보건학석사 학위논문

Carcinogens in petroleum-derived products: focusing on benzene and ethylbenzene

석유계 화학물질 함유제품 중 발암성분 포함에 관한 연구: 벤젠과 에틸벤젠을 중심으로

2020 년 8 월

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Abstract

Carcinogens in petroleum-derived products: focusing on benzene and ethylbenzene

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Background Petroleum-derived products (PDPs) are widely used in the workplace. PDPs are known to contain benzene and ethylbenzene, which were categorized as Group 1 and Group 2B, respectively, by the International Agency for Research on Cancer. Some workplace processes proceed at a high temperature. For example, manufacturing and automobile processes occur at temperatures ranging from 120°C to 180°C. In this context, the goals of our study were to 1) qualitatively screen carcinogens in PDPs and quantitatively measure benzene and ethylbenzene and 2) evaluate increases in number and concentrations of carcinogens with increases in temperature.

Methods 30 PDPs were selected using the Chemical Abstracts Service number of high-use chemicals. They were categorized into four groups: Viscous Liquid of Lubricant (VL), Aerosol of Lubricant (AL), Semisolid of Grease (SG), and Aerosol of Remover (AR). Analysis was conducted to evaluate carcinogens in the bulk sample, and headspace analysis was performed to elucidate the volatile carcinogens with rising temperature. To screen carcinogens and to quantify target compounds, qualitative and quantitative analyses were performed using gas chromatography (GC, 7890A, Agilent Technology, USA) -mass spectrometry (MS, 5975C Series, Agilent Technology, USA) with benzene and ethylbenzene being the target chemicals for quantitative analysis.

Results As temperature increased, the number of carcinogens increased. One chemical (Carcinogen 1A) was identified in each of VL and AR, two chemicals (Carcinogen 1B) were detected in SG, and three chemicals (Carcinogen 1B) were identified in AL at 180℃. Benzene was detected in 13 products (43.33%) and ethylbenzene was detected in 29 products (96.67%) among the 30 PDPs. Benzene concentrations in some PDPs were increased as the temperature increased compared to the analysis of the bulk samples (20% (2/10) in VL, 30% (3/10) in AL, and 50% (2/4) in AR). Ethylbenzene concentrations in some PDPs were increased as temperature increased compared to the analysis of the bulk samples (80% (8/10) in VL, 60% (6/10) in AL, and 16.67% (1/6) in SG, and 50% (2/4) in AR).

Conclusions Benzene and ethylbenzene are required to be removed from PDPs to the extent possible. If they are difficult to eliminate, we suggest that their presence is stated on the Material Safety Data Sheets to inform workers. The concentration of benzene and ethylbenzene in VL was the highest as temperature increased within the four groups. When the temperatures are high, the use of VL of PDPs should be avoided to minimize exposure to carcinogens. If these products are used in confined workplaces, it is necessary to allow sufficient ventilation and to inform workers of chemical hazards before entering the workplace.

Keywords: Petroleum-derived products, Carcinogens, Benzene, Ethylbenzene, GC-MS, Headspace analysis

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Contents

List of Tables

List of Figures

1. Introduction

Petroleum-derived products (PDPs) exist all around us in our daily lives and are used worldwide. In total, 354,209 tons of PDPs were supplied in the United States in 2019 (US EIA, 2019). In Korea, PDPs are widely used in the workplace as a variety of products. Many industrial products related to the Material Safety Data Sheets (MSDSs) are managed by various platforms, such as Toxfree (https://toxfree.kr/). Toxfree has product information that is used at workplaces and lists the components of products. According to the Toxfree database, 29% of products (4,421 of 15,301) contain petroleum substances. However, when classified as chemicals, only 3% (123 of 3,780) were classified as petroleum chemicals (Yoon et al., 2019).

Many epidemiological studies have reported that petroleum workers who made PDPs were associated with elevated rates of cancer than were non-exposed workers (Sathiakumar et al., 1995; Kirkeleit et al., 2007; Heibati et al., 2017). These PDPs are known to contain benzene and ethylbenzene. The International Agency for Research on Cancer (IARC) categorizes benzene as Group 1 ("Carcinogenic to humans"), ethylbenzene as Group 2B ("Possibly carcinogenic to humans") (IARC, 2020).

Numerous studies have focused on the benzene concentrations in PDPs. Cleaning products have been shown to contain 1,700–15,000 ppm (Kwak., 2014), aerosol cans of brake cleaner 1–930 ppm (Fries et al., 2018), and lubricants 11,000 ppm (Choi et al., 2019). Benzene and ethylbenzene are among the primary volatile organic compounds (VOCs). It is generally known that VOCs increase as temperature rises. As the temperature increased, VOC concentrations in commercial fuel oil samples increased (Anyakudo et al., 2018), and VOC concentrations around a petrochemical complex also increased (Cetin et al., 2003). Some workplace processes are performed at high temperatures. For example, the automotive painting process is operated from 125°C to 160°C (Akafuah et al., 2016) and the furnace process in a continuous annealing line is conducted at approximately 800°C in steel mills (Ginzburg VB and Ballars R, 2000).

Therefore, it is necessary to study carcinogens in PDPs at high temperatures. Numerous analyses of the benzene content in PDPs have been conducted. However, there is still considerable uncertainty regarding the compositions or concentrations of benzene and ethylbenzene based on the temperature of the manufacturing process.

In this context, the goals of the study were to 1) qualitatively screen carcinogens in PDPs and quantitatively measure benzene and ethylbenzene and 2) evaluate increases in number and concentrations of carcinogens with increases in temperature.

2. Materials and Methods

2.1. The outline of this study

The methodological outline of this study is shown in **Figure 1**. 84 PDPs were collected, which were readily available on the market and commonly used in the workplace. Tens of thousands of chemicals are used in the workplace; however, "chemicals to be managed under the Law," consist of only 171 kinds and 1,197 hazardous substances. Therefore, Yoon et al. (2018) suggested detailed guidelines to classify all chemicals by health hazards. As per the guide, 16 petroleum chemicals were designated as Special Management Materials among the chemicals in the Korea Survey of Distribution of Chemicals (KSDC) database. These chemicals were classified as Carcinogen 1A ("Known to have carcinogenic potential humans") or Carcinogen 1B ("Presumed to have carcinogenic potential for humans") by the Globally Harmonized System of classification and labeling of chemicals (UNECE, 2019). Among the 16 chemicals, "Distillates (petroleum), hydrotreated-heavy-paraffinic (CAS No: 64742-54-7)" and "Distillates (petroleum), hydrotreated-light-paraffinic (CAS No: 64742-55-8)" are the most frequently used in the KSDC database (Yoon et al., 2019). Using mainly these two types of chemicals, 30 PDPs were filtered from the collected PDPs.

The 30 PDPs were categorized into four groups. S-01 to S-10 belonged to the Viscous Liquid of Lubricant (VL) group, S-11 to S-20 belonged to Aerosol of Lubricant (AL) group, S-21 to S-26 belonged to the Semisolid of Grease (SG) group, and S-27 to S-30 belonged to the Aerosol of Remover (AR) group (**Table 1**). Further details regarding composition and product use in PDPs were provided in the supplementary material (**Table A-1**). The 30 PDPs were analyzed qualitatively and quantitatively. Qualitative analysis was conducted to identify other carcinogens and quantitative analysis of benzene and ethylbenzene was performed. The first step was the qualitative and quantitative analysis of the bulk samples. The second step was the qualitative and quantitative analysis of PDPs according to temperature conditions. Temperature conditions were established from room temperature to high temperature to identify volatile substances in the PDPs. The highest temperature condition was set at 180°C, which was based on automotive processes.

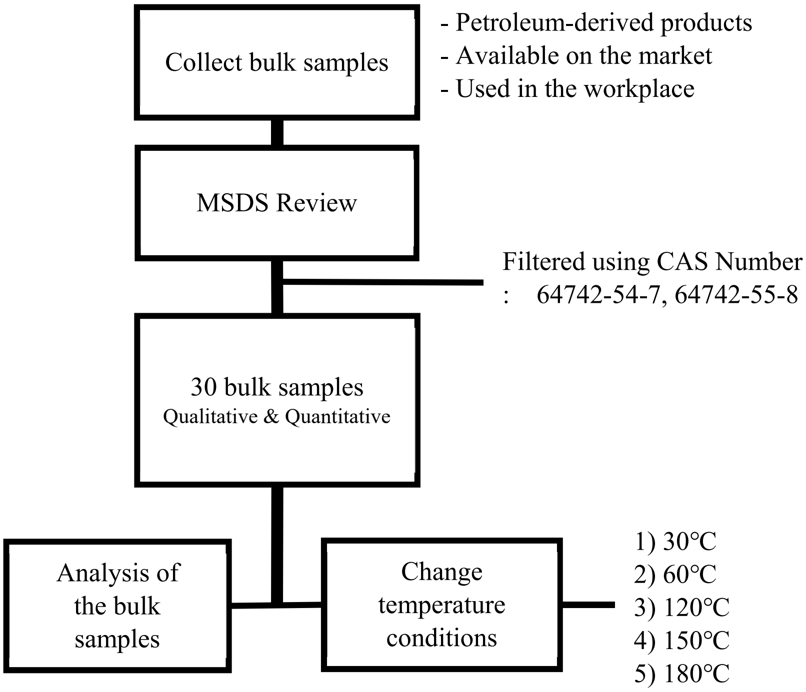


Figure 1. The outline of this study

Abbreviations**:** CAS, Chemical Abstracts Service.

Note: CAS Numbers were the most frequently used chemicals in Korea Survey of Distribution of Chemicals database among the 16 petroleum chemicals that have designated as Special Management Materials through guidelines (Yoon et al., 2019).

Temperature conditions were established from room temperature to high temperature to find volatile substances in PDPs. The highest temperature condition was set at 180℃ referred to automotive processes.

Table 1. The basic characteristic of information about 30 petroleum-derived products.

Product use (State of matter)	N	Major petroleum chemical composition of PDPs		EU CLP	K MOEL
		Chemical name	CAS No		
Lubricant (Viscous Liquid)	10	Distillates (petroleum), hydrotreated heavy paraffinic	64742-54-7	Carc. 1B	Carc. 1B
		Distillates (petroleum), hydrotreated light paraffinic	64742-55-8	Carc. 1B	Carc. 1B
Lubricant (Aerosol)	10	Distillates (petroleum), hydrotreated heavy paraffinic	64742-54-7	Carc. 1B	Carc. 1B
		Distillates(petroleum), hydrotreated light	64742-47-8	-	-
Grease (Semisolid)	6	Distillates (petroleum), hydrotreated heavy paraffinic	64742-54-7	Carc. 1B	Carc. 1B
		Residual oils (petroleum), hydrotreated	64742-57-0	Carc. 1B	Carc. 1B
Remover (Aerosol)	4	Ligroine; petrodeum ether	8032-32-4	Carc. 1B	Carc. 1B
		Distillates(petroleum), hydrotreated light	64742-47-8	-	-

***Abbreviations*:** PDPs, Petroleum derived products; N, Numbers of PDPs; CAS, Chemical Abstracts Service; EU CLP, European Union Regulation on Classification, Labelling, and Packaging; KMOEL, Ministry of Employment and Labor in Korea.

Note: 30 PDPs were categorized into four groups. Representative chemicals among the chemicals which were mostly contained in each group were presented.

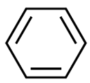
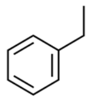
EU CLP Carcinogen classifications − Carcinogen 1A: Known to have carcinogenic potential humans, classification is largely based on animal evidence, Carcinogen 1B: Presumed to have carcinogenic potential for humans, classification is largely based on animal evidence, Carcinogen 2: Suspected human carcinogens.
KMOEL Carcinogen classifications − Carcinogen 1A: Known to have carcinogenic potential humans, classification is largely based on animal evidence, Carcinogen 1B: Presumed to have carcinogenic potential for humans, classification is largely based on animal evidence, Carcinogen 2: Suspected human carcinogens.

2.2. Chemicals and reagents

As target quantitation compounds, benzene (Purity: ≥99.9%) was obtained from Sigma-Aldrich (USA), and ethylbenzene (Purity: ≥99.0%) was obtained from Fluka (Switzerland). Their physicochemical properties, target, and qualifier ion (m/z) were presented in **Table 2**.

HPLC grade of methylene chloride (Purity: ≥99.8%) and methanol (Purity: ≥99.8%) was obtained from J.T. Baker (USA). Methylene chloride was used as a solvent for analyzing bulk samples, and methanol was used as a solvent of stock solution for evaluating volatile carcinogens in PDPs.

Table 2. A list of target quantitation compounds and their physicochemical information.

Parameter	Benzene	Ethylbenzene
CAS No.	71-43-2	100-41-4
Chemical formula	C_6H_6	C_8H_{10}
Boiling point (°C)	80	136
Vapor Prssure (mmHg)	94.8	9.6
Quantitation ion	78	91
Confirmation ion	51	106
Chemical structure		

2.3. Sample preparation and analysis

2.3.1. Identification carcinogens in PDPs

To prevent the loss of benzene and ethylbenzene from the PDPs owing to evaporation, all items were refrigerated at 4°C. VOCs contained in PDPs were analyzed after dilution with 1/100 of methylene chloride. Diluted samples were mixed vigorously with the aid of a vortex for a few minutes to ensure proper homogenization of the sample and were sonicated for 30 minutes at room temperature before analysis. A stock solution of benzene and ethylbenzene was prepared using methylene chloride as a solvent. During sample analysis, lab blanks were included in the sequence every five samples to assess instrument drift and performance.

Gas chromatography (GC, 7890A, Agilent Technology, USA) -mass spectrometer (MS, 5975C Series, Agilent Technology, USA) was performed for analysis of bulk samples. A volume of 1 μl extracted sample was injected on the split mode (3:1) by autosampler (Combi PAL, CTC Analytics, Switzerland). DB-624 UI column which has 30 m in length, 0.25 mm in inner diameter, 1.40 μm in film thickness was used for analysis (122-1334 UI, Agilent Technology, USA). The target and qualifier ions for the Selected Ion Monitoring analysis were split into two different ion groups based on compound elution order and retention time. The specific GC-MS conditions were shown in **Table 3** (EPA, 2017).

Table 3. The conditions of GC-MS for analysis of bulk samples.

Parameter	Conditions
Instrument	Gas chromatography – Mass spectrometer (7890A -5975C, Agilent Technology, USA)
Injector	Autosampler (PAL COMBI-xt, Switzerland)
Inlet temperature	225℃
Injector volume	1 μl
Split ratio	3:1
Column	DB-624 (30 m x 0.25 mm x 0.25 μm, Agilent, USA)
Carrier Gas	Helium (Purity: ≥99.999%), 1.3 ml/min
Column Temperature	35℃ (hold 3 minutes) → 6 ℃/min, 100℃ → 12 ℃/min, 180℃ → 20 ℃/min, 200℃ (hold 7 minutes)
Transfer line and the Ion source Temperature	230℃
MS Mode	Selected Ion Monitoring / Scan
MS Quad / Source	150℃ / 230℃
Scan range	35 - 225 m/z
Solvent delay	5.00 minutes

2.3.2. Identification volatile carcinogens in PDPs with increasing temperature

The full evaporation technique was employed to identify the volatile components with increases in temperature and to overcome matrix effects (Markelov and Guzowski, 1993). Samples were prepared by weighing 0.1 g sample into 20 ml headspace vial. The vial and its content were sealed with an aluminum-coated polytetrafluoroethylene (PTFE)/silicone septum. A headspace syringe which has volume 2.5 ml, scale 60 mm (MSH 02-00B, Hamilton, Germany) was used for this analysis.

Samples were agitated for 10 min and 500 rpm at 30℃, 60℃, 120℃, 150℃, and 180℃. Standard solutions of benzene and ethylbenzene were prepared using methanol as a solvent. The prepared 10 μl of standard solution was filled into 20 ml headspace vial. Standard solutions were agitated for 10 minutes and 500 rpm at 180℃. After agitation, an injection of 500 μl of the headspace gas was performed into the GC-MS at the rate of 1000 μl/s with headspace syringe heated for 95℃ by autosampler. During sample analysis, lab blanks were included in the sequence every 10 samples to assess instrument drift and performance. The specific headspace GC-MS conditions were shown in **Table 4** (Anyakudo et al., 2018).

Table 4. The conditions of headspace GC-MS.

Parameter	Conditions
Instrument	Gas chromatography – Mass spectrometer (7890A -5975C, Agilent Technology, USA)
Injector	Autosampler (PAL COMBI-xt, Switzerland)
Inlet temperature	250℃
Injector volume	500 μl
Split ratio	30:1
Column	DB-5MS UI (30 m x 0.25 mm x 0.25 μm, Agilent, USA)
Carrier Gas	Helium (Purity: ≥99.999%), 1.0 ml/min
Column Temperature	40℃ (hold 1 min) → 10 ℃/min, 245℃ (hold 2 min)
Transfer line and the ion source Temperature	250℃
MS Mode	Selected Ion Monitoring / Scan
MS Quad / Source	150℃ / 230℃
Scan range	35 - 250 m/z

2.4. Quality control and data analysis

2.4.1. Quality control

Quality control was performed to evaluate the accuracy and precision of the analysis. Relative standard deviations (%RSD) was determined by analyzing the 5 ppm (bulk sample) and 50 ppm (headspace) of the standard solution over five repetitions. We confirmed that the %RSD of benzene and ethylbenzene was within the 20% limit recommended by the US Environmental Protection Agency (EPA, 2017).

The limit of detection (LOD) was three times the standard deviation based on seven replicates of the lowest level of the standard solution (EPA, 2015). The LOD of benzene was 0.62 ppm and that of ethylbenzene was 0.88 ppm for bulk samples. The LOD of benzene was 0.14 ppm and that of ethylbenzene was 0.11 ppm in the headspace analysis (**Table 5**).

Table 5. Results of quality control.

Analysis	Compounds	LOD	Accuracy (%)	RSD (%)	r^2
Bulk sample	Benzene	0.62	101.15	2.55	1.0000
	Ethylbenzene	0.88	101.97	2.43	0.9999
Headspace	Benzene	0.14	99.66	5.05	1.0000
	Ethylbenzene	0.11	99.77	6.70	1.0000

***Abbreviations*:** LOD, The limit of detection; RSD, Relative Standard Deviation; r^2, The correlation coefficient.

2.4.2. Data analysis

R software (version 3.5.3, R Foundation for Statistical Computing, Austria) was used to perform the statistical analyses. A database containing concentrations of benzene and ethylbenzene based on temperature conditions was transformed using a logarithmic function. Not detected (ND) values were set to 1/2 that of the LOD for data analysis (Hornung and Reed, 1990). An Analysis of variance (ANOVA) was used to compare the concentrations of benzene and ethylbenzene based on temperature among the product state of the material (liquid, aerosol, and semisolid). This was followed by Tukey's HSD post hoc test. The level of significance was set to be at $p < 0.05$.

The MS Workstation data files were translated into MassHunter Data format using GC-MS translator (Agilent Technology, USA) to acquire more accurate qualitative analysis. Because of many overlapping chromatograms of total ion chromatogram (TIC) in the analysis results, every TICs was extracted by the Unknown Analysis software (version B.09.00 / Build 9.0.647.0, Agilent Technology, USA) as a deconvoluted ion chromatogram (DIC), which is a structure used to potential match the mass spectrum provided by the W11N17 (Wiley11-Nist17, Wiley, Hoboken, USA). All DICs were used for the identification of unknown compounds detected in the analysis results based on the matching rate (> 80%) of mass spectra archived in the W11N17 library.

The following databases were used to identify carcinogens in PDPs. (1) Tox-Info database which has IARC and National Toxicology Program (NTP) (NIFDS, 2020), (2) European Union Regulation on Classification, Labelling, and Packaging

(EU CLP) database (Annex VI ATP 13) (ECHA, 2020), and (3) Korea Occupational Safety and Health Agency (KOSHA, 2020).

3. Results

3.1. Qualitative analysis in PDPs

Qualitative analysis was also conducted in PDPs. Although more than several hundred mass spectra were generated from the DIC in each temperature condition, approximately 90 compounds per temperature condition were well-matched (>80%) with the W11N17 library.

The higher the temperature, the greater the number of carcinogens. Carcinogen 1A which was classified by EU CLP regulations (EP & EC, 2008) was not identified at 30℃ but was detected from 60℃ to 180℃. At 180℃, carcinogens were most frequently detected, and the ratio of carcinogens 1A and 1B was 66.67% (6 of 9) (**Figure 2**). One chemical classified as carcinogen 1A was identified in each of VL and AR, two chemicals classified as carcinogen 1B were detected in SG, and three chemicals classified as carcinogen 1B were found in AL at 180℃ (**Table 6**). Qualitative analysis results by each PDP were provided in the supplementary material (**Table A-2**).

Table 6. Results of qualitative analysis by groups according to temperature conditions. Petroleum-derived products were categorized into four groups.

Temp (℃)	Lubricant (Viscous Liquid)		Lubricant (Aerosol)		Grease (Semisolid)		Remover (Aerosol)		IARC	NTP	EU CLP	KMOEL
	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate				
Bulk	Ethylbenzene (100-41-4)	1/10	Ethylbenzene (100-41-4)	2/10					Group 2B	-	-	Carc. 2
	Benzene,(1-methylethyl)- (98-82-8)	2/10							Group 2B	-	-	Carc. 2
							1,3-Butadiene (106-99-0)	1/10	Group 1	K	Carc. 1A	Carc. 1A
30	Ethylbenzene (100-41-4)	3/10	Ethylbenzene (100-41-4)	1/10					Group 2B	-	-	Carc. 2
			Propane, 1-bromo- (106-94-5)	1/10					-	-	-	Carc. 2
					Ethene, 1,1-dichloro- (75-35-4)	1/6	Ethene, 1,1-dichloro- (75-35-4)	1/4	Group 3	-	Carc. 2	Carc. 2
					Methylene chloride (75-09-2)	3/6	Methylene chloride (75-09-2)	1/4	Group 2B	R	Carc. 2	Carc. 2
60	Ethylbenzene (100-41-4)	2/10	Ethylbenzene (100-41-4)	1/10					Group 2B	-	-	Carc. 2
	Benzene (71-43-2)	1/10							Group 1	K	Carc. 1A	Carc. 1A
	Benzene,(1-methylethyl)- (98-82-8)	2/10							Group 2B	-	-	Carc. 2
			Styrene (100-42-5)	1/10					Group 2B	R	-	Carc. 2
			Propane, 1-bromo- (106-94-5)	1/10					-	-	-	Carc. 2

Temp (℃)	Lubricant (Viscous Liquid)		Lubricant (Aerosol)		Grease (Semisolid)		Remover (Aerosol)		IARC	NTP	EU CLP	KMOEL
	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate				
60					Methylene chloride (75-09-2)	3/6	Methylene chloride (75-09-2)	1/4	Group 2B	R	Carc. 2	Carc. 2
					Ethene, 1,1-dichloro- (75-35-4)	1/6	Ethene, 1,1-dichloro- (75-35-4)	1/4	Group 3	-	Carc. 2	Carc. 2
120	Ethylbenzene (100-41-4)	3/10	Ethylbenzene (100-41-4)	1/10					Group 2B	-	-	Carc. 2
	Propane, 2-nitro- (79-46-90)	1/10	Propane, 2-nitro- (79-46-9)	1/10			Propane, 2-nitro- (79-46-9)	1/4	Group 2B	R	Carc. 1B	Carc. 1B
	Benzene,(1-methylethyl)- (98-82-8)	2/10							Group 2B	-	-	Carc. 2
	Benzene (71-43-2)	2/10							Group 1	K	Carc. 1A	Carc. 1A
			Cyclohexanone (108-94-1)	1/10					Group 3	-	-	Carc. 2
					Ethene, 1,1-dichloro- (75-35-4)	1/6	Ethene, 1,1-dichloro- (75-35-4)	1/4	Group 3	-	Carc. 2	Carc. 2
					Methane, dichloro- (75-09-2)	3/6	Methane, dichloro- (75-09-2)	1/4	Group 2B	R	Carc. 2	Carc. 2
					Oxirane, methyl- (75-56-9)	3/6			Group 2B	R	Carc. 1B	Carc. 1B
150	Ethylbenzene (100-41-4)	3/10	Ethylbenzene (100-41-4)	1/10					Group 2B	-	-	Carc. 2
	Propane, 2-nitro- (79-46-9)	1/10							Group 2B	R	Carc. 1B	Carc. 1B

Temp (℃)	Lubricant (Viscous Liquid)		Lubricant (Aerosol)		Grease (Semisolid)		Remover (Aerosol)		IARC	NTP	EU CLP	KMOEL
	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate				
150	Benzene (71-43-2)	2/10							Group 1	K	Carc. 1A	Carc. 1A
	Benzene,(1-methylethyl)- (98-82-8)	2/10							Group 2B	-	-	Carc. 2
			1,3-Butadiene (106-99-0)	1/10					Group 1	K	Carc. 1A	Carc. 1A
			Methyl Isobutyl Ketone (108-10-1)	1/10					Group 2B	-	-	Carc. 2
			Cyclohexanone (108-94-1)	1/10					Group 3	-	-	Carc. 2
			(CH3)2CHCH2ONO (542-56-3)	1/10					-	-	Carc. 1B	Carc. 1B
			Propane, 1-bromo- (106-94-5)	1/10					-	-	-	Carc. 2
					Ethene, 1,1-dichloro- (75-35-4)	1/6	Ethene, 1,1-dichloro- (75-35-4)	1/4	Group 3	-	Carc. 2	Carc. 2
					Oxirane, methyl- (75-56-9)	2/6			Group 2B	R	Carc. 1B	Carc. 1B
					Methylene chloride (75-09-2)	3/6	Methylene chloride (75-09-2)	1/4	Group 2B	R	Carc. 2	Carc. 2
							Pyridine (110-86-1)	1/4	Group 3	-	-	Carc. 2
							Trichloromethane (67-66-3)	1/4	Group 2B	R	Carc. 2	Carc. 2

Temp (℃)	**Lubricant (Viscous Liquid)**		**Lubricant (Aerosol)**		**Grease (Semisolid)**		**Remover (Aerosol)**		IARC	NTP	EU CLP	KMOEL
	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate				
180	Ethylbenzene (100-41-4)	3/10	Ethylbenzene (100-41-4)	1/10					Group 2B	-	-	Carc. 2
	Aziridine (151-56-4)	1/10							Group 2B	-	Carc. 1B	Carc. 1B
	Benzene,(1-methylethyl)- (98-82-8)	3/10							Group 2B	-	-	Carc. 2
	Benzene (71-43-2)	2/10							Group 1	K	Carc. 1A	Carc. 1A
			Propane, 1-bromo- (106-94-5)	1/10					-	-	-	Carc. 2
			Methyl Isobutyl Ketone (108-10-1)	1/10	Methyl Isobutyl Ketone (108-10-1)	2/6			Group 2B	-	-	Carc. 2
			2,4-Hexadienal, (E,E)- (142-83-6)	1/10					Group 2B	-	-	Carc. 2
			Hydrazine, 1,2-dimethyl- (540-73-8)	3/10	Hydrazine, 1,2-dimethyl- (540-73-8)	1/6			Group 2A	-	Carc. 1B	Carc. 1B
			Oxirane, methyl- (75-56-9)	1/10	Oxirane, methyl- (75-56-9)	3/6			Group 2B	R	Carc. 1B	Carc. 1B
			Propane, 2-nitro- (79-46-9)	1/10			Propane, 2-nitro- (79-46-9)	1/4	Group 2B	R	Carc. 1B	Carc. 1B
					Ethene, fluoro- (75-02-5)	2/6			Group 2A	R	-	Carc. 1B
					Methylene chloride (75-09-2)	3/6	Methylene chloride (75-09-2)	1/4	Group 2B	R	Carc. 2	Carc. 2

Temp (℃)	Lubricant (Viscous Liquid)		Lubricant (Aerosol)		Grease (Semisolid)		Remover (Aerosol)		IARC	NTP	EU CLP	KMOEL
	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate	Compound (CAS No.)	Detection rate				
180							1,3-Butadiene (106-99-0)	1/4	Group 1	K	Carc. 1A	Carc. 1A
							Trichloromethane (67-66-3)	1/4	Group 2B	R	Carc. 2	Carc. 2
							Ethene, 1,1-dichloro- (75-35-4)	1/4	Group 3	-	Carc. 2	Carc. 2

Abbreviations**:** CAS, Chemical Abstracts Service; IARC, International Agency for Research on Cancer; NTP, National Toxicology Program; EU CLP, European Union Regulation on Classification, Labelling, and Packaging; KMOEL, Ministry of Employment and Labor in Korea.

Note**:** The carcinogen information and classification were based on criteria suggested by each agency.

IARC Carcinogen classifications − Group 1: Carcinogenic to humans, Group 2A: Probably carcinogenic to humans, Group2B: Possibly carcinogenic to humans, Group 3: Not classifiable as to its carcinogenicity to humans, Group 4: Probably not carcinogenic to humans.

NTP Carcinogen classifications − K: Know to be a human carcinogens, R: Reasonable anticipated to be a human carcinogens.

EU CLP Carcinogen classifications − Carcinogen 1A: Known to have carcinogenic potential humans, classification is largely based on animal evidence, Carcinogen 1B: Presumed to have carcinogenic potential for humans, classification is largely based on animal evidence, Carcinogen 2: Suspected human carcinogens.

KMOEL Carcinogen classifications − Carcinogen 1A: Known to have carcinogenic potential humans, classification is largely based on animal evidence, Carcinogen 1B: Presumed to have carcinogenic potential for humans, classification is largely based on animal evidence, Carcinogen 2: Suspected human carcinogens.

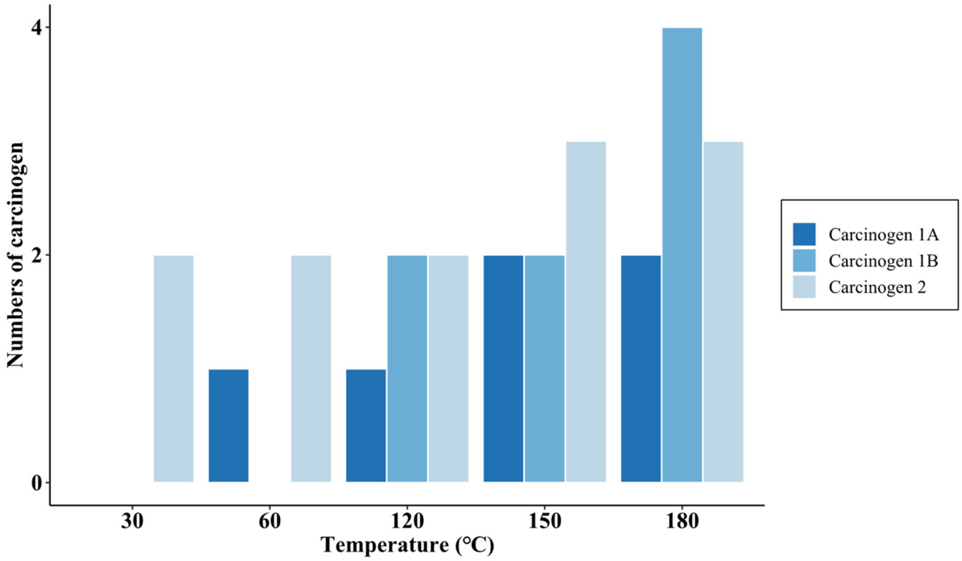


Figure 2. The number of carcinogens increased as temperature rose

Abbreviations**:** EU CLP, European Union Regulation on Classification, Labelling, and Packaging.

Note**:** The carcinogenic information and classification were based on criteria provided by EU CLP.

EU CLP Carcinogen classifications − Carcinogen 1A: Known to have carcinogenic potential humans, classification is largely based on animal evidence, Carcinogen 1B: Presumed to have carcinogenic potential for humans, classification is largely based on animal evidence, Carcinogen 2: Suspected human carcinogens.

3.2. Quantitative analysis of benzene and ethylbenzene in PDPs

3.2.1. Concentrations of benzene and ethylbenzene in PDPs

Benzene was detected in 13 of the 30 (43.33%) PDPs. The highest benzene concentrations were 11.82 ppm in lubricants for a 2 stroke motorcycle engine oil (S-08), followed by 6.09 ppm in a sticker stain remover (S-30) and 4.78 ppm in lubricants for a 2 stroke motorcycle engine oil (S-03). Ethylbenzene was detected in 29 of the 30 (96.67%) PDPs. The highest ethylbenzene concentrations were 364.60 ppm in lubricants for a 2 stroke motorcycle engine oil (S-08) followed by 143.96 ppm in lubricants for a 2 stroke motorcycle engine oil (S-03). Further details about quantitative analysis results by each PDP were provided in the supplementary material (**Table A-1**).

In the four groups, benzene was most often detected in AL (70%, 7 of 10) followed by AR (50%, 2 of 4). VL (ND–11.82 ppm) had the highest average concentrations, followed by AR (ND–6.09 ppm), AL (ND–4.07 ppm), and SG (ND–2.37 ppm). Ethylbenzene was detected in all samples except for one sample in AL (S-19). VL (2.99–364.60 ppm) had the highest average concentrations, followed by AL (ND–135.37 ppm), AR (3.81–18.30 ppm), and SG (ND–4.42 ppm). The average concentrations of benzene and ethylbenzene were the highest in VL and lowest in SG (**Table 7**).

Table 7. Benzene and ethylbenzene concentrations in petroleum-derived products by groups. Petroleum-derived products were categorized into four groups.

Product use (State of matter)	**Benzene**			**Ethylbenzene**		
	Detected in products	Concentrations (ppm, v/v)		Detected in products	Concentrations (ppm, v/v)	
		AM±SD	Range		AM±SD	Range
Lubricant (Viscous Liquid)	3/10 (30%)	6.22±4.10	ND – 11.82	10/10 (100%)	54.87±111.27	2.99 – 364.60
Lubricant (Aerosol)	7/10 (70%)	2.69±0.76	ND – 4.07	9/10 (90%)	23.96±39.85	ND – 135.37
Grease (Semisolid)	2/6 (33.33%)	2.21±0.16	ND – 2.37	6/6 (100%)	4.12±0.23	3.77 – 4.42
Remover (Aerosol)	2/4 (50%)	4.30±1.79	ND – 6.09	4/4 (100%)	7.79±6.08	3.81 – 18.30

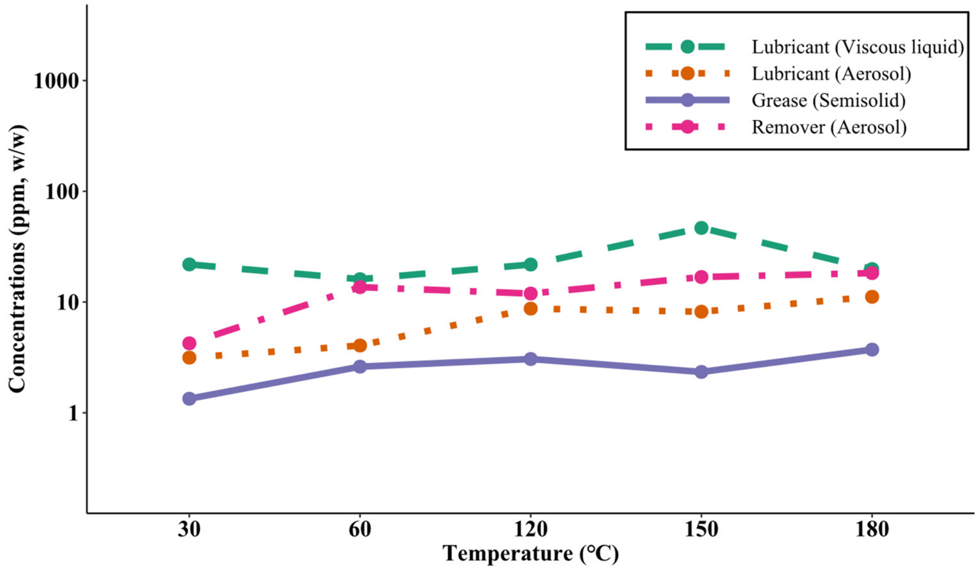
***Abbreviations*:** v/v, Volumetric ratio; AM±SD, Arithmetic Mean±Standard Deviation; Min, Minimum; Med, Median; Max, Maximum.

***Note*:** The limit of detection of the benzene and ethylbenzene as follows: benzene, 0.62 ppm; ethylbenzene, 0.88 ppm.

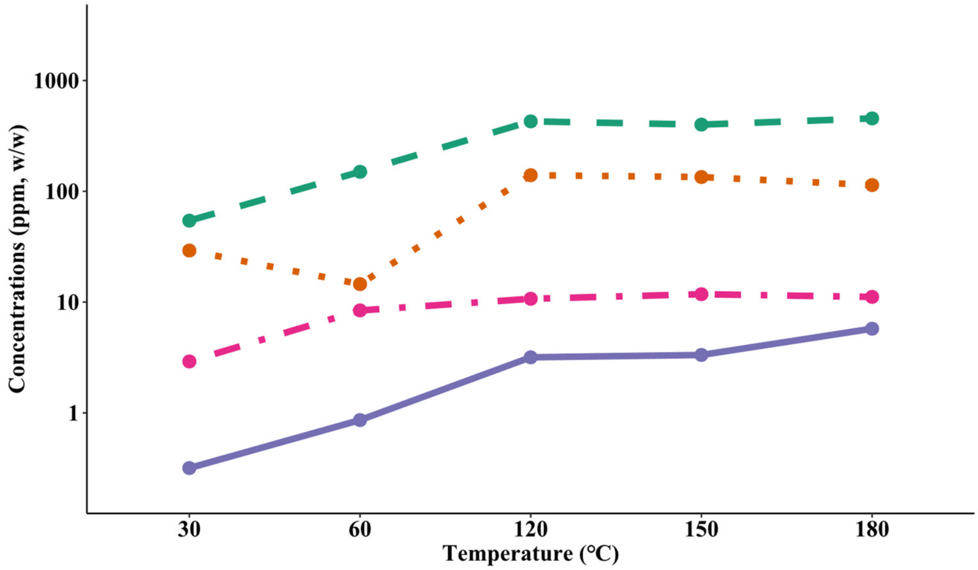
3.2.2. Concentrations of benzene and ethylbenzene in PDPs as a function of temperature

Benzene concentrations in some PDPs increased with increasing temperature compared to that of the bulk sample, specifically S-03 and S-08 in VL, S-12, S-14, and S-15 in AL, and S-26 and S-30 in AR. Benzene was ND in AL for S-13, S-17, and S-19 when analyzing bulk samples; however, benzene concentrations increased with increasing temperature (**Table A-1, Table A-3**). Benzene concentrations in VL, AL, and AR increased as temperature increased compared to that of the bulk sample. SG groups increased at 60°C but not 30°C compared to that of the bulk sample. The highest concentrations occurred at 150°C, except for that of the SG group (**Table 7, Figure 3-(a)**).

Ethylbenzene concentrations in some PDPs increased with increasing temperature among the PDPs in which ethylbenzene was detected by analyzing the bulk sample for all PDPs, except S-01 and S-06 in VL, S-16, S-17, S-19, and S-20 in AL, S-24 in SG, and S-26 and S-30 in AR (**Table A-1, Table A-3**). Ethylbenzene concentrations in VL, AR, and SG increased from 60°C to 180°C compared to that of the bulk sample. AL groups increased at all temperatures, except 60°C, compared to that of the bulk sample (**Table 7, Figure 3-(b)**).



(a) Benzene

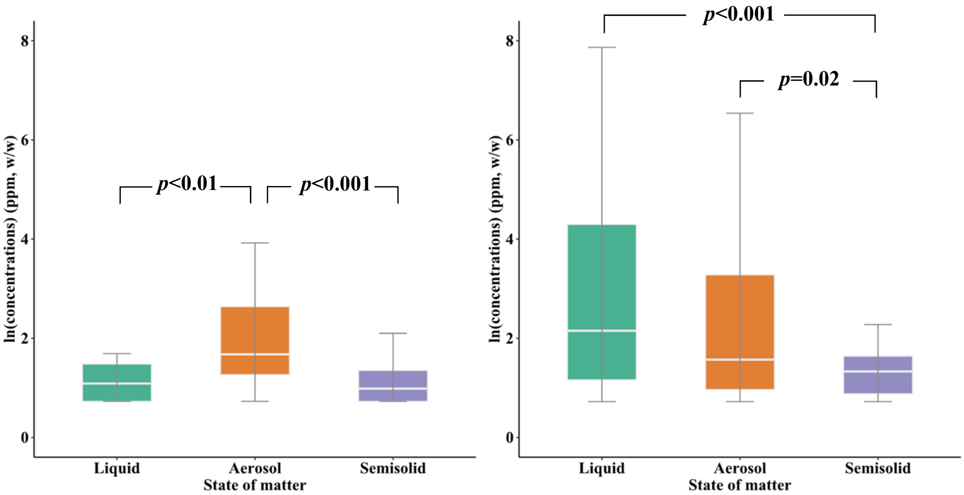


(b) Ethylbenzene

Figure 3. Concentrations of benzene and ethylbenzene in petroleum-derived products according to temperature conditions. Petroleum-derived products were categorized into four groups. (a) benzene concentrations by groups (b) ethylbenzene concentrations by groups. The y-axis is a log scale.

***Abbreviations*:** w/w, weight ratio.
***Note*:** The limit of detection of the benzene and ethylbenzene as follows: benzene, 0.14 ppm; ethylbenzene, 0.11 ppm.

An ANOVA revealed a significant difference among the state of matter of the product in the concentration of benzene and ethylbenzene (p<0.001). Significant differences were observed between aerosols and liquids (p<0.01) and aerosols and semisolids (p<0.001) in benzene concentrations (**Figure 4-(a)**). Regarding ethylbenzene concentrations, significant differences were observed between aerosols and semisolids (p=0.02) and liquids and semisolids (p<0.001) (**Figure 4-(b)**).



(a) Benzene (b) Ethylbenzene

Figure 4. Box plots of benzene and ethylbenzene concentrations according to temperature conditions by state of matters of the products. (a) significance was observed between aerosol and liquid (p<0.01) and aerosol and semisolid (p<0.001), and (b) significance was observed between aerosol and semisolid (p=0.02) liquid and semisolid (p<0.001).

Abbreviations**:** w/w, weight ratio.
Note**:** Values shown are median (line within box), 25th and 75th percentiles (bottom and top of box, respectively), minimum (lower bars on whiskers), maximum (upper bars on whisker), and outliers (dots).

4. Discussion

Our main goals were to screen carcinogens, identify benzene and ethylbenzene quantitatively in PDPs and evaluate increases in the number and concentrations of carcinogens with increasing temperature. Qualitative analysis revealed that the number of carcinogens increased as temperature rose. There was only one carcinogen classified by the EU CLP in the 30 PDPs detected by analyzing the bulk sample. However, two carcinogens were identified at 30°C and nine were detected at 180°C, which was the highest temperature in the analysis conditions. The quantitative analysis showed that benzene was detected in 70% of products in AL, 50% in AR, 33.33% in SG, and 30% in VL. Ethylbenzene was identified in all PDPs except one. Benzene and ethylbenzene concentrations rose steadily from 30°C to 120°C in AL and SG.

Conversely, the concentrations of benzene and ethylbenzene in some PDPs decreased or remained constant at 180°C. There are several possible explanations for this result. First, the equilibrium between the sample (condensed) phase and gas phase (headspace) is important in headspace techniques (Kolb and Ettre, 2006). It is believed that thermal equilibrium had not been established between the condensed phase and headspace in the vial at 180°C. Second, the PDP matrix was complex (Mushrush, 1995; Oppenlaender et al., 2007). The adsorption rates of benzene and ethylbenzene may not have been optimized because of other chemicals.

Concentrations of benzene and ethylbenzene were the highest in S-08 followed by S-03. These two products are in the VL group and are used for small engines, such as weed mowers, leaf blowers, and chainsaws. Weed mowers and leaf blowers are hand-held machines. With hand-held machines, the effect on the health of toxic substances in the exhaust is locally amplified by their stationary use very close to the worker (Neri et al., 2016). It should be purified like any other PDPs such that the concentrations of benzene and ethylbenzene remaining as impurities are removed.

As a result of the ANOVA, the aerosol type was significantly different from the liquids and semisolids in terms of benzene and had the highest concentrations. For ethylbenzene, a significant difference occurred between aerosols and semisolids and between liquids and semisolids. Both benzene and ethylbenzene appeared to be at their lowest concentrations in semisolids. The concentrations of benzene and ethylbenzene did not volatilize well.

Several studies have described benzene concentrations in PDPs. The cleaning products contained 1,700–15,000 ppm according to reports published in 2009 and 2010 (Kwak., 2014). The lubricant contained 11,000 ppm, as suggested by a report published in 2013 (Choi et al., 2019). Aerosol cans of the brake cleaner contained 1–930 ppm (Fries et al., 2018). In this study, the average concentration of benzene in PDPs was 6.23 ppm (ND–11.82 ppm).

There are reasons as to why the benzene concentrations in PDPs were lower than those detected in previous studies. First, filtered PDPs were readily available on the market for consumers. Household chemical products undergo a hazard and risk assessment following the Safety of Household Chemical Products and Biocidal Products Act (ME, 2020) before they are sold on the market. Therefore, industrial chemical PDPs that are not managed under this law tend to have higher concentrations of benzene and ethylbenzene. According to a recent study that investigated the health hazards of cleaner agents used in the workplaces, benzene was detected in four of the five cleaner products. The benzene concentrations of the four products were 700, 1,700, 2,100, and 9,300 ppm (Jeong et al., 2018-b). Second, the benzene concentrations in the PDPs were gradually reduced. Exposure criteria have been reduced worldwide with an awareness of benzene risk. Studies have shown that continuous exposure to 1 ppm during working hours increases mortality from leukemia (Crump, 1994; Paxton et al., 1994). The time-weighted average (TWA) of 0.5 ppm exposure showed that the incidence of deaths from leukemia that was not significantly different from that of the non-exposure groups. To prevent the risk of developing leukemia from occupational exposure to benzene, the current guidelines for benzene exposure is threshold limit value (TLV)-TWA 0.5 ppm, TLV-Short Term Exposure Limit (STEL) 2.5 ppm (Paustenbach et al., 1992). In Korea, exposure criteria for benzene were also revised from TLV-TWA 1 ppm and TLV-STEL 5 ppm (MoEL, 2013) to TLV-TWA 0.5 ppm and TLV-STEL 2.5 ppm (MoEL, 2016-a). The concentration of benzene in gasoline has gradually been decreased from 6.0% in 1992 to 0.7% in 2009 after the risk of benzene was recognized (Sheen, 2001; ME, 2012).

Benzene and ethylbenzene were not listed on the 30 MSDSs for the PDPs as ingredients because carcinogens must be specified in the MSDS when they represent 0.1% or higher in the mixture (MOEL, 2016-b). However, because only trace levels of benzenes can cause cancer, many epidemiological studies have suggested maintaining a low exposure standard (ppb level) to prevent diseases caused by occupational exposure to benzene (Alexander and Leonard, 2006; Weisel, 2010; Ciarrocca et al., 2012). Therefore, benzene should be listed as an ingredient on

MSDSs, as suggested by Kopstein, even if the benzene concentrations in the PDPs are much less than 0.1% (Kopstein, 2006).

The number of carcinogens increased as the temperature rose. The workplace temperature varies depending on the work process. Some manufacturing processes are conducted at high temperatures in confined places, such as automotive processes, and workers often enter these spaces for maintenance. Aromatic hydrocarbons, such as benzene, exist in high concentrations at high temperatures because they are relatively very stable compared to aliphatic hydrocarbons (Kilppenstein et al., 2007). Therefore, workers are more easily exposed to high concentrations of benzene or ethylbenzene.

This study had several limitations. First, VOCs evaporate easily when sampling propellant spray products because of the compressed gas in the propellant spray products. To minimize loss, the propellant spray products are collected into the mouth of the vial with the cap closing as rapidly as possible. Second, the headspace analysis technique was not optimized at 180℃. Therefore, the concentrations of benzene and ethylbenzene decreased after 150℃.

It is suggested that further study should be undertaken in the following areas. First, it is necessary to quantify chemicals that were present in the qualitative analysis using reagents. Second, it is necessary to identify volatile carcinogens in PDPs considering vapor pressure and to evaluate volatile carcinogens in PDPs above 180℃ (for example, the furnace process is performed at 800℃).

5. Conclusion

This study conducted a quantitative and quantitative analysis of benzene and ethylbenzene in PDPs and identified an increase in the concentrations of benzene and ethylbenzene according to temperature. Furthermore, it was found that the number of carcinogens increased as the temperature rose. Benzene and ethylbenzene needed to be eliminated as much as possible in PDPs. If it is impossible to remove, we suggest that it is clearly stated in the MSDS because workers have the right to understand their risk. Various carcinogens appeared at high temperatures compared to that of the bulk samples. PDPs, such as lubricants and removers, contained trace levels of benzene and ethylbenzene. If these products are used in confined workplaces, it is necessary to provide sufficient ventilation and to inform workers of the chemical hazards before entering the manufacturing area.

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Appendices

Table A-1. The basic information about 30 petroleum-derived products and their benzene and ethylbenzene concentrations.

ID No.	Manu-facturer	Product use	State of matter	Result of analysis in bulk sample: Concentrations of benzene (ppm, v/v)	Result of analysis in bulk sample: Concentrations of ethylbenzene (ppm, v/v)	Major components of product: CAS No.	Major components of product: Chemical name	Major components of product: Concentration (%)
S-01	A	Lubricants (Engine Cleaner Oil)	Viscous Liquid	ND	3.50	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	100
S-02	A	Lubricants	Viscous Liquid	ND	11.61	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	90.0-97.0
						-	Trade secret	1.0-5.0
S-03	A	Lubricants (2 Stroke Motorcycle Engine Oil)	Viscous Liquid	4.78	143.96	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	80.0-90.0
						-	Trade secret	1.0-5.0
S-04	B	Transmission oil	Viscous Liquid	ND	2.99	64742-55-8	Distillates (petroleum), hydrotreated light paraffinic	30.0-40.0
S-05	B	Engine oil	Viscous Liquid	ND	4.26	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	< 90.0
						848301-69-9	Fischer-Tropsch	< 90.0
S-06	B	Engine oil	Viscous Liquid	2.08	4.13	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	25.0-35.0
						36878-20-3	bis(nonylphenyl)amine	1.0-3.0
S-07	C	Lubricants (Engine Cleaner Oil)	Viscous Liquid	ND	4.11	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	84.0-99.6
						-	additive mixture	0.2-3.0
S-08	C	Lubricants (2 Stroke Motorcycle Engine Oil)	Viscous Liquid	11.82	364.60	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	45.0-55.0
						9003-27-4	Polyisobutylene	20.0-30.0
						-	Trade secret	2.0-5.0

ID No.	Manu-facturer	Product use	State of matter	Result of analysis in bulk sample: Concentrations of benzene (ppm, v/v)	Result of analysis in bulk sample: Concentrations of ethylbenzene (ppm, v/v)	Major components of product: CAS No.	Major components of product: Chemical name	Major components of product: Concentration (%)
S-09	C	Lubricants	Viscous Liquid	ND	4.34	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	79.0-85.0
						-	additive mixture	12.0-17.0
S-10	D	Gasoline & Diesel Engine Oil	Viscous Liquid	ND	5.23	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	>76.8
						-	Mixed performance additive	12.0-13.5
S-11	E	Lubricant	Aerosol	2.20	7.87	64742-55-8	Distillates (petroleum), hydrotreated light paraffinic	20.0-30.0
						75-28-5	Isobutane	20.0-30.0
S-12	E	Lubricant	Aerosol	4.07	135.37	75-28-5	Isobutane	70.0-80.0
						63148-62-9	Silicone grease	3.0-7.0
S-13	F	Lubricant	Aerosol	ND	4.07	106-97-8	Butane	40.0-60.0
						64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	30.0-40.0
S-14	F	Lubricant	Aerosol	2.36	19.02	106-97-8	Butane	40.0-50.0
						64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	1.0-5.0
S-15	F	Lubricant	Aerosol	3.67	21.56	64742-47-8	Distillates(petroleum), hydrotreated light	40.0-50.0
						64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	1.0-10.0
S-16	G	Lubricant	Aerosol	2.10	6.15	64742-47-8	Distillates(petroleum), hydrotreated light	65.0-70.0
						64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	20.0-25.0

ID No.	Manu-facturer	Product use	State of matter	Result of analysis in bulk sample: Concentrations of benzene (ppm, v/v)	Result of analysis in bulk sample: Concentrations of ethylbenzene (ppm, v/v)	Major components of product: CAS No.	Major components of product: Chemical name	Major components of product: Concentration (%)
S-17	H	Lubricant	Aerosol	ND	12.20	64742-47-8	Distillates(petroleum), hydrotreated light	30.0-35.0
						64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	16.0-25.0
S-18	H	Lubricant	Aerosol	2.13	3.89	64742-47-8	Distillates(petroleum), hydrotreated light	30.0-35.0
						106-97-8	Butane	18.0-23.0
S-19	H	Lubricant	Aerosol	ND	ND	64742-47-8	Distillates(petroleum), hydrotreated light	30.0-40.0
						64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	10.0-20.0
S-20	I	Lubricant	Aerosol	2.27	5.49	64742-47-8	Distillates (petroleum), hydrotreated light	40.0-49.0
						64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	15.0-22.0
S-21	A	Grease	Semisolid	2.04	4.24	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	35.0-42.0
						64742-57-0	Residual oils (petroleum), Hydrotreated	30.0-35.0
S-22	C	Grease	Semisolid	ND	4.26	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	72.0-80.0
						64742-52-5	Distillates (petroleum), hydrotreated heavy naphthenic	10.0-15.0
S-23	F	Grease	Semisolid	ND	3.77	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	70.0-80.0
						64742-57-0	Residual oils (petroleum), Hydrotreated	10.0-20.0

ID No.	Manu-facturer	Product use	State of matter	Result of analysis in bulk sample: Concentrations of benzene (ppm, v/v)	Concentrations of ethylbenzene (ppm, v/v)	Major components of product: CAS No.	Chemical name	Concentration (%)
S-24	F	Grease	Semisolid	ND	4.42	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	40.0-50.0
						9002-92-0	Polyoxyethylene lauryl ether	35.0-45.0
S-25	J	Grease	Semisolid	ND	3.83	64742-62-7	Residual oils (petroleum), solvent-dewaxed	40.0-50.0
						64742-65-0	Distillates (petroleum), solvent-dewaxed heavy paraffinic	30.0-40.0
S-26	K	Grease	Semisolid	2.37	4.18	64742-54-7	Distillates (petroleum), hydrotreated heavy paraffinic	80.0-90.0
						4485-12-05	Lithium stearate	10.0-20.0
S-27	E	Adhesive remover	Aerosol	2.51	4.83	106-97-8	Butane	15.0-25.0
						64742-47-8	Distillates(petroleum), hydrotreated light	10.0-15.0
S-28	E	Adhesive remover	Aerosol	ND	4.23	68476-85-7	LPG	50.0-60.0
						64742-47-8	Distillates(petroleum), hydrotreated light	15.0-25.0
S-29	F	Paint remover	Aerosol	ND	3.81	75-09-2	Methylene chloride	50.0-60.0
						115-10-6	Dimethyl ether	40.0-50.0
						64742-47-8	Distillates(petroleum), hydrotreated light	1.0-5.0
S-30	F	Sticker stain remover	Aerosol	6.09	18.30	64742-47-8	Distillates(petroleum), hydrotreated light	30.0-40.0
						106-97-8	Butane	30.0-40.0

Abbreviations: v/v, Volumetric ratio.

***Note*:** Two or three representative chemicals were showed among the chemicals which were presented in Material Safety Data Sheet. The limit of detection of the benzene and ethylbenzene as follows: benzene, 0.62 ppm; ethylbenzene, 0.88 ppm.

Table A-2. Results of qualitative analysis by each petroleum-derived product according to temperature condition.

ID No. \ Temp (℃)	Compounds (CAS No.) 30	60	120	150	180	IARC	NTP	EU CLP	KMOEL
S_02	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Group 2B	-	-	Carc. 2
S_03		Benzene (71-43-2)	Benzene (71-43-2)	Benzene (71-43-2)	Benzene (71-43-2)	Group 1	K	Carc. 1A	Carc. 1A
		Benzene, (1-methylethyl)- (98-82-8)	Benzene, (1-methylethyl)- (98-82-8)	Benzene, (1-methylethyl)- (98-82-8)	Benzene, (1-methylethyl)- (98-82-8)	Group 2B	-		Carc. 2
	Ethylbenzene (100-41-4)		Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Group 2B	-	-	Carc. 2
S_06			Propane, 2-nitro- (79-46-9)	Propane, 2-nitro- (79-46-9)		Group 2B	R	Carc. 1B	Carc. 1B
S_08			Benzene (71-43-2)	Benzene (71-43-2)	Benzene (71-43-2)	Group 1	K	Carc. 1A	Carc. 1A
		Benzene, (1-methylethyl)- (98-82-8)	Benzene, (1-methylethyl)- (98-82-8)	Benzene, (1-methylethyl)- (98-82-8)	Benzene, (1-methylethyl)- (98-82-8)	Group 2B	-		Carc. 2
	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Group 2B	-	-	Carc. 2
					Aziridine (151-56-4)	Group 2B	-	Carc. 1B	Carc. 1B
S_11					Hydrazine, 1,2-dimethyl- (540-73-8)	Group 2A	-	Carc. 1B	Carc. 1B
					Methyl Isobutyl Ketone (108-10-1)	Group 2B	-	-	Carc. 2
S_12			Cyclohexanone (108-94-1)	Cyclohexanone (108-94-1)		Group 3	-	-	Carc. 2

ID No. \ Temp (℃)	Compounds (CAS No.) 30	60	120	150	180	IARC	NTP	EU CLP	KMOEL
S_12					2,4-Hexadienal, (E,E)- (142-83-6)	Group 2B	-	-	Carc. 2
	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Ethylbenzene (100-41-4)	Group 2B	-		Carc. 2
S_13	Propane, 1-bromo- (106-94-5)	Propane, 1-bromo- (106-94-5)		Propane, 1-bromo- (106-94-5)	Propane, 1-bromo- (106-94-5)	-	-	-	Carc. 2
		Styrene (100-42-5)				Group 2B	R	-	Carc. 2
				1,3-Butadiene (106-99-0)		Group 1	K	Carc. 1A	Carc. 1A
S_15			Propane, 2-nitro- (79-46-9)		Propane, 2-nitro- (79-46-9)	Group 2B	R	Carc. 1B	Carc. 1B
				(CH3)2CHCH2ONO (542-56-3)		-	-	Carc. 1B	Carc. 1B
S_17					Hydrazine, 1,2-dimethyl- (540-73-8)	Group 2A	-	Carc. 1B	Carc. 1B
S_19				Methyl Isobutyl Ketone (108-10-1)		Group 2B	-	-	Carc. 2
					Hydrazine, 1,2-dimethyl- (540-73-8)	Group 2A	-	Carc. 1B	Carc. 1B
					Oxirane, methyl- (75-56-9)	Group 2B	R	Carc. 1B	Carc. 1B
S_21	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methane, dichloro- (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-20	Group 2B	R	Carc. 2	Carc. 2
S_22			Oxirane, methyl- (75-56-9)	Oxirane, methyl- (75-56-9)		Group 2B	R	Carc. 1B	Carc. 1B

ID No. \ Temp (℃)	Compounds (CAS No.) 30	60	120	150	180	IARC	NTP	EU CLP	KMOEL
S_23			Oxirane, methyl- (75-56-9)	Oxirane, methyl- (75-56-9)		Group 2B	R	Carc. 1B	Carc. 1B
S_24	Ethene, 1,1-dichloro- (75-35-4)	Ethene, 1,1-dichloro- (75-35-4)	Ethene, 1,1-dichloro- (75-35-4)	Ethene, 1,1-dichloro- (75-35-4)					
	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Group 2B	R	Carc. 2	Carc. 2
					Ethene, fluoro- (75-02-5)	Group 3	-	Carc. 2	Carc. 2
					Methyl Isobutyl Ketone (108-10-1)	Group 2B	-	-	Carc. 2
					Oxirane, methyl- (75-56-9)	Group 2B	R	Carc. 1B	Carc. 1B
S_26	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Group 2B	R	Carc. 2	Carc. 2
			Oxirane, methyl- (75-56-9)		Oxirane, methyl- (75-56-9)	Group 2B	R	Carc. 1B	Carc. 1B
					Hydrazine, 1,2-dimethyl- (540-73-8)	Group 2A	-	Carc. 1B	Carc. 1B
					2-Pentanone, 4-methyl- (108-10-1)	Group 2B	-	-	Carc. 2
					Ethene, fluoro- (75-02-5)	Group 2A	R	-	Carc. 1B
S_27				Pyridine (110-86-1)		Group 3	-	-	Carc. 2
S_28			Propane, 2-nitro- (79-46-9)		Propane, 2-nitro- (79-46-9)	Group 2B	R	Carc. 1B	Carc. 1B
					1,3-Butadiene (106-99-0)	Group 1	K	Carc. 1A	Carc. 1A

ID No. \ Temp (℃)	Compounds (CAS No.)					IARC	NTP	EU CLP	KMOEL
	30	60	120	150	180				
S_29	Ethene, 1,1-dichloro- (75-35-4)	Ethene, 1,1-dichloro- (75-35-4)	Ethene, 1,1-dichloro- (75-35-4)	Ethene, 1,1-dichloro- (75-35-4)	Ethene, 1,1-dichloro- (75-35-4)	Group 3	-	Carc. 2	Carc. 2
				Trichloromethane (67-66-3)	Trichloromethane (67-66-3)	Group 2B	R	Carc. 2	Carc. 2
S_30	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Methylene chloride (75-09-2)	Group 2B	R	Carc. 2	Carc. 2

***Abbreviations*:** CAS, Chemical Abstracts Service; IARC, International Agency for Research on Cancer; NTP, National Toxicology Program; EU CLP, European Union Regulation on Classification, Labelling, and Packaging; KMOEL, Ministry of Employment and Labor in Korea.

***Note*:** The carcinogen information and classification were based on criteria suggested by each agency.

IARC Carcinogen classifications − Group 1: Carcinogenic to humans, Group 2A: Probably carcinogenic to humans, Group2B: Possibly carcinogenic to humans, Group 3: Not classifiable as to its carcinogenicity to humans, Group 4: Probably not carcinogenic to humans.

NTP Carcinogen classifications − K: Know to be a human carcinogens, R: Reasonable anticipated to be a human carcinogens.

EU CLP Carcinogen classifications − Carcinogen 1A: Known to have carcinogenic potential humans, classification is largely based on animal evidence, Carcinogen 1B: Presumed to have carcinogenic potential for humans, classification is largely based on animal evidence, Carcinogen 2: Suspected human carcinogens.

KMOEL Carcinogen classifications − Carcinogen 1A: Known to have carcinogenic potential humans, classification is largely based on animal evidence, Carcinogen 1B: Presumed to have carcinogenic potential for humans, classification is largely based on animal evidence, Carcinogen 2: Suspected human carcinogens.

Table A-3. Concentrations of benzene and ethylbenzene in petroleum-derived products according to temperature conditions.

Temp (℃) / ID No.	Concentrations of benzene (ppm, w/w)					Concentrations of ethylbenzene (ppm, w/w)				
	30	**60**	**120**	**150**	**180**	**30**	**60**	**120**	**150**	**180**
S-01	<LOD	0.94	1.83	0.70	2.52	<LOD	<LOD	0.89	1.14	4.02
S-02	<LOD	0.65	2.02	<LOD	1.45	6.90	23.45	102.27	113.01	126.27
S-03	23.32	46.11	78.33	67.09	71.91	140.62	473.43	1,553.96	1,450.14	1,752.73
S-04	<LOD	0.19	1.49	<LOD	1.48	0.20	1.08	5.73	6.29	9.62
S-05	<LOD	0.22	1.48	<LOD	1.37	0.33	1.70	7.89	8.90	12.01
S-06	0.39	1.48	3.42	1.91	2.97	<LOD	0.73	3.84	4.23	6.30
S-07	<LOD	<LOD	1.40	<LOD	0.91	0.25	1.31	5.87	8.86	9.47
S-08	41.89	78.81	126.02	117.13	114.21	285.72	845.05	2,583.64	2,386.95	2,606.96
S-09	<LOD	0.32	1.26	<LOD	0.82	0.20	1.15	4.96	5.46	7.24
S-10	<LOD	<LOD	0.86	<LOD	0.99	0.87	3.26	13.99	16.52	20.13
S-11	1.36	3.22	3.88	2.19	11.95	0.41	2.09	3.32	2.58	8.26
S-12	8.96	8.59	22.92	20.38	13.52	135.45	82.19	1,160.32	896.58	688.73
S-13	1.00	1.64	1.94	2.72	3.04	6.70	13.17	33.92	44.11	44.83
S-14	5.82	5.13	12.01	12.27	14.33	20.24	23.92	101.82	128.80	118.71
S-15	11.01	12.58	31.33	32.38	48.49	11.97	19.56	79.83	105.81	211.99
S-16	0.41	0.88	1.62	1.55	1.94	<LOD	0.23	0.81	13.44	28.05
S-17	0.22	1.21	1.66	1.53	1.26	<LOD	1.26	1.37	<LOD	0.93
S-18	0.29	1.28	2.42	1.95	2.49	0.60	1.76	13.00	16.58	32.79
S-19	1.50	3.79	5.37	3.81	3.46	<LOD	0.83	2.68	2.27	2.63
S-20	0.92	2.22	4.14	3.00	3.13	<LOD	0.36	1.59	1.36	2.46
S-21	0.68	1.39	5.28	1.15	1.32	<LOD	0.41	2.19	2.14	2.74
S-22	<LOD	<LOD	1.44	0.18	2.61	<LOD	<LOD	0.74	0.65	1.53

Temp (℃) / ID No.	Concentrations of benzene (ppm, w/w)					Concentrations of ethylbenzene (ppm, w/w)				
	30	60	120	150	180	30	60	120	150	180
S-23	<LOD	2.16	1.40	<LOD	0.27	<LOD	0.36	1.89	1.79	2.94
S-24	<LOD	<LOD	<LOD	<LOD	<LOD	0.22	1.17	4.78	4.46	6.32
S-25	<LOD	<LOD	1.03	<LOD	0.31	<LOD	0.60	2.54	3.23	4.02
S-26	2.00	4.29	6.15	5.68	14.07	0.41	1.77	6.93	7.73	16.98
S-27	0.78	2.35	5.43	4.18	4.11	<LOD	<LOD	0.48	0.24	0.41
S-28	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0.44	0.78	0.70
S-29	<LOD	<LOD	0.43	<LOD	<LOD	<LOD	1.74	17.23	18.20	19.97
S-30	7.70	24.93	29.93	29.46	32.43	2.91	15.09	24.73	27.95	23.50

Abbreviations**:** w/w, weight ratio; LOD, The limit of detection.
Note**:** The LOD of the benzene and ethyl benzene as follows: benzene, 0.14 ppm; ethylbenzene, 0.11 ppm.

국문초록

석유계 화학물질 함유제품 중 발암성분 포함에 관한 연구: 벤젠과 에틸벤젠을 중심으로

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연구 배경: 세계적으로 석유계 화학물질 함유 제품 시장의 규모는 크며 국내 화학물질 유통량 조사 결과 석유계 화학물질의 사용량도 많다. 석유계 화학물질 함유 제품은 사업장에서 다양하고 광범위하게 사용되는데, 여러 역학 연구에서는 석유계 화학물질 함유 제품 관련 작업자들이 그렇지 않은 작업자들보다 암 발병률이 높다고 보고했다. 석유계 화학물질 함유 제품에는 발암성 물질인 벤젠과 에틸벤젠이 포함되는데, 이 물질들은 휘발성 유기화합물로 온도가 상승함에 따라 발생하는 농도가 증가하는 경향이 있다. 작업장의 공정은 다양한데 제조업이나 자동차 공장에서는 고온 공정도 있다. 이에 본 연구는 석유계 화학물질 함유 제품 내 발암성 물질을 확인하고 온도가 상승함에 따라 증가하는 발암성 물질의 농도와 수를 파악하는 것이다.

연구 방법: 국내 화학물질 유통량 조사 결과, 사용량이 높은 석유계 화학물질의 CAS 번호를 기준으로 석유계 화학물질 함유 제품 30개를 선정했다. 30개의 제품은 점성이 있는 액체 윤활유 (VL), 에어로졸 윤활유 (AL), 반고체 윤활유 (SG), 그리고 에어로졸 제거제 (AR) 4가지 형태로 분류했다. 제품 내 발암성 물질을 파악하기 위한 벌크 제품 분석 방법과 온도에 따라 휘발되는 발암성을 평가하기 위해 헤드스페이스 분석 방법을 이용했다. 기체 크로마토그래피 질량분석기를 활용하여 정성 및 정량 분석을 동시에 진행했는데, 정성분석을 통해 발암성 물질을 파악했고 벤젠과 에틸벤젠을 대상으로 정량분석했다.

연구 결과: 정성분석 결과, 온도가 상승할수록 발암물질의 수도 증가했다. EU CLP 기준에 근거한 발암물질은 30℃에서 검출되지 않았지만 60℃부터 180℃까지 검출되었으며, 180℃에서는 발암물질이 9개로 가장 많이 검출되었다. 9개의 발암물질 중 1A와 1B에 해당하는 물질은 6개 (66.67%)였다. 정량분석 결과, 석유계 화학물질 함유 제품 30개 중 벤젠은 13개 (43.33%) 제품에서, 에틸벤젠은 29개 (96.67%) 제품에서 검출되었다. VL에서는 20% (2/10), AL에서는 30% (3/10), 그리고 AR에서는 50% (2/4)의 제품들이 온도가 상승하며 벌크 제품 분석 결과보다 벤젠 농도가 증가했다. VL에서는 80% (8/10), AL에서는 60% (6/10), SG에서는 16.67% (1/6) 그리고 AR에서는 50% (2/4)의 제품들이 온도가 상승하며 벌크 제품 분석 결과보다 에틸벤젠 농도가 증가했다.

결론: 정량분석 결과, VL은 벌크 제품 분석과 헤드스페이스 분석에서 벤젠과 에틸벤젠의 농도가 가장 높았다. 작업자는 VL을 고온의 공정에서 사용하게 될 경우 노출되지 않도록 해야 한다. 석유계 화학물질 함유 제품을 밀폐된 공정에서 사용하게 될 경우, 들어가기 전에 충분한 환기가

필요하며 작업자에게 화학물질의 위험성을 알려야 할 필요가 있다. 또한 이러한 제품 내 벤젠이나 에틸벤젠은 가능한 제거해야 하고 제거가 불가능할 경우 물질안전보건자료에 함유량을 제시하여 작업자가 알 수 있게 해야 한다. 마지막으로 석유계 화학물질 함유 제품 내 벤젠 및 에틸벤젠 함량에 대한 관리가 필요하며 다른 발암성 물질에 대해서도 주의가 필요하다.

주요어: 석유계 화학물질 함유 제품, 발암성 물질, 벤젠, 에틸벤젠, 기체크로마토그래피 질량분석기, 헤드스페이스 분석 방법

학번: 2018-22343