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Case Report

A Study for Health Hazard Evaluation of Methylene Chloride Evaporated from the Tear Gas Mixture

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This study explored the health hazard of those exposed to methylene chloride by assessing its atmospheric concentration when a tear gas mixture was aerially dispersed. The concentration of methylene chloride ranged from 311.1–980.3 ppm (geometric mean 555.8 ppm), 30 seconds after the dispersion started. However, the concentration fell rapidly to below 10 ppm after dispersion was completed. The concentration during the dispersion did not surpass the National Institute for Occupational Safety and Health (NIOSH) 'immediately dangerous to life or health' value of 2,300 ppm, but did exceed the American Conference of Governmental Industrial Hygienists (ACGIH) excursion limit of 250 ppm. Since methylene chloride is highly volatile (vapor pressure, 349 mmHg at 20°C), the post-dispersion atmospheric concentration can rise instantaneously. Moreover, the o-chlorobenzylidenemalononitril e formulation of tear gas (CS gas) is an acute upper respiratory tract irritant. Therefore, tear gas mixtures should be handled with delicate care.

Key Words: Methylene chloride, CS tear gas, Tear gas mixture, Health hazard evaluation

Introduction

Tear gases such as o-chlorobenzylidenemalononitrile (CS), dibenzoxazepine (CR) and phenacyl chloride (CN) are commonly used for riot control [1-6] since they stimulate the corneal nerves in the eyes to cause tearing. The present study used CS gas. The gas was discovered in the U.S. in 1928; it is designated after the initial of discoverers Corson and Stoughton [2-4]. CS gas, a substance causing eye irritation, excessive lacrimation and burn injury, has been used in controlling riots for the past four decades [5,6]. CS is a powder at room temperature but is used mostly as an aerosol.

Despite this long history of use, CS gas has recently come under greater scrutiny since it can be applied as a mixture that contains a suspected human carcinogen, methylene chloride. CS is soluble in organic solvents such as methylene chloride; at room temperature, the solubility is approximately 39% by weight [4]. Methylene chloride is a colorless and volatile liquid (vapor pressure, 349 mmHg at 20°C), which is easily miscible with many other solvents. The organic compound is widely-used as a paint stripper and degreaser. Compared to related chlorinated solvents such as carbon tetrachloride and chloroform, methylene chloride has relatively low acute toxicity. However, an acute exposure to methylene chloride primarily depresses the central nervous system. The compound is considered a weak animal carcinogen based on the observations of liver and lung cancer in exposed mice, and benign mammary gland tumors in rats after chronic inhalation at high concentrations (≥ 1,000

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ppm) [7]. Methylene chloride has been classified as an A2 agent (a suspected human carcinogen) by the Ministry of Labor of Korea, Group 2B (possible carcinogenic to humans) by the International Agency for Research on Cancer, and A3 (confirmed animal carcinogen with unknown relevance to humans) by the American Conference of Governmental Industrial Hygienists (ACGIH) [8-10].

This study explored the health hazard of those exposed to methylene chloride by assessing its atmospheric concentration when a tear gas mixture was dispersed similar to the real-life use.

Materials and Methods

The dispersion experiment for tear gas mixture was conducted in a vacant lot located in Incheon, Korea. The dispersion vehicle was equipped with a tank containing 50 L of tear gas mixture and a tank containing 2,500 L of water. The tear gas mixture and water were released from separate nozzles at controlled rates and were mixed in a ratio of 1 : 50 just prior to dispersal (2,000 L/min) into the atmosphere using a water cannon (gun). Dispersal was toward three dummies 16 meters away. The distance between the dummies was three meters. The tear gas mixture was dispersed three times with a 3-minute interval. The dispersion time per round was 30 seconds. The authors referred to the National Institute for Occupational Safety and Health (NIOSH) manual of analytical method No. 1005 on sampling and analyzing methylene chloride. In order to minimize the loss of the samples due to breakthrough, two charcoal tubes were connected in series [11]. Sampling was conducted at the respiratory region of the dummies. In addition to personal air sampling, real-time monitoring for concentration changes of methylene chloride during the dispersion experiment was also conducted using a photoacoustic multi-gas monitor (INNOVA Air Tech Instrument, models 1312 and 1309). Monitoring was conducted with a 40-second interval at the middle dummy.

Results

Real-time monitoring of methylene chloride concentration levels

A real-time gas monitor was used to follow the concentration levels of methylene chloride in the atmosphere while the tear gas mixture was being dispersed. The concentration was the highest (178-430 ppm) immediately after the dispersion started and decreased rapidly after dispersion was completed (Fig. 1). Differences of methylene chloride concentrations among the dispersion rounds were due to the sampling interval of the real-time gas monitor. Although an exact estimation of the concentration levels of methylene chloride was difficult to determine, the result shows the air-borne concentration pattern of dispersed methylene chloride.

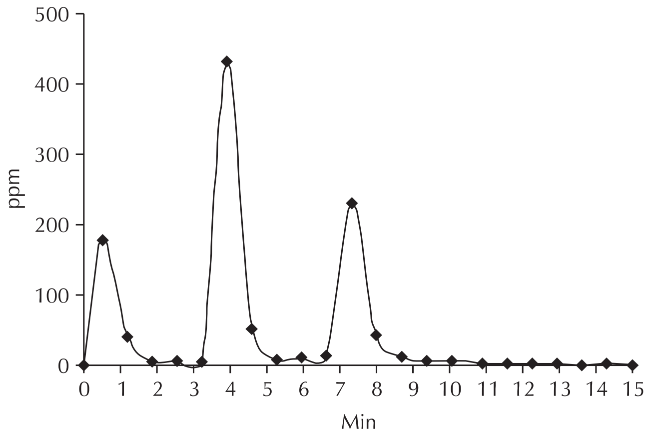

Fig. 1. Concentration levels of methylene chloride by time.

Monitoring methylene chloride concentration levels by a personal air sampling device

Table 1 shows the concentration levels of methylene chloride evaluated by a personal air sampling device, which was set at the respiratory region of the dummies. The concentration of methylene chloride ranged from 311.1-980.3 ppm (geometric mean 555.8 ppm), 30 seconds after the dispersion started. However, the concentration fell rapidly upon the conclusion of dispersion. The reason that the concentration of the second or third dispersion round was lower than that of the first dispersion round was that the sampling time for each round was different. The sampling time of second or third dispersion round spanned from the starting time of the first dispersion round to the finishing time of each dispersion round.

Discussion

The concentration during the first dispersion round was very high at 311.1-980.3 ppm (geometric mean 555.8 ppm). However, it decreased over time as illustrated in (Table 2). It is assumed that due to its high volatility, methylene chloride rapidly evaporated into the atmosphere upon dispersion, raising the initial concentration levels. However, the compound was also rapidly diffused into the atmosphere, dropping the concentration over time.

The limits set by the Ministry of Labor of Korea and the ACGIH are based on an 8-hour time weighted average level (TWA), not on the short term exposure limit (STEL). There-

Table 1. Concentration levels of methylene chloride as monitored by a personal air sampling device

Dispersion time (min)	Sampling time (min)	No. of samples	Concentration, GM (ppm)	Concentration, range (ppm)	Dispersion round
0-0.5	0-0.5	6	555.8	311.1-980.3	One
3.5-4.0	0-4.0	6	98.5	63.5-136.4	Two
7.0-7.5	0-7.5	6	69.9	58.0-88.5	Three
	7.5-15	4	2.8	2.4-3.1	
	15-25	6	0.9	0.8-1.0	

GM: geometric mean.

Table 2. Concentration levels of methylene chloride by time

Time	30 sec	4 min	7.5 min	15 min
Concentration (ppm)	555.8 (980.3 max)	98.5	69.9	36.3

fore, it was not appropriate to apply these limits to the concentration levels of methylene chloride dispersed for a short time. According to this study, the 15-minute exposure concentration was 36.3 ppm, which is below the Occupational Safety and Health Administration (OSHA) limit of 125 ppm and the Health and Safety Executive (HSE) limit of 300 ppm [12,13]. NIOSH recommends that the methylene chloride level be kept as low as possible, stating that 2,300 ppm is the immediately dangerous to life or health (IDLH) concentration [14]. Presently, the methylene chloride concentrations did not exceed the IDLH value. However, the concentration while the mixture was being sprayed was still very high (980.3 ppm maximum). The ACGIH recommends that exposure to materials without the TWA-STEL should not exceed 30 min if the concentrations are three times higher than the TLV-TWA. If the concentrations are more than five times higher than the TLV-TWA, no exposure is tolerable. This recommendation aims to prevent the compounds without the TWA-STEL values from causing adverse health effects owing to instant high concentration. Therefore, it seems necessary to take measures such as replacing the compound with low-risk materials.

Conclusions

This study kept track of the methylene chloride concentration levels in the atmosphere when a tear gas mixture was dispersed similar to the real-life use. The concentration of methylene chloride ranged from 311.1-980.3 ppm (geometric mean 555.8 ppm), 30 seconds after dispersion started. However, the concentration fell rapidly to below 10 ppm when the dispersion was over. The concentration during the dispersion did not surpass the NIOSH IDLH level (2,300 ppm). However, the concentration exceeded the ACGIH excursion limit (250 ppm). The ACGIH recommends that worker exposure level should not exceed the excursion limit in any circumstances with an aim to avoid health hazards due to the high concentrations. Acute methylene chloride exposure primarily depresses the central nervous system. The compound is considered a weak animal carcinogen. Moreover, CS gas is a well known acute irritant to upper respiratory tract. Therefore, the tear gas mixture should be handled with delicate care.

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