

Exposure Assessment of ETBE in Gas Station Workers and Gasoline Tanker Truck Drivers

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Abstract: Exposure Assessment of ETBE in Gas Station Workers and Gasoline Tanker Truck Drivers:

Yoko EITAKI, *et al.* Department of Preventive Medicine and Public Health, School of Medicine, Keio University—Objectives:

In order to measure occupational exposure concentrations of ethyl *tertiary*-butyl ether (ETBE), we developed a diffusive sampling method for monitoring ETBE and performed an ETBE exposure assessment. **Methods:** The applicability of diffusive samplers was examined by exposing the samplers to ETBE vapor in test chambers. The personal exposure levels of workers and airborne concentrations were measured at 4 gas stations. **Results:** The ETBE sampling rate for the diffusive samplers (VOC-SD, Sigma-Aldrich Japan) was 25.04 m³/min (25°C). Compared with the active sampling method, the diffusive samplers could be used for short-term measurements and in environments containing a mixture of organic solvents. The geometric mean (GM) of TWA-8h ETBE was 0.08 ppm (0.02–0.28 ppm) in 28 gas station workers and 0.04 ppm (0.01–0.21 ppm) in 2 gasoline tanker truck drivers. With regard to ETBE airborne concentrations, the GM was 4.12 ppm (0.93–8.71 ppm) at the handles of hanging pumps but dropped to less than 0.01 ppm (less than 0.01–0.01 ppm) at the side of a public road. **Conclusion:** The diffusive sampling method can be used for the measurement of occupational ETBE exposure. The threshold limit of TLV-TWA 5 ppm recommended by the ACGIH was not exceeded in any of the workers in this study.

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Ethyl *tertiary*-butyl ether (ETBE; CAS No. 637-92-3; molecular weight, 102.18; boiling point, 72.78 °C) is synthesized from 2-methylpropene (CH₂C(CH₃)₂, CAS No. 115-11-7) derived from petroleum and plant-derived ethanol and is thus considered a biofuel. Japan began selling ETBE-blended gasoline on a trial basis in April 2007. The number of stores selling ETBE-blended gasoline has gradually increased, and Japan supplied 780,000 kl of ETBE in fiscal 2010.

Some toxicological data on the hazards of ETBE are available. In a 4-week inhalation study, a no-observed-adverse-effect level (NOAEL) of 500 ppm was indicated for neurotoxic effects in rats¹. In a 90-day inhalation study, a NOAEL of 500 ppm was indicated for testicular lesions in male rats². Additionally, in a 2-hour male volunteer inhalation study at 0, 5, 25, and 50 ppm, slight but statistically significant decreases were observed in pulmonary function measurements at 25 and 50 ppm. Therefore, 5 ppm is the NOAEL for pulmonary function in humans³. ACGIH recommended a threshold limit value-time weighted average (TLV-TWA) of 5 ppm for occupational exposure to ETBE. However, sufficient data were not available to recommend carcinogenicity notations in 2000⁴.

The results of carcinogenicity tests were released in 2010. There were no incidences of tumors in a 2-year oral administration study in male and female rats. The incidences of hepatic adenoma increased in a 2-year inhalation study in male rats, and the NOAEL was 1,500 ppm. Fifteen parts per million was recommended as a reference value for ETBE carcinogenicity, and this value was obtained by multiplying the NOAEL from this study by 1/100 as an uncertainty factor, 1/10 for the species difference and 1/10 for individual differences⁵.

This study aimed to assess exposure to ETBE of gas station workers and gasoline tanker truck drivers who, because of their occupations, are assumed to be exposed to relatively high concentrations of ETBE. Initially, we performed an experiment to examine the applicability of

diffusive samplers. Thereafter, we conducted exposure measurements at 4 gas stations.

Materials and Methods

Experimental examination of the diffusive samplers

Diffusive samplers (VOC-SD, Sigma-Aldrich Japan, Tokyo, Japan) were attached with perforated holders (No. 28222-U, Sigma-Aldrich Japan, Tokyo, Japan) to prevent the fine pores in the surfaces of the diffusive samplers from touching the workers' clothes. The diffusive samplers were exposed to ETBE vapor in test chambers at 3 concentrations, low, medium and high, for 1, 2, 4 and 8 h.

This test chamber system has been used to confirm the sampling rates of other volatile organic compounds for diffusive samplers⁶⁻⁹. The ETBE vapor in exposure chambers was generated by bubbling air through liquid ETBE, followed by dilution of the dense ETBE vapor with fresh air. The ETBE concentrations in each chamber were confirmed using an active sampling method with pumps (Pocket Pump, SKC, Eighty Four, PA, USA) and activated carbon tubes (No.258, GASTEC, Ayase, Kanagawa, Japan) once every hour. The room temperature was maintained at 25 °C, and the relative humidity was kept at 57%.

After sampling, the absorbents from diffusive samplers and activated carbon tubes were extracted with 1 ml of carbon disulfide (>98%, Wako Pure Chemical Industries, Osaka, Japan) spiked with 1.5 ppm (volume/volume) *tertiary*-butyl benzene (CAS No. 98-06-6, >98.0%, Tokyo Chemical Industry, Tokyo, Japan) as an internal standard. The extract was introduced to a gas chromatography column equipped with a flame ionization detector (GC/FID, GC6890, Agilent Technologies, Santa Clara, CA, USA) set as shown in Table 1. The calibration curve showed linearity at concentrations from 0 to 112.3 µg/ml with a good correlation ($r=1.00$). The limit of quantification of the analytical instrument was 0.1 µg/ml.

The recoveries of the activated carbon tubes were determined as follows: a known amount of ETBE liquid (1.2 µg or 120 µg) was added to the first layers ($n=4$, respectively); fresh air was passed through the tubes at a flow rate of 50 ml/min for 1 h; the layers were extracted; and the amount of ETBE in the first and second layers was quantified with a GC/FID.

The extraction efficiencies of the diffusive samplers were determined as follows. A known amount of ETBE liquid (1.2 µg or 120 µg) was added to the absorbents ($n=4$, respectively), after which they were allowed to stand for 1 h for absorption of the compound. The absorbents were then extracted, and the amount of ETBE was quantified with a GC/FID.

Diffusive and active sampling of airborne ETBE were performed simultaneously at concentrations of approximately 5 ppm for 15 min to confirm whether the

sampling rate of the diffusive samplers was constant in the short-term exposure ($n=9$ each).

The diffusive samplers, attached with or without perforated holders, were exposed to airborne ETBE at concentrations of approximately 5 ppm for 15 min to confirm the rate at which the sampling rates varied ($n=9$ each).

Diffusive sampling and active sampling were performed simultaneously in the vapor generated by bubbling air through ETBE-blended gasoline, as opposed to pure ETBE liquid, at several concentrations for 1 h. The ETBE-blended gasoline was kindly supplied by the Petroleum Association of Japan. The purpose of this test was to confirm that other volatile compounds contained in gasoline did not inhibit ETBE absorption on the surface of the absorbent and that the diffusive samplers were able to maintain a constant sampling rate ($n=6$ each).

Field study

Four gas stations selling ETBE-blended gasoline were investigated for 2 days in February and March 2009. ETBE was blended with regular gasoline at a proportion of 7%. Premium gasoline, light diesel oil and kerosene did not include ETBE. None of the gas stations we investigated had introduced a stage 2 vapor recovery system, which would collect the vapor that blows out from car tanks when gasoline is pumped.

Four to 6 workers were selected from each gas station. Their personal exposures were measured throughout their shifts, including during pump operation, car washing, kerosene delivery and break times. The personal exposures of 2 gasoline tanker truck drivers were measured while unloading at a gas station. Unloading from the tanker trucks to underground tanks required approximately 1 h, including the unloading of light diesel oil and other fuels not containing ETBE. Personal exposures while loading at the oil refinery and driving between the refinery and gas stations were not measured. The workers fastened the diffusive samplers to their collars for measurement. Placement and replacement of the samplers was done by researchers, and the workers were asked not to touch the samplers to avoid contamination with gasoline liquid on their hands. None of the workers used respirators.

Airborne ETBE concentrations were measured in the vicinities of pumps fixed to the ground, pumps hanging from a canopy, maintenance rooms and indoor cash registers at the gas stations and at the side of a public road. The diffusive samplers were suspended at a height of 1–1.5 m from the ground for approximately 12 h, from opening to closing of the store. Both personal exposures and airborne concentrations were measured using the diffusive samplers with perforated holders attached.

After measurement, the absorbent was removed from the samplers and extracted with 1 ml carbon disulfide (low benzene grade, Sigma-Aldrich Japan, Tokyo, Japan)

Table 1. Instrumental parameters of GC for ETBE analysis

	Experimental measurement	Environmental measurement
Type of detector	Flame ionization detector	Mass spectrometer
Injection volume	2 μ l	1 μ l
Injection condition	250°C, split mode (split ratio 5:1)	250°C, pulsed split mode (split ratio 1:1)
Carrier gas	Helium 5 ml/min	Helium 1.2 ml/min
Oven temperature	35°C (13 min)→7°C/min→160°C (0 min)→ 20°C/min→250°C (3 min)	35°C (10 min)→5°C/min→125°C (0 min)→ 20°C/min→260°C (5 min)
Column	DB-1, 60 m × 0.53 mm × 1 mm, Agilent Technologies, Santa Clara, CA, USA	DB-1, 60 m × 0.25 mm × 1.5 mm, Agilent Technologies, Santa Clara, CA, USA
Detector temperature	260°C	250°C
Ionization method	–	Electron Impact ionization
Ions	–	ETBE: quantify m/z = 59, qualify m/z = 87 Toluene-d8: quantify m/z = 100, qualify m/z = 99

spiked with 2 μ g/ml toluene-d8 (1 mg/ml methanol solvent, Kanto Chemical, Tokyo, Japan) as an internal standard. The extract was introduced to a gas chromatography column equipped with a mass spectrometer (GC/MS, GC 6890/MSD 5973N, Agilent Technologies, Santa Clara, CA, USA) set as shown in Table 1. The calibration curve obtained was linear at concentrations of 0–114 μ g/ml with a good correlation ($r=0.999$). The limit of quantification of the analytical instrument was 0.01 μ g/ml.

Statistical analysis

For comparison of the 2 sampling methods, orthogonal regression models were conducted using the JMP version 7 statistical software to consider the error of the variable X. Other linear regression models were conducted using Microsoft Office Excel 2003.

Results

Experimental examination of the diffusive samplers

When the ETBE levels from the diffusive samplers (μ g) were plotted on the y-axis against the exposure duration (h) on the x-axis, it was found that the amount of ETBE collected was linearly related to the exposure duration (Fig. 1). The regression lines were used to calculate correlation coefficients, all of which were >0.99 . The calculated slopes were 20.23, 31.65, and 51.37 at concentrations of 3.6, 4.6 and 8.4 ppm, respectively.

Linearity was also observed when the same data were rearranged against the exposure concentrations (ppm) on the x-axis, and the regression lines were used to calculate

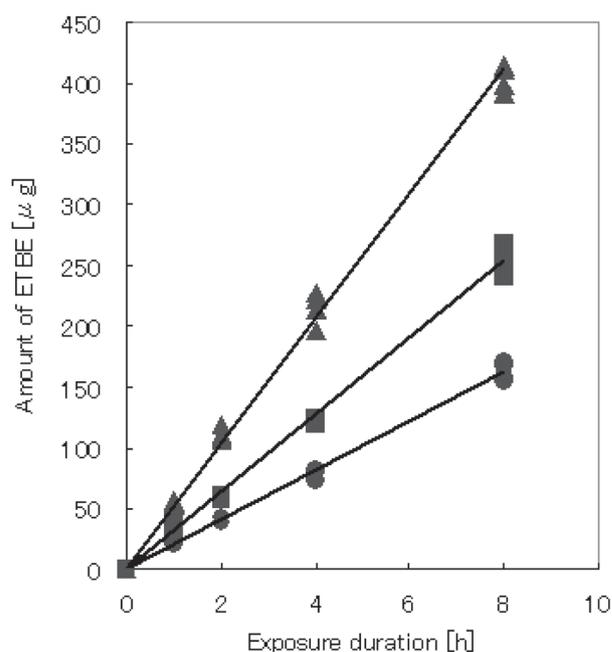


Fig. 1. Correlation between the amount of ETBE collected in the diffusive sampler (μ g) and the exposure duration (h). ●: Chamber concentration of 3.6 ppm, $y=20.23x$, $r=1.00$. ■: Chamber concentration of 4.6 ppm, $y=31.65x$, $r=1.00$. ▲: Chamber concentration of 8.4 ppm, $y=51.37x$, $r=1.00$.

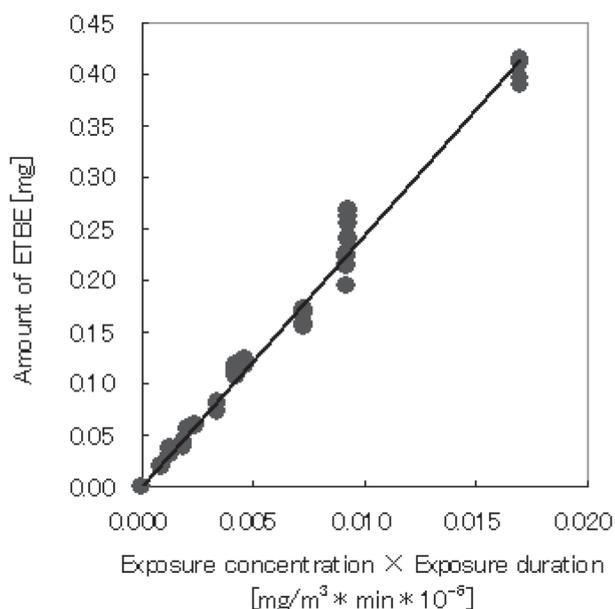


Fig. 2. Correlation between the amount of ETBE collected in the diffusive sampler (mg) and the product of exposure concentration (mg/m^3) and exposure duration (min) using 10^{-6} as the factor to convert from m^3 to ml. Equation: $y=25.04x$, $r=0.99$.

correlation coefficients of >0.97 . The calculated slopes were 6.65, 12.77, 24.03, and 48.93 at the exposure durations of 1, 2, 4 and 8 h, respectively.

The amount of ETBE collected was expressed as a function of exposure concentration and exposure duration. The ETBE collected in the diffusive samplers (mg) was plotted on the y-axis against the product of exposure concentration (mg/m^3), and exposure duration (min), using 10^{-6} as the factor to convert the units on the x-axis from m^3 to ml (Fig. 2). Linearity was observed, and the regression line was used to calculate a correlation coefficient of >0.99 . The slope of the regression line, 25.04, was the sampling rate of ETBE (ml/min) in the case of the diffusive samplers attached with a perforated holder.

The average ETBE recoveries, at the concentrations of $1.2 \mu\text{g}/\text{ml}$ and $120 \mu\text{g}/\text{ml}$ from the activated carbon tubes were 92.5 and 101.4%, respectively, and the coefficients of variance (CVs) were 10.0 and 4.8%, respectively. ETBE was not detected in the second layers of the tubes. The average ETBE extraction efficiencies at the concentrations of $1.2 \mu\text{g}/\text{ml}$ and $120 \mu\text{g}/\text{ml}$ of the diffusive samplers were 93.6% and 101.6%, respectively, and the CVs were 0.9 and 2.8%, respectively. The average ETBE concentrations in each chamber measured by the active sampling method once every hour were 3.6, 4.6 and 8.4 ppm, and the CVs for the 8-h measurements were 6.0, 11.9 and 10.9%, respectively.

The validation of short-term exposure was examined at concentrations from 2.6 to 5.9 ppm, as measured by active sampling. The airborne ETBE concentrations obtained using diffusive sampling were plotted on the y-axis against those obtained using active sampling on the x-axis. The orthogonal regression analysis yielded the linear equation: $y=0.98x + 0.12$, with $r=0.99$; the variance ratio was 1. The confidence interval of the slope was between 0.80 and 1.20 when the significance level was 0.1.

The effect of perforated holders was examined at concentrations from 3.7 to 9.2 ppm, and measurements were recorded using diffusive samplers with perforated holders attached. The amounts of ETBE collected using diffusive samplers with perforated holders were plotted on the y-axis against collections made without perforated holders on the x-axis. The linear regression analysis yield the linear equation: $y=0.73x$, with $r=0.95$. Attachment of the perforated holders to diffusive samplers reduced the amount of ETBE collected to 73%.

The effect of other volatile organic compounds was examined at concentrations from 0.3 to 4.5 ppm, as measured by active sampling. The airborne ETBE concentrations measured by diffusive sampling were plotted on the y-axis against those measured by active sampling on the x-axis. The orthogonal regression analysis yielded the linear equation: $y=1.16x + 0.03$, with $r=1.00$; the variance ratio was 1. The confidence interval of the slope was between 1.13 and 1.19 at the significance level of 0.1.

Field study

In the field study, GC/MS was used for determination of ETBE because it is superior to GC/FID in terms of selectivity. Figure 3 shows typical chromatograms of the airborne samples collected at the gas stations. Some peaks overlapped with the ETBE peak on the total ion chromatogram for which all mass numbers were scanned. On the other hand, no peaks overlapped with the ETBE peak on the selected ion chromatogram for which only the ETBE quantifying ion of $m/z=59$ was counted. Consequently, the amount of ETBE was not overestimated when it was determined with GC/MS in the select ion mode.

The limit of quantification for the personal exposures and airborne ETBE concentrations in the 8-hour measurements was calculated as 0.001 ppm, factoring in the sampling rate of the diffusive sampler and the limit of quantification of GC/MS.

Table 2 shows profiles of the gas stations examined in the present study and the measurements of the personal exposures of the workers and airborne ETBE concentrations.

Airborne ETBE concentrations

The handles of hanging pumps had the highest airborne

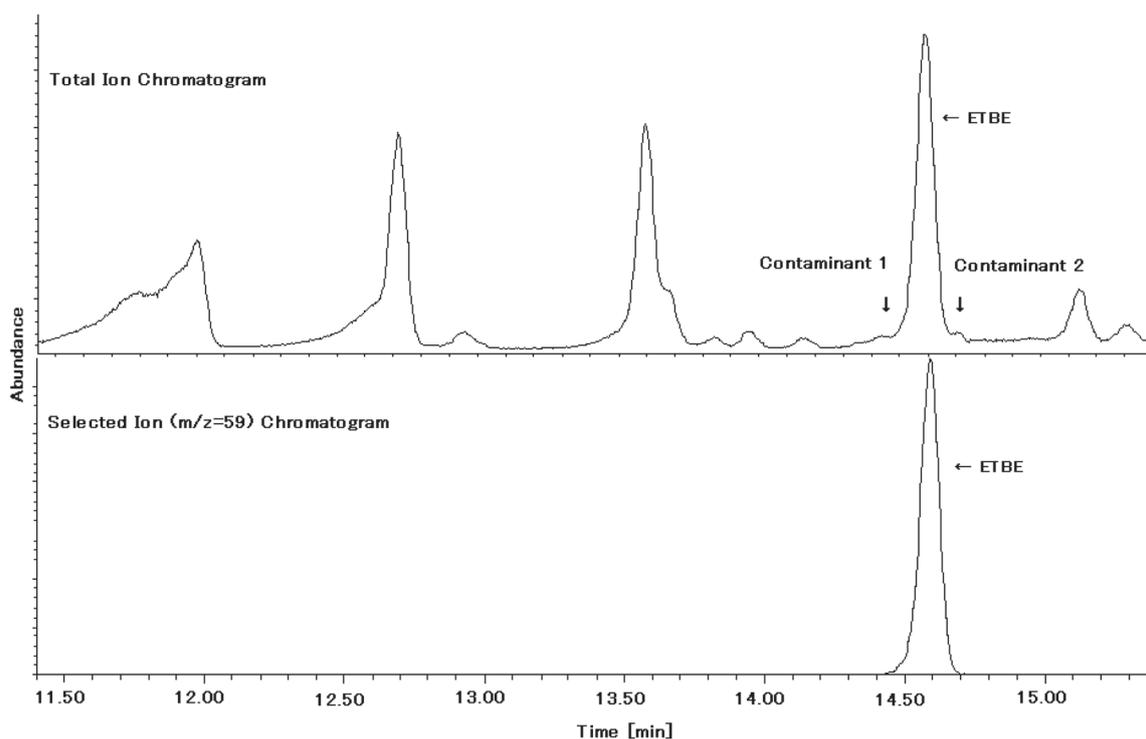


Fig. 3. Chromatograms of an airborne sample collected at a gas station analyzed with GC/MS. Some peaks are overlapping with the ETBE peak in the total ion chromatogram (upper). The ETBE peak is free from overlapping peaks in the selected ion chromatogram (lower).

ETBE concentrations (geometric mean (GM), 4.12 ppm) because measurements were recorded close to the fuel nozzles, at a distance of approximately 50 cm. Lower concentrations of ETBE were found in the vicinity of ground-fixed pumps (GM, 0.06 ppm) than close to the handles of hanging pumps, because measurements were recorded at a distance of 1–2 m from the fuel nozzles.

The maintenance rooms were surrounded by walls on 3 sides but were open on 1 side, allowing ETBE vapor to diffuse into the atmosphere immediately, if ETBE-blended gasoline leaked inside. Additionally, the maintenance rooms were located at a great distance from the pumps suspected to be the main sources of ETBE vapor. Consequently, the airborne concentrations here dropped to a GM of less than 0.01 ppm.

Low concentrations (GM, 0.01 ppm; range, less than 0.01–0.16 ppm) of ETBE were found in areas where the workers entered during their working hours, in the vicinities of ground-fixed pumps (GM, 0.06 ppm; range, 0.02–0.16 ppm), in the vicinities of unloading holes (GM, 0.01 ppm; range, less than 0.01–0.01 ppm), at indoor cash registers (GM, 0.01 ppm; range, less than 0.01–0.01 ppm) and in maintenance rooms (GM, less than 0.01 ppm; range, less than 0.01–0.01 ppm).

Measurements were recorded at the side of a public road to observe the effects of the gas station on the surrounding

neighborhood; low concentrations were found in the neighborhood (GM, less than 0.01 ppm; range, less than 0.01–0.01 ppm).

Workers' personal exposure

For the gas station workers, the GM of their personal exposures taken as 8-hour time-weighted averages (TWA-8h) was 0.08 ppm for all 4 gas stations. However, all of the workers worked for over 8 h on the measurement days, including the casual staff. High concentrations (GM, 4.12 ppm) were found at the pump handles, which are usually close to vapor-generating sources. However, the level of exposure to ETBE of gas station workers was lower than the levels measured at the pumps. In Japan, the pumps at full-service gas stations continue to pump gasoline even if the operators lose their grip after they insert the nozzle. However, the pumps at self-service gas stations have an accident prevention mechanism that stops pumping if the operator releases the handle. Additionally, gas station workers usually let go of the pump nozzle so that they can wipe the windows of the car or to check the tire pressure while they wait for pumping to complete. This allows workers to keep away from the source of gasoline vapor as it is generated and may help to reduce the overall exposure of gas station workers to ETBE during the course of their shifts.

Table 2. Profiles of the gas stations examined in the present study and measurements of the personal exposures of the workers and airborne samples

	Store A	Store B	Store C	Store D	Total
Weather, temperature and relative humidity on the first day	Rainy 10°C 56–85%	Cloudy 11°C 50–78%	Fine 8°C 10–40%	Rainy 9°C 58–78%	–
Weather, temperature and relative humidity on the second day	Rainy 10°C 58–76%	Cloudy 11°C 30–50%	Cloudy 5°C 28–78%	Fine 11°C 22–42%	–
Amount of regular gasoline pumped per day	2.3 kl	3.8 kl	5.0 kl	2.2 kl	3.3 kl on average
Percentage of regular gasoline in daily sales	70%	70%	70%	30%	–
Type and number of pumps	Hanging 4 Ground-fixed 0	Hanging 0 Ground-fixed 4	Hanging 2 Ground-fixed 3	Hanging 4 Ground-fixed 0	–
Number of sides open at store	2	2	1	2	–
Gas station workers' personal exposures TWA-8h*					
n	8	6	8	6	28
GM	0.06	0.22	0.08	0.05	0.08
GSD	1.75	1.20	1.81	1.53	2.05
Range	0.03–0.13	0.17–0.28	0.02–0.15	0.03–0.10	0.02–0.28
Tanker truck drivers' personal exposures TWA-8h					
n	1	0	1	0	2
GM	0.21	–	0.01	–	0.04
GSD	–	–	–	–	10.65
Range	–	–	–	–	0.01–0.21
Handles of hanging pumps					
n	6	0	4	4	14
GM	4.71	–	2.38	5.80	4.12
GSD	1.71	–	2.22	1.17	1.88
Range	2.25–8.71	–	0.93–6.18	4.65–6.80	0.93–8.71
Vicinity of ground-fixed pumps					
n	0	6	4	0	10
GM	–	0.04	0.12	–	0.06
GSD	–	1.78	1.64	–	2.13
Range	–	0.02–0.09	0.06–0.16	–	0.02–0.16
Indoor cash registers					
n	1	1	1	1	4
GM	0.01	< 0.01	< 0.01	0.01	0.01
GSD	–	–	–	–	2.51
Range	–	–	–	–	< 0.01–0.01
Maintenance rooms					
n	2	2	2	2	8
GM	0.01	< 0.01	< 0.01	0.01	< 0.01
GSD	1.36	3.97	1.57	1.14	3.44
Range	0.01–0.01	< 0.01–0.01	< 0.01–< 0.01	0.01–0.01	< 0.01–0.01
Side of a public road					
n	2	2	2	2	8
GM	0.01	0.01	< 0.01	< 0.01	< 0.01
GSD	1.40	1.60	2.75	1.10	3.33
Range	0.01–0.01	0.01–0.01	< 0.01–0.01	< 0.01–< 0.01	< 0.01–0.01

Units : ppm. n: number of measurements. GM: geometric mean. GSD: geometric standard deviation. *: TWA-8h=Averaged exposure concentration × working time / 8 h.

The exposure of 1 of the 2 gasoline tank truck drivers to ETBE was 1.10 ppm during a 90-minute unloading operation, whereas that of the other was 0.08 ppm during a 43-minute unloading operation. The exposure level during the unloading operation at 1 gas station was converted to a TWA-8h based on the assumption that the driver was not exposed to ETBE for the rest of his shift. The TWA-8h was calculated to be the lower exposure level of GM 0.04 ppm. However, we did not measure exposure during the loading of gasoline into tanker trucks at oil refineries; additionally, the chances for exposure would increase if a driver were to unload at several stations in 1 day.

Discussion

Experimental exposure and vapor generation

The average CV for the concentration of ETBE vapor in the chambers was 10% at concentrations 3.6–8.4 ppm during the examination. The chambers were sufficiently stable to be used as exposure chambers, which is consistent with other studies using the same type of system with CVs of 14% (dimethylformamide, 2.6–58.6 ppm)⁶, 5% or less (1-butanol, 0–400 ppm)⁷, 5% or less (2-bromopropane, 0–1,500 mg/m³.⁸) and less than 5% (dichloromethane, 0–400 ppm)⁹.

Sampling rate of the diffusive sampler

Some investigators have argued that sampling rates can be calculated by applying some characteristic value of a compound with a known sampling rate, such as the molecular weight, to theoretical formulas. That is, compounds with similar molecular weights would have similar sampling rates. The ETBE sampling rate obtained in this study is 25.04 ml/min. The sampling rate without a perforated holder was calculated as 34.30 ml/min because the perforated holder decreased the collection efficiency of the diffusive sampler to 73%. The manufacturer of the VOC-SD diffusive sampler has published the sampling rates of certain compounds, such as 37.33 ml/min for methyl isobutyl ketone (molecular weight (MW), 100.16), 39.84 ml/min for heptane (MW, 100.21) and 38.52 ml/min for ethyl benzene (MW, 106.17). Therefore, it can be shown that the sampling rate obtained in this examination of ETBE (MW 102.17) is close to the sampling rates of compounds with similar molecular weights.

Validation tests

To prove the validity of the diffusive sampling method, we showed that equivalent values were obtained using the diffusive sampling method and the active sampling method, because the active sampling method has been commonly used for workplace measurements. We used the 2 methods simultaneously, and applied the values for the ETBE airborne concentration, determined by each

method, to an orthogonal regression analysis. The variance ratio was taken to be 1 because the extraction and analytical steps for GC/FID are the same for both methods, and therefore, the measurement errors should also be the same. The slope of the regression line is close to 1, and the lower and upper confidence intervals of the slope are 0.8 to 1.25, respectively, when the significance level is 0.1, indicating the equivalence of these 2 sampling methods.

Workers' personal exposure

In the present study, the highest TWA-8h for a gas station worker was 0.28 ppm, and that for a tanker truck driver was 0.21 ppm. None of the examined workers had a TWA-8h exceeding TLV 5 ppm, the threshold recommended by the ACGIH. In addition, when the TLV for ETBE is regarded as a permissible exposure level and the action level of ETBE is defined as one-half the value of the permissible exposure level, each maximum value does not exceed the action level. The action level is the point at which certain provisions to prevent exposure must be initiated¹⁰.

We also attempted to estimate the upper limit of the sample population and assess the results considering day-to-day fluctuations. The Ministry of Health, Labour and Welfare of Japan has issued guidelines for assessing the occupational exposure of workers to hazardous materials¹¹. According to these guidelines, either the maximum measurement value or the estimated upper limit of the 90% confidence interval in a t-distribution, whichever is higher, is applied to estimate the maximum of TWA-8h. For gas station workers, the estimated upper limit (0.29 ppm) is higher than the maximum measurement value (0.28 ppm) and is lower than TLV 5 ppm. This means that the present exposure risk is low. We examined only 2 tanker truck drivers in the present study, and this number is insufficient for assessment by this method.

Matsunaga *et al.* proposed a personal exposure assessment method that takes day-to-day exposure fluctuations into account¹². The day-to-day fluctuations in personal exposure are derived from systematic errors and random errors. Systematic errors consist of changes in the working method, the opening or closing of windows in the workplace, performance degradation of ventilating systems, and so on. Random errors consist of changes in the workload, wind direction and velocity, temperature and humidity. It can be assumed that the frequency distribution of a series of TWA-8h values for 1 worker over several months would show a lognormal distribution, if the systematic errors were negligible.

The 95% upper limit (X_{95}) and arithmetic mean (μ) of the distribution of TWA-8h values, which were estimated from the GM and geometric standard deviations (GSD) of the measured values, were used for evaluation. X_{95} is used for toxicities that have greater effects at the maximum

concentration than at the average concentrations, such as allergic toxicity, acute toxicity, and subacute toxicity; μ is an index of the accumulative exposure¹³.

For assessment of exposure of gas station workers, either the GSD calculated at each gas station (1.20–1.81 ppm) or the GSD calculated for all gas station workers (2.05 ppm) could be used to calculate X_{95} or μ , indicating a 95% chance of not exceeding the threshold limit. Similarly, the 2 tanker truck drivers were assessed using the GSD (10.65 ppm). The calculated values for X_{95} and μ showed a 50–95% chance of not exceeding the threshold limit, and reexamination is necessary.

In Europe and the United States, a compound of similar structure, methyl tertiary-butyl ether (MTBE, $\text{CH}_3\text{OC}(\text{CH}_3)_3$, CAS No. 1634-04-4), was added to gasoline for oxygenation or octane enhancement purposes in the 1990s. Immediately thereafter, the problem of MTBE in gasoline entering groundwater from leaks in the old gas station tanks was realized. Therefore, the use of MTBE has declined in recent years.

The International Programme on Chemical Safety reviewed the effects of MTBE¹⁴. The median of long-term (30 min to 8 h) exposure levels was 0.5 ppm in the gas station workers examined. The median of long-term exposure levels was 0.5 ppm (range, 0.01–6.2 ppm) in the gasoline tanker truck drivers examined. However, the loading of MTBE-blended gasoline into trucks and the delivery of gasoline were included in the data obtained for the tanker truck drivers' exposure levels, in addition to the measurements taken while unloading at gas stations. A comparison of these data showed that the present ETBE measurements are fractions of the MTBE measurements.

In addition, measurement of the exposure of tanker truck drivers to MTBE was conducted in summer and winter in Helsinki, Finland¹⁵, and there was a seasonal difference, the geometric mean of the breathing-zone concentration of MTBE was 4.3 mg/m³ in October (the air temperature was -4.9 °C), and 6.4 mg/m³ in August (14.1 °C). Organic solvents are vaporized more easily at a higher air temperature. The mean air temperature is 27–29 °C in summer in Tokyo and Osaka; therefore, airborne ETBE concentrations and workers' ETBE exposure will be higher in summer than those shown in the results of the present study.

In conclusion, the VOC-SD diffusive sampler can be used for measurement of exposure to ETBE for 15 min to 8 h. The ETBE sampling rate of a VOC-SD attached with a perforated holder is 25.04 ml/min. A low concentration of ETBE, 0.001 ppm, can be determined in an 8-hour measurement. In the field study, the GM of TWA-8h ETBE was 0.08 ppm (0.02–0.28 ppm) in 28 gas station workers. Even when considering individual day-to-day fluctuations or when estimating the maximum of the population, the probability of exceeding the TLV of 5 ppm is low. The GM of TWA-8h ETBE was 0.04 ppm (0.01–

0.21 ppm) for the 2 gasoline tanker truck drivers. None of the workers in this study exceeded the TLV. However, further studies need to be conducted to assess a larger number of tanker truck drivers. The airborne concentrations were from less than 0.01 to 0.01 ppm at the side of a public road; hence, the effect of ETBE released from the gas station on the surrounding neighborhood was negligible.

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