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Development of a Sampling and Analysis Method for 4-Vinyl-1-cyclohexene in Air

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Abstract: Development of a Sampling and Analysis Method for 4-Vinyl-1-cyclohexene in Air: Pornpimol KONGTIP, *et al.* Department of Occupational Health and Safety, Faculty of Public Health, Mahidol University, Thailand—The purpose of this research was to develop an applicable sampling and analytical method to determine airborne 4-vinyl-1-cyclohexene concentrations which are usually found in the atmosphere of polybutadiene factories. A solid sorbent tube, containing two sections (100 mg in the front and 50 mg in the back) of activated coconut-shell charcoal was chosen for sampling 4-vinyl-1-cyclohexene vapor. The 4-vinyl-1-cyclohexene in the charcoal samples was desorbed with carbon disulfide and analyzed by gas chromatography equipped with a flame ionization detector. The suitable air flow rate, adsorption capacity, sample storage stability, desorption efficiency and reliability of the method for sampling and analysis of 4-vinyl-1-cyclohexene were evaluated. The method was applied to sampling and analysis of 4-vinyl-1-cyclohexene in the rubber industry. The results indicated a suitable air flow rate of 0.3 to 1.5 *l*/min. The adsorption capacity of 4-vinyl-1-cyclohexene on 100 mg of charcoal was 0.2134 mg. The 4-vinyl-1-cyclohexene adsorbed on the charcoal was stable for 7 d at room temperature or 21 d in a refrigerated condition. The average percent desorption efficiency of 4-vinyl-1-cyclohexene ranged from 90.45% to 97.04% with the loaded amount ranging from 0.412 to 8.250 μg using 1 m*l* carbon disulfide. The limit of detection of 4-vinyl-1-cyclohexene was 0.044 ng. The average percent recoveries (n=6) of 4-vinyl-1-cyclohexene adsorbed on charcoal ranging from 0.46 to 8.87 μg were 96.78–102.87% with relative standard deviations (RSDs) of 0.34–1.92%, respectively. The concentrations of 4-vinyl-1-cyclohexene ranged from 0.011 to 0.105 mg/m^3 in the working environment of a polybutadiene factory.
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Occupational exposure to 4-vinyl-1-cyclohexene may occur at workplaces where 4-vinyl-1-cyclohexene, acrylonitrile/butadiene/styrene, or rubber compounds are produced or used. In a survey of 17 sites in the USA used by companies for the production of crude or refined butadiene, or generation and isolation of 4-vinyl-1-cyclohexene, approximately 1,300 employees were potentially exposed to 4-vinyl-1-cyclohexene[1)]. In the past, the highest concentrations of 4-vinyl-1-cyclohexene were found in personal air samples of polymer production workers (styrene/butadiene and vinylnorbornene production) at about 5 ppm and in those of Russian rubber workers at a mean of 271 to 542 ppm[2)]. The production of polybutadiene around the world is approximately 2 million tons per year and usage is especially high in the process of tire production which generates 4-vinyl-1-cyclohexene. In 1976, the composition of curing effluents from rubber stock during simulated vulcanization was studied in the laboratory. Many poisonous compounds were found in the final products such as methylbenzene, 4-vinyl-1-cyclohexene, 1,5-cyclooctadiene and 1,5,9-cyclododecatriene[3, 4)].

Statistics of the Customs Department, Ministry of Finance, Thailand, show that Thailand imported chemical substances in the group of butadiene, isoprene and 4-vinyl-1-cyclohexene in the amount of approximately 9,898 tons in the year 2002. This group of chemical substances is used in several chemical industries, such as those producing plastic polymers (ABS copolymer), epoxy resin and polyallyl ester. In Thailand, approximately 550 employees may be exposed to 4-vinyl-1-cyclohexene, according to the statistics of the Department of Industrial Works, Ministry of Industry.

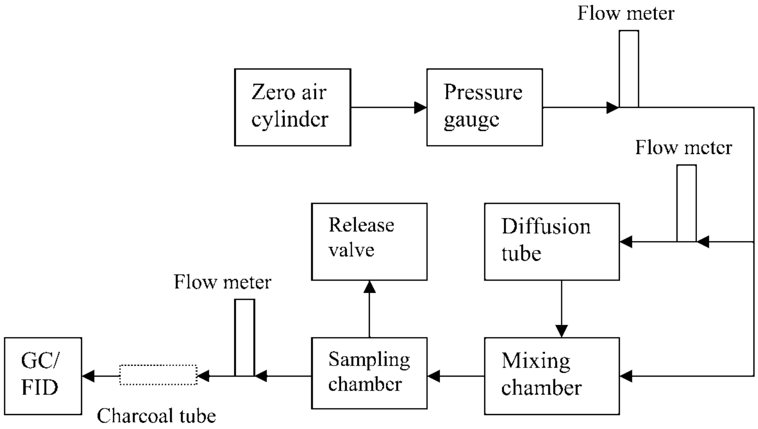

Fig. 1. Schematic diagram of instrumentation required for 4-vinyl-1-cyclohexene generation, capture and analysis.

The physical and chemical properties of 4-vinyl-1-cyclohexene are as follows: molecular weight, 108.18; specific gravity (Water =1), 0.832; boiling point, 128°C; vapor pressure (25°C), 14.03 mmHg; vapor density (Air =1), 3.76 and water solubility, insoluble[5]. Exposure to 4-vinyl-1-cyclohexene is caused by inhalation, ingestion and skin absorption. It is an irritant, and it defats the skin on direct contact. It is also an anesthetic and CNS depressant. When ingested, it presents a low to moderate pulmonary aspiration hazard[6]. Workers inhaling a mean of 271 to 542 ppm 4-vinyl-1-cyclohexene were reported to suffer from keratitis, rhinitis, headache, hypotonia, leukopenia, neutrophilia, and lymphocytosis[2]. Additionally, 4-vinyl-1-cyclohexene is classified as possibly carcinogenic to humans (Group 2B) by International Agency for Research on Cancer (IARC)[7].

Recently, the use of 4-vinyl-1-cyclohexene in chemical processes has increased and it is now generated as a by-product in the process of polybutadiene production. Thus, the evaluation of 4-vinyl-1-cyclohexene exposure of operators in the working environment has become necessary[8]. Since the American Conference of Governmental Industrial Hygienists (ACGIH) has already recommended a Threshold Limit Value (TLV), the ACGIH may have tried to develop an analytical method for 4-vinyl-1-cyclohexene vapor. However, at the present time there is no accessible reference method for the sampling and analysis of 4-vinyl-1-cyclohexene vapor in air. This study aimed to develop a solid sorbent sampler method for determining concentrations of 4-vinyl-1-cyclohexene vapors and apply it to measurements in a polybutadiene factory.

Methods

Apparatuses and chemical reagents

A Shimadzu GC-14B gas chromatograph (GC) with a DB-1 capillary column (30 m × 0.53 mm I.D.), equipped with a flame ionization detector and an integrator (Shimadzu C-R7A, Shimadzu, Kyoto, Japan) was used. The carrier gas was helium at a flow-rate of 10 ml/min. The GC condition was isothermal with column temperature of 70°C, injector temperature of 200°C and detector temperature of 200°C.

A personal air sampling pump (224-PCXR8, SKC), and a 5-liter Tedlar air bag (SKC), charcoal tube (100 mg/50 mg) (Cat.226-01) (SKC Inc., Eighty Four, Pa., USA) were used for air sampling. 4-Vinyl-1-cyclohexene and carbon disulfide were purchased from Merck (Darmstadt, Germany).

The calibration curve of 4-vinyl-1-cyclohexene in air

A static system was chosen to generate known concentrations of 4-vinyl-1-cyclohexene in dry air to set up a calibration curve for gas chromatography. The 4-vinyl-1-cyclohexene liquid, diluted with carbon disulfide to the desired concentration, was spiked into 5-liter Tedlar bags containing zero air at various concentrations ranging from 7.5 to 225 ppb 4-vinyl-1-cyclohexene in air. In the experiment, preconditioning of the bags was performed by flushing out the bags several times with a 4- vinyl-1-cyclohexene at the desired concentrations, with at least one of the air flushes remaining in the bag overnight.

The generation of standard 4-vinyl-1-cyclohexene in air by a dynamic system

4-Vinyl-1-cyclohexene in dry air was prepared at 4 concentrations, namely 10 (0.1TLV), 50 (0.5TLV), 100 (1TLV) and 200 (2TLV) ppb. Zero air was generated at a flow rate of approximately 1,000 m*l*/min. The zero air line was divided into 2 lines. The first line went to a diffusion tube containing liquid 4-vinyl-1-cyclohexene. The 4-vinyl-1-cyclohexene was diffused and mixed with the zero air in the mixing chamber. The second air line was used to dilute the chemical to the desired concentration in the mixing chamber which was connected to a sampling chamber (Fig. 1). The vapor concentration of 4-vinyl-1-cyclohexene generated stabilized in the sampling chamber within 2 h. The concentration of 4-vinyl-1-cyclohexene generated was analyzed by GC using a calibration curve of standard 4-vinyl-1-cyclohexene in air.

The investigation of suitable air flow rate for sampling of 4-vinyl-1-cyclohexene

The charcoal tube was placed in line to a port of the sampling chamber containing 200 ppb 4-vinyl-1-cyclohexene vapor. Air containing 4-vinyl-1-cyclohexene was collected in the charcoal tube at a flow rate of 0.1 *l*/min for 100 *l*. After the sampling was completed, the charcoal tube was sealed with parafilm M, capped with plastic caps and kept in a refrigerated condition. The experiment was repeated four times.

The experiment to find a suitable air flow rate for sampling of 4-vinyl-1-cyclohexene was repeated at flow rates of 0.3, 0.5, 1.0, 1.5 and 2.0 *l*/min. The charcoal tubes were desorbed with 1 m*l* carbon disulfide and 4-vinyl-1-cyclohexene vapor adsorbed was analyzed by GC.

The adsorption capacity of charcoal

The adsorption capacity was investigated by measuring the time(s) taken for 4-vinyl-1-cyclohexene to break through the adsorbent material, the presence of the 4-vinyl-1-cyclohexene being measured in the effluent air under a controlled flow rate. When the charcoal tube was placed in line between the sampling chamber and the GC at time 0, the known concentration of chemical in the influent air stream would be adsorbed onto the charcoal tube. When 5% of the 4-vinyl-1-cyclohexene was measured in the effluent air, we judged that breakthrough had occurred. The monitoring continued until the charcoal tube was saturated with the 4-vinyl-1-cyclohexene. A representative diagram of the experiment is shown in Fig. 1. The breakthrough experiment using the charcoal tube was conducted at a flow rate of 0.5 *l*/min with a volatilized 4-vinyl-1-cyclohexene concentration of 200 ppb in dry air. The back-up section and urethane foam plug were removed from the charcoal tube before the charcoal tube was placed in line. After the charcoal began adsorbing 4-vinyl-1-cyclohexene in air, 1.0 of m*l* effluent air was injected into the GC by a gas tight syringe to check for breakthrough of 4-vinyl-1-cyclohexene. The breakthrough time, volume, and capacity of trapped 4-vinyl-1-cyclohexene were investigated.

Calibration curve of 4-vinyl-1-cyclohexene in carbon disulfide

The calibration curve of 4-vinyl-1-cyclohexene in carbon disulfide ranged from 0.165 to 12.375 μg/m*l* and was analyzed by GC. The LOD (Limit of detection) and LOQ (Limit of quantitation) were calculated following the National Institute for Occupational Safety and Health (NIOSH) method[9].

The desorption and analysis of 4-vinyl-1-cyclohexene from charcoal

The front and back sections of the charcoal tube that adsorbed 4-vinyl-1-cyclohexene were separated into separate vials. The chemical was desorbed for 30 minutes by 1 m*l* carbon disulfide and 1 μl of carbon disulfide was injected into the GC.

Determination of desorption efficiency

The desorption efficiency of 4-vinyl-1-cyclohexene was determined by liquid spiking of 4-vinyl-1-cyclohexene at 0.412, 2.062, 4.125 and 8.250 μg onto the front section of each charcoal tube. These spiked charcoal tubes were stored overnight, desorbed with 1 m*l* carbon disulfide, then analyzed by GC.

Determination of sample storage stability

A sample storage stability test was carried out by spiking 0.412, 2.062, 4.125 and 8.250 μg of standard 4-vinyl-1-cyclohexene onto charcoal. All the spiked charcoal tubes were wrapped immediately with parafilm M and capped. Half were kept at room temperature (27.4-29.2°C) while the other half were kept at a refrigerated temperature (4.0-6.0°C). The charcoal tubes were desorbed and analyzed after storage of 1, 3, 7, 10, 14 and 21 d at room and refrigerated temperatures.

The accuracy and precision of the sampling and analysis method of 4-vinyl-1-cyclohexene

Known concentrations of 4-vinyl-1-cyclohexene in dry air were generated at concentrations of approximately 10, 50, 100 and 200 ppb. Air containing various concentrations of 4-vinyl-1-cyclohexene was collected on a charcoal tube at a flow rate of 0.5 *l*/min for 20 min. The samples were analyzed by GC and the accuracy and precision of the method were calculated.

Application of the method in a polybutadiene factory

The working environment of a polybutadiene factory was selected for sampling 4-vinyl-1-cyclohexene vapor. Air samples in three areas of the working environment, namely, mixing, bead building and the extrusion process, were collected for 10 samples in each area. Then, the samples were desorbed with carbon disulfide and analyzed by GC following the method described above.

Statistical analysis

The general characteristics of all data were analyzed in terms of mean, standard deviation (SD) and relative

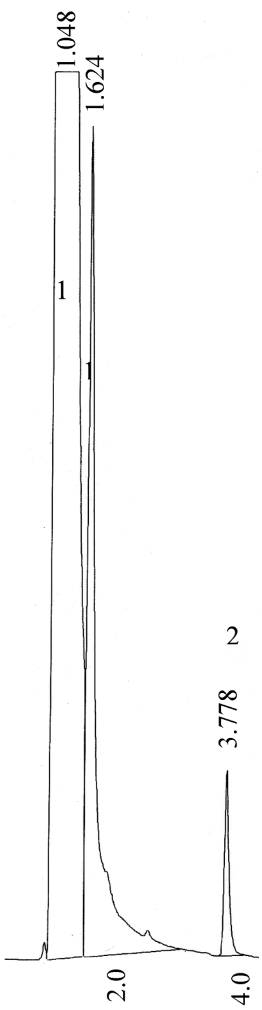

Fig. 2. Chromatogram of standard 4-vinyl-1-cyclohexene in carbon disulfide: (1) carbon disulfide (2) 4-vinyl-1-cyclohexene.

standard deviation (RSD).

Results

Calibration curve of 4-vinyl-1-cyclohexene in air and in carbon disulfide

The calibration curves of 4-vinyl-1-cyclohexene in air ranging from 7.5 to 225 ppb and in carbon disulfide ranging from 0.17 to 12.38 μg/m*l* were prepared. The chromatograms of 4-vinyl-1-cyclohexene in air and in carbon disulfide were similar. The chromatogram of 4-vinyl-1-cyclohexene in carbon disulfide is shown in Fig. 2. The retention time of 4-vinyl-1-cyclohexene was 3.78 min. Linear relationships were found between the peak area of 4-vinyl-1-cyclohexene and 4-vinyl-1-cyclohexene concentrations both in air and in carbon disulfide (Table 1). From the regression curve of low concentrations of 4-vinyl-1-cyclohexene in carbon disulfide, the LOD and LOQ were estimated to be 0.044 and 0.148 ng, respectively.

The generated 4-vinyl-1-cyclohexene vapor by dynamic system

The generated 4-vinyl-1-cyclohexene concentrations in air by the dynamic system were close to the target concentration (Table 2). The dynamic of known concentrations of 4-vinyl-1-cyclohexene (10, 50, 100 and 200 ppb) was used for the assessment of suitable air flow rate, adsorption capacity, accuracy and precision of the sampling and analysis method of 4-vinyl-1-cyclohexene.

The suitable air flow rate of 4-vinyl-1-cyclohexene sampling

The average percent recoveries of 4-vinyl-1-cyclohexene from charcoal ranged from 91.26% to 100.85 % (Fig.3). Suitable air flow rates for sampling of 4-vinyl-

Table 1. Calibration curves of 4-vinyl-1-cyclohexene in air and in carbon disulfide

Calibration curve	Concentration range	Slope	Y-intercept	Correlation coeff. (r) (n=4)
4-vinyl-1-cyclohexene in air	7.5–225 ppb	43.19	819.72	0.999
4-vinyl-1-cyclohexene in carbon disulfide	0.17–12.38 µg/m*l*	1,000	87.338	0.999

Table 2. Concentrations of 4-vinyl-1-cyclohexene generated in air using the dynamic system

Target conc. (ppb)	Generated conc. (ppb) (Mean ± SD)	%RSD (n=4)
10 (0.1TLV)	10.4 ± 0.15	1.44
50 (0.5TLV)	50.5 ± 0.18	0.36
100 (1TLV)	100.7 ± 0.39	0.38
200 (2TLV)	200.8 ± 0.47	0.23

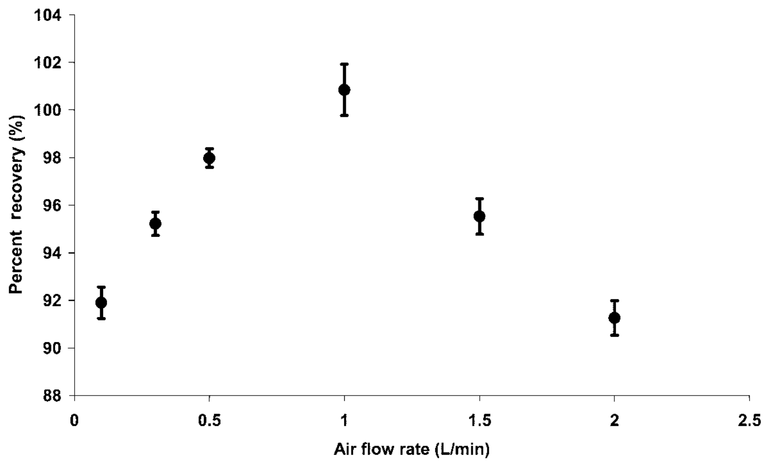

Fig. 3. Percent recoveries of 4-vinyl-1-cyclohexene from charcoal tubes after sampling of 200 ppb 4-vinyl-1-cyclohexene vapor in 100 *l* air at flow rates of 0.1, 0.3, 0.5, 1.0, 1.5 and 2 *l*/min.

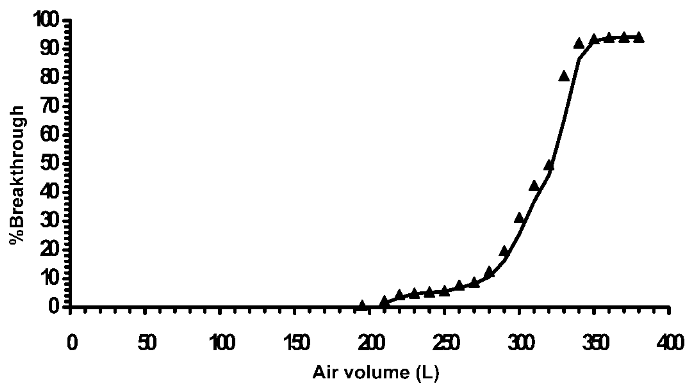

Fig. 4. Breakthrough curve of 200 ppb 4-vinyl-1-cyclohexene in dry air adsorbed on 100 mg of charcoal at a flow rate of 0.5 *l*/min when using 1.0 m*l* of effluent air injected into the gas chromatograph.

1-cyclohexene ranged from 0.3 to 1.5 *l*/min because these air flow rates gave the desired 95% percent recoveries.

The adsorption capacity of charcoal for 200 ppb 4-vinyl-1-cyclohexene

At 5% breakthrough, the average breakthrough time of 4-vinyl-1-cyclohexene for charcoal (100 mg) was 480 min. The average mass loading of 4-vinyl-1-cyclohexene adsorbed on the 100 mg of charcoal was 0.2134 mg. The average adsorption capacity of charcoal was 0.002134 mg 4-vinyl-1-cyclohexene/mg charcoal (in dry air at 24.5°C). In the first stage of the breakthrough curve (0 to 10 % breakthrough), the slope of the curve was increased slightly and it increased dramatically after sampling of 240 *l* and showed complete saturation at the volume of 350 *l* or 700 min (Fig. 4).

The desorption efficiency

The average percent desorption efficiencies of spiked 4-vinyl-1-cyclohexene ranging from 0.412 to 8.250 μg were 90.45 to 97.04 %, respectively (Table 3).

Sample storage stability

The percent recovery was nearly 100% within 3 d at room temperature and in the refrigerated condition. However, the percent of recovery decreased after 7 d of storage both at room temperature and in the refrigerated condition (Fig. 5).

The suitable duration for storage of samples was selected as recovery loss percentages of less than 10 %. At 0.412 μg 4-vinyl-1-cyclohexene, the charcoal tube containing 4-vinyl-1-cyclohexene was stable for 14 d at room temperature and in the refrigerated condition. At 2.062, 4.125 and 8.250 μg 4-vinyl-1-cyclohexene, the

Table 3. Desorption efficiency of spiked 4-vinyl-1-cyclohexene on charcoal

Chemical added (μg)	Chemical found (μg) (Mean ± SD)	% Desorption efficiency (Mean ± SD)(n= 4)
0.413	0.37 ± 0.062	90.45 ± 2.39
2.063	1.92 ± 0.058	93.30 ± 0.68
4.125	3.88 ± 0.026	94.09 ± 1.12
8.250	8.01 ± 0.115	97.04 ± 2.28

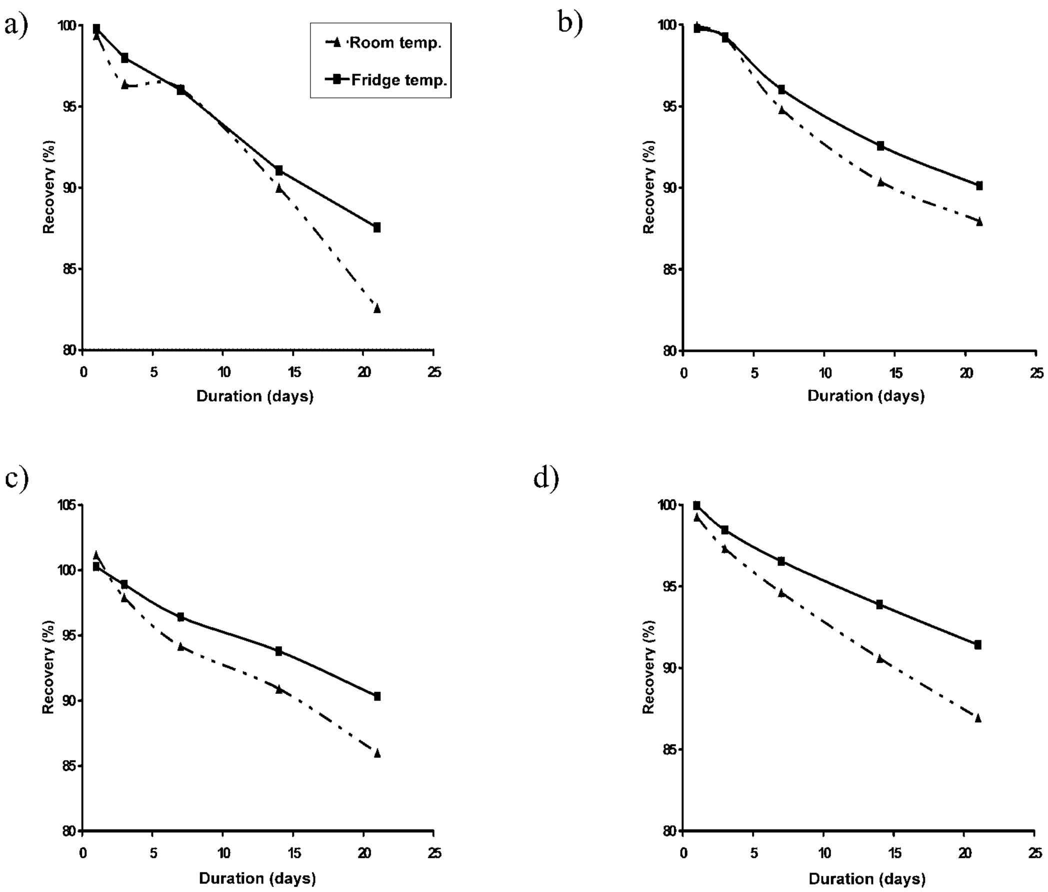

Fig. 5. Storage stability of four loading levels of spiked 4-vinyl-1-cyclohexene on charcoal tube at room and refrigerated temperatures: a) 0.412 μg 4-vinyl-1-cyclohexene, b) 2.062 μg 4-vinyl-1-cyclohexene, c) 4.125 μg 4-vinyl-1-cyclohexene, and d) 8.250 μg 4-vinyl-1-cyclohexene.

charcoal tube could be stored for 14 d at room temperature and 21 d at refrigerated temperature.

The accuracy and precision of the sampling and analysis method of 4-vinyl-1-cyclohexene in air

The average percent recoveries (n=6) of 4-vinyl-1-cyclohexene adsorbed on charcoal ranging from 0.46 to 8.87 μg were 96.78–102.87 %, with RSDs of 0.34–1.92%, respectively (Table 4).

Application of the method in the polybutadiene factory

The working environment of a polybutadiene factory was selected for sampling 4-vinyl-1-cyclohexene vapor. The chromatogram of 4-vinyl-1-cyclohexene in the working environment of a polybutadiene factory is shown in Fig. 6. The results show that the concentrations of 4-vinyl-1-cyclohexene in mixing, bead building, and extrusion ranged from 0.0117 to 0.183, 0.0111 to 0.105 and 0.0376 to 0.078 mg/m^3, respectively. The concentration of 4-vinyl-1-cyclohexene in the working environment of

Table 4. The recovery of sampling and analysis method of 4-vinyl-1-cyclohexene in air

μg adsorbed (Mean ± SD)	μg recovered (Mean ± SD)	%Recovery (n=6)	%RSDs
0.460 ± 0.007	0.445 ± 0.005	96.78	0.39
0.232 ± 0.008	2.223 ± 0.050	99.59	1.92
4.448 ± 0.017	4.576 ± 0.007	102.87	0.43
8.873 ± 0.021	8.788 ± 0.048	99.03	0.34

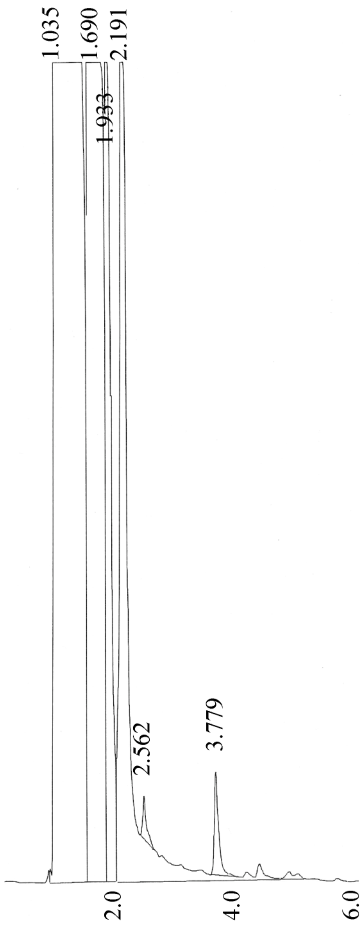

Fig. 6. Chromatogram of 4-vinyl-1-cyclohexene sampled in the working environment of a polybutadiene industry.

the polybutadiene factory was very low in comparison to the Threshold Limit Value-Time-Weighted Average (TLV-TWA) of 0.1 ppm or 0.442 mg/m^3.

Discussion

4-Vinyl-1-cyclohexene in air was sampled at various air flow rates from 0.1 to 2.0 *l*/min with a charcoal tube. Air flow rates suitable for sampling 4-vinyl-1-cyclohexene were 0.3 and 1.5 *l*/min, because these air flow rates gave percent recoveries of 95.22 to 100.85. The percent recoveries increased when the sampling air flow rate (0.1 to 1.0 *l*/min) increased because the 200 ppb 4-vinyl-1-cyclohexene concentration had constant mole equivalent. If the air flow rate increases, mass rate increases (mass rate=mole equivalent × flow rate). Mass rate is the mole of gas per unit time[10]. However, the percent recoveries decreased when the air flow rate was increased from 1 to 2 *l*/min because the micropores in the charcoal could not catch the 4-vinyl-1-cyclohexene vapor which diffuses very quickly. The back section of the charcoal tube was found to contain 4-vinyl-1-cyclohexene. The average masses of 4-vinyl-1-cyclohexene in the back section of the charcoal tube at 1.5 and 2.0 *l*/min were 3.17 ± 0.30 and 4.35 ± 0.16 μg, respectively. Furthermore, 4-vinyl-1-cyclohexene flowed rapidly through the charcoal tube.

With regard to the sample storage stability of 4-vinyl-1-cyclohexene, four loading levels of liquid spiked samples on charcoal tubes were prepared and stored under two conditions, at room temperature and in a refrigerated condition. The suitable duration for storage was selected at percent recovery losses of less than 10%. Charcoal tubes containing 0.412-μg 4-vinyl-1-cyclohexene were stable for 14 d both at room temperature and in the refrigerated condition. In addition, charcoal tubes containing 4-vinyl-1-cyclohexene ranging from 2.06 to 8.25 μg were stable for 14 d at room temperature and 21 d in the refrigerated condition.

The migration of 4-vinyl-1-cyclohexene from the front to the back sections of the charcoal tube occurred over 14 d at mass loading levels of 4.12 and 8.25 μg, and over 21 d at mass loading levels of 0.412 to 8.25 μg at room temperature. When the charcoal tube loaded with large amounts of 4-vinyl-1-cyclohexene were stored at room temperature for long periods of time, it was probable that chemical vaporization occurred, followed by migration of the chemical from the front to the back section of the charcoal tube. However, in the refrigerated condition, the migration was so small that 4-vinyl-1-cyclohexene could not be detected on the back section of the refrigerated charcoal tube.

To prevent the migration and loss of 4-vinyl-1-

cyclohexene samples collected on the charcoal tube, the sample should not be stored for more than 7 d at room temperature or more than 21 d in a refrigerated condition. It is highly recommended that charcoal tubes containing 4-vinyl-1-cyclohexene be stored in a refrigerated condition and analyzed within 7 d in order to obtain reliable results.

Conclusion

4-Vinyl-1-cyclohexene vapor can be sampled using a charcoal tube and analyzed by GC. The method detailed above for sampling and analysis of 4-vinyl-1-cyclohexene has high accuracy and precision and can be used for monitoring low concentrations of 4-vinyl-1-cyclohexene in a working environment.

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