.S.A)
Injector	type: split/splitless injector	Ionization mode: EI (70 eV)
	inj. temp: 250°C	Ion source temp.: 230°C
	column flow: 1 mL/min	interface temp.: 200°C
	split ratio: splitless	Acquisition type: SIM mode (78 m/z)
Oven	37°C for 3 min	
	20°C at 80°C/min	
	60°C at 200°C/min, for 2 min	
	Total Run Time 9.15 min	

Table 2. Instrument conditions for analyzing benzene concentrations in air samples

Analytical device	SHIMADZU GC-2010 Plus
Column	HP-INNOWAX
Carrier gas	Nitrogen (N_2)
Injection temperature	200°C
Split ratio	100:1
Detector temperature	250°C
Oven	Same as shown in Table 1

Table 3. Five steps for the chemical hazard risk management (CHARM)

Advance preparation	Investigate safety and health information necessary for the evaluation
Identification hazardous factors	Identify hazardous risk factors through checklist, existing health data, and actual workplace surveys
Risk estimation	Calculate the magnitude of the hazard by estimating the hazard rating and exposure level rating
Determining the risk	Determine if the estimated risk rating is acceptable
Establish/implement risk reduction measures	Reduce risk ratings to as low a level as practicable and establish and implement appropriate measures

Time-Weighted Average (TWA standard). After sample collection was completed, both ends of the activated carbon tube were sealed and labeled, transported to the analysis room, stored frozen, and analyzed within one week. Table 2 represents conditions of the analysis device.

Table 4. Determination of risk level in chemical hazard risk management (CHARM)

Exposure \ Hazard	4	3	2	1
4	16	12	8	4
3	12	9	6	3
2	8	6	4	2
1	4	3	2	1

Benzene-related risk assessment

The risk assessment regarding benzene was conducted using Chemical Hazard Risk Management (CHARM), one of the chemical risk assessment techniques. The CHARM was developed to be used in all businesses of different scales in South Korea based on Control of Substances Hazardous to Health Essentials (COSHH Hessentials) developed by the Health & Safety Executive, UK (HSE).

CHARM is divided into five stages as shown in Table 3. The score for estimating risk level is given by a combination of exposure level (grades 1 to 4) and hazard level (grades 1 to 4) and the risk level is finally classified into grades 1 to 16[11].

For rating exposure level, it is first investigated whether the chemical has caused occupational diseases in the work process, then the exposure level is reviewed, the amount used and the physical characteristics such as scattering and volatility are confirmed.

The rating of hazard level is determined using classification information of Carcinogenicity, Mutagenicity and Reproductive Toxicity (CMR), exposure standards, and R-phrase and H-code provided by MSDS. In the case of CMR materials, the hazard rating is always the fourth grade and when exposure criteria, R-phrase, and H-code are applied, they are classified into four grades according to the corresponding criteria.

In particular, unlike COSHH Essentials or other control banding techniques, CHARM can determine an exposure level using the work environment measurement data, which are classified into four exposure levels. Less than 10% of the exposure standard is classified as level 1, 10% or more and less than 50% are level 2, 50% or more and less than 100% are level 3, and those exceeding the exposure standard are classified as level 4.

Finally the risk level (1: low, 2: medium, 3: high, 4: very high) is determined by multiplying the exposure level and the hazard level in accordance with Table 4. The final scores of the CHARM risk assessment are classified as shown in Table 5.

Table 5. Contents of chemical hazard risk management (CHARM) by score

Calculated risk	Risk level	Risk information	Acceptable or not	Improvement
1–2	1	Low risk	Unacceptable	Immediately
3–4	2	Medium risk		As soon as possible
5–11	3	High risk	Acceptable or unacceptable*	According to an annual plan
12–16	4	Very high risk	Acceptable	when needed

*Unacceptable: If a person with occupational disease among chemicals with a risk size of 4 has occurred or the chemical is a carcinogenicity, mutagenicity and reproductive toxicity (CMR) substance.

Results

Workplace status of printing business of South Korea

As presented in Table 6, the 25 sites evaluated on-site are located in the metropolitan area of South Korea. The size of the workplace was 21 small businesses with less than 5 employees, 1 place with 5 to 10 employees, 3 place with 10 or more employees. The temperature range of the survey site was 19.8°C to 31.3°C. The amount of petroleum-based cleaner used was 15 to 8,500 l/month. Ventilation equipment was not used in 14 of the 25 workplaces.

In the case of ventilation equipment, even if it is installed on site, if it does not operate normally due to damage or incorrect design, it is indicated that ventilation equipment is not used. The components of the cleaning agent used were found to be 2 benzene, 12 toluene, 6 hard naphthas, 7 mixed substances, and no n-hexane.

Concentration of benzene in cleaning agent

As a result of analyzing the bulk sample of the cleaning agent, benzene was detected in all 25 samples. The minimum and maximum contents of benzene were detected as 0.0016% (w/w) and 0.2719% (w/w), respectively. The chemical contained in the MSDS of the cleaning agent with the minimum content was toluene, and the cleaning agent with the maximum content was a mixed material. The maximum concentration of benzene for each substance is shown in Fig. 1. It was analyzed that the content of benzene in three samples (two mixed substances and one hard naphtha) exceeded 0.1% as shown in Fig. 2.

Exposure level of benzene in the air

As a result of measuring benzene concentration in the air, benzene was detected in 3 samples out of 25 samples as shown in Fig. 3. The minimum and maximum concentrations of exposed benzene were 0.011 ppm and 0.0474 ppm, respectively. All of the detected concentrations of benzene were 0.5 ppm or less of the exposure standard.

Benzene-related risk assessment

In this study, two methods were used to determine the exposure level of benzene. One is to reflect the property of the benzene and the other is to use actual benzene measurement data in the air, which is a unique characteristics of CHARM. Table 7 presents the risk assessment results of the three samples in which benzene was detected in the air. The hazard level was found to be the 4th grade for benzene which is a CMR substance in all 3 cleaning agents. All exposure levels (possibility) when using actual benzene measurement data were found to be the 1st grade, with less than 10% of 0.5 ppm which is the standard for benzene exposure in South Korea. As represented in Table 8, on the other side, they were rated the 2nd grade when using its physical characteristics such as volatility (boiling point: 80°C)

Discussion

As the health risks of benzene have been identified, studies on organic solvents, cleaning agents and petroleum products that may contain benzene have continued from the past to the present[12, 13)]. However, most of the previous studies on cleaning agents focused on manufacturing sites or internal experiments at laboratories[14, 15)].

Therefore, it can be considered that the fact that this study was conducted in the printing industry is different from the existing studies. Most of the workplaces surveyed in this study were small-scale workplaces. Due to these characteristics, it is known that there is a lack of awareness of work environment management and safety and health. In this study, the highest value among the air samples detected with benzene was 0.0474 ppm, which is close to 10% of 0.5 ppm based on benzene exposure standard in South Korea. In addition, in previous studies[16, 17)], it was reported that both individual sensitivity and response characteristics to benzene were different. Based on this, it is judged that workers who are sensitive to benzene exposure even when the concentration of benzene in the air is below the exposure standard would exhibit health hazard. In par-

Table 6. Workplace status of printing business investigated in this study

Workplace No.	Description in MSDS		Monthly usage (L)	Workplace temperature (°C)	Local ventilation installation	Number of workers	Benzene in product (%)	Benzene concentration in workplace (ppm)
	Substance	Content (%)					Measured value	
A	Toluene	100	300	25.2	○	19	0.0016	**0.0264**
B	LSR	60–80	15	25.7	○	2	0.0046	-
	Toluene	20–40						
C	HSR	40–60	16,000	26	×	25	**0.1379**	-
	LSR	25–45						
	Toluene	3–7						
D	Toluene	100	3,200	20.5	×	4	0.0046	-
E	Toluene	100	8,500	19.8	○	21	0.0309	-
F	Toluene	100	3,200	21.6	○	3	0.0356	-
G	LSR	100	420	22.4	○	3	0.0037	-
H	LSR	100	120	22.8	○	4	**0.134**	-
I	LSR	100	360	21.7	○	4	0.0053	-
J	LSR	100	420	26.6	○	3	0.0239	-
K	LSR	100	450	22.4	×	3	0.0034	-
L	Toluene	100	30	23.8	×	2	0.0067	-
M	Toluene	100	680	25.4	○	3	0.0071	-
N	LSR	30	75	26.1	○	4	0.0068	-
	Toluene	70						
O	Toluene	100	1,600	21.6	○	9	0.0066	-
P	Toluene	100	380	20.8	○	3	0.0076	-
Q	LSR	80	120	22.6	×	2	**0.2719**	**0.0173**
	Toluene	20						
R	LSR	50	40	24.1	○	1	0.0077	-
	Toluene	50						
S	LSR	70	800	23.5	○	4	0.0072	-
	Toluene	30						
T	Toluene	100	280	24.5	○	3	0.0578	**0.0474**
U	LSR	100	370	26.9	○	3	0.007	-
V	Toluene	100	20	27.1	○	1	0.007	-
W	Toluene	100	1,100	24.2	○	4	0.0069	-
X	LSR	20	2,400	26.3	○	4	0.0239	-
	Toluene	80						
Y	Toluene	100	240	26.3	○	4	0.0035	-

MSDS: Material Safety Data Sheet; HSR: Heavy Straight Run Naptha LSR: Light Straight Run Naptha.

ticular, although benzene was not indicated on the MSDS, benzene was detected in all 25 samples, and considering the fact that 0.1% or more, which is obligatory to indicate on the MSDS, was detected in 3 samples, measures such as the labeling obligation for a small amount of benzene should be sufficiently taken in the process of using and manufacturing petroleum cleaning agents.

In addition, considering that benzene was not detected in the air sample at 0.2719% (w/w) of benzene in the bulk sample whereas it was detected in the air sample at 0.0016% (w/w) of benzene in the bulk sample, it seems that environmental factors such as the management situation of the workplace, the amount of work, the working method or type, rather than the benzene concentration in the bulk sample, have a greater effect on the possibility of exposure to benzene in the air.

As a result of the risk assessment using the CHARM technique, when the work environment measurement result was used, the risk of benzene was all graded 4. However, when the handling amount of benzene and its physicochemical characteristics were used under the assumption that there is no work environment measurement result, the risk of benzene was up to grade 8 depending on the presence or absence of the application of the local

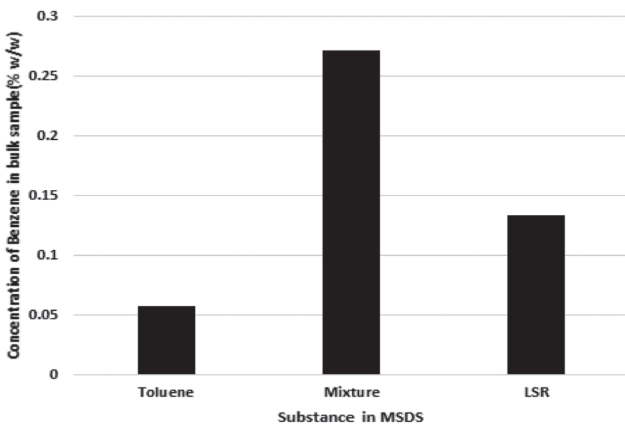

Fig. 1. Maximum concentration of benzene by substance in Material Safety Data Sheet (MSDS).
LSR: Light Straight Run Naptha.

ventilation facility. In case of CHARM, if the risk result is grade 4 or higher, it is a step that requires continuous management.

Since benzene is a CMR substance and its hazard level is always class 4, it is necessary to establish pertinent measures for reducing benzene exposure level such as enclosing, process change and ventilation system[18]. Furthermore, although the importance of wearing appropriate respirators is mentioned as a way to prevent benzene exposure[19, 20], all employees surveyed in this study are working without wearing respirators, which requires health management.

In order to reduce exposure to benzene, the proper training on the dangers of benzene, etc. should be conducted

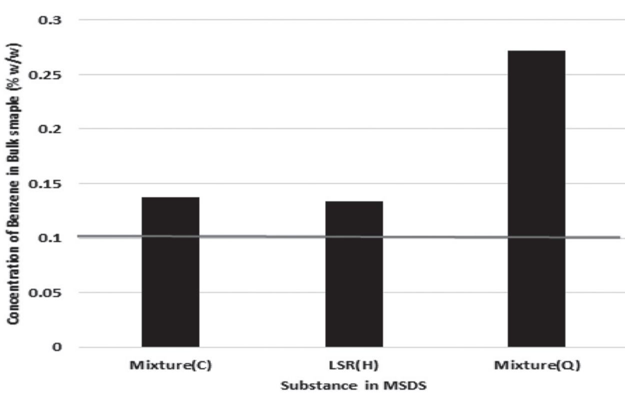

Fig.2. Substances with a benzene content exceeding 0.1% benzene.
LSR: Light Straight Run Naptha; MSDS: Material Safety Data Sheet.

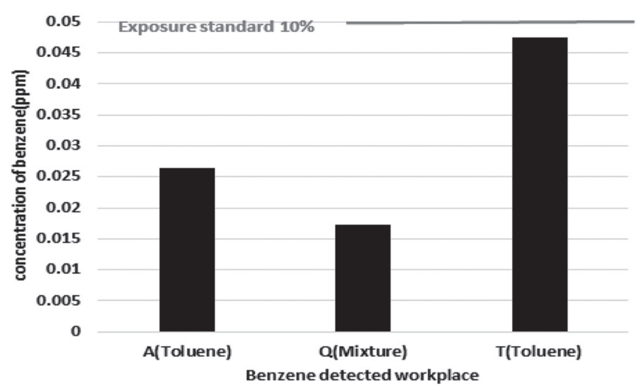

Fig.3. Concentration of benzene in local samples.

Table 7. Benzene risk assessment by cleaning agents in printing businesses where benzene is detected in the air

Area	Business No.	Reflection of work environment measurement results			Reflect physical properties of benzene		
		Exposure	Hazard	Risk	Exposure	Hazard	Risk
Metropolitan area	A	1 (5.28%)	4	**4**	2	4	**8**
	Q	1 (3.46)	4	**4**	2	4	**8**
	T	1 (9.48%)	4	**4**	2	4	**8**

Metropolitan area: Seoul city, Incheon city and Gyeonggi-do.
( ): Exposure level/Exposure Criteria × 100.

Table 8. Volatile rating

Process temperature	3 (High)	2 (Medium)	1 (Low)
If the process temperature is room temperature (20°C)	Boiling point <50°C	50°C≤ Boiling point ≤150°C	150°C< Boiling point
If the process temperature is not room temperature (X°C)	Boiling point <(2x+10)°C	(2x+10)°C≤ Boiling point ≤(5x+50)°C	(5x+50)°C≤ Boiling point

periodically and consideration should be given to changing the cleaning agent to another product. In addition, if possible, processes and facilities that use cleaning agents should be isolated and sealed and proper work clothes and gloves should be recommended since benzene causes skin irritation.

There is a limit to represent the worst case of printing businesses with the highest amount of cleaning agents because only 25 sites out of total 17,622 printing businesses in South Korea are randomly selected and number of insufficient measurements and short survey period of 3 months are allowed due to COVID-19 quarantine. In addition, since air samples were evaluated only by area sampling method, personal sample measurement is required in the future for a more practical exposure assessment. Furthermore, an additional evaluation of the period with the highest workload is required since the workload in the printing industry changes more frequently than in the manufacturing industry. For representing the overall status of the printing industry of South Korea, it is necessary to assess workplaces in other regions such as Busan and Daejeon because this study was conducted only at workplaces in the metropolitan area.

According to previous studies[21, 22], since the distribution or exposure of chemicals, etc. varies by season, additional studies considering particular seasons are needed Finally, four cleaning agents including n-hexane were selected in the research design stage, but there were no workplaces using n-hexane in the actual workplace. In the case of n-hexane, since it is a substance that has been found to be toxic through animal experiments[23, 24], it is considered that additional exposure assessment at workplaces using n-hexane-based petroleum-based cleaning agents is necessary in the future.

Conclusion

All 25 cleaning agents surveyed in this study contained benzene, and three of them contained 0.1% or more. Considering that more than 0.1% benzene is detected in petroleum-based cleaner products that are not obliged to be labeled on MSDS if the component content is less than 0.1%, it is suggested that all petroleum-based cleaners should be able to label benzene on MSDS through accurate sample analysis. The benzene was not detected in the air at work sites where a relatively high concentration of benzene was detected in the bulk sample whereas the benzene was detected in the air in a workplace where benzene was detected at a relatively low concentration in the bulk sample. Based on these results, it is considered that in addition to the contents of the chemicals, the methods used in actual work, work environment management and protective equipment are important for pertinently reducing air exposure level of benzene. Regardless of the level of benzene exposure, the risk assessment results showed that improvement and management were needed in grades 4 to 8. In particular, in the case of printing businesses in South Korea, small businesses account for the majority, so it is necessary to prepare health management measures in various fields such as respiratory protection and local ventilation system.

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