ORIGINAL ARTICLES

Determination Method for Methyl Iodide Using Diffusive Sampler and Capillary GC With Thermal Desorption Injector and FID

Sei-ichiro KANNO

National Institute of Industrial Health
21-1, Nagao 6-chome, Tama-ku Kawasaki 214, Japan

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Abstract: A determination method for methyl iodide in the work place has been developed, using a diffusive sampler and a capillary gas chromatograph with a thermal desorption cold trap injector and an FID. The sampler consists of a glass tube (6 mm o.d., 4 mm i.d., 16 cm length) packed with porous polymer beads. The diffusion path of the sampler is made of a 3 mm i.d., 52 mm length poly (terafluoroethylene) tube inserted in the glass tube. The sampling rate of the sampler for methyl iodide was 4.6 ml/h, and variations caused by temperature, relative humidity, and wind speed were found to be small and negligible. The sample could be stored for at least two weeks without significant loss. A time-weighted average concentration of methyl iodide in the range of sub ppm to ppm for two to six hours can be measured by this method. The average concentration of methyl iodide for a period of a few seconds can also be measured by grab sampling, i.e., injecting 20 ml of air directly into the sampler.

Key words: Personal Sampler-Diffusive Sampler-Methyliodide-Thermal Desorption-GC

INTRODUCTION

Methyl iodide (MeI) is a colorless liquid used as a methylating agent. it is a suspected carcinogen. The administrative level assigned for it is 5 ppm in Japan.

There are several analytical methods for methyl iodide using an active charcoal sampler or direct sampling or a detection method using an electron capture detector. Methyl iodide, however, is easily hydrolyzed on an activated charcoal surface or decomposes in the bag used for direct sampling of air (see footnote).

1 A Part of methyl iodide, adsorbed by a sampler packed with graphite adsorbent (Carbotrap or Carbosieve) and stored for three days, decomposed, and methanol was produced. The concentration of methyl iodide stored in a Tedler bag wrapped with aluminum foil decreased by more than 30% within a day.
Therefore, these methods have serious limitations. In this study, a tube-type diffusive sampler and a gas chromatographic analysis with thermal desorption have been applied to analyze methyl iodide in the atmosphere. The major advantages of the tube-type sampler are that sampling rate is not affected by wind speed because of its low sampling rate and that it can be used as a grab sampler by injecting sampled air by gas-tight syringe.

**Experimental**

*Sampler (Fig. 1)*

The sampler was made of a glass tube (borosilicate glass, 6 mm o.d., 4 mm i.d., 16 cm length) packed with 400 mg of porous polymer beads (Porapak Q, 50/80 mesh, Waters Associates, Inc., Milford). A stainless steel screen (100 mesh) was placed 52 mm from one end of the tube, then a Teflon tube (3 mm i.d., 52 mm length) was inserted. The polymer beads were poured from the other end of the tube and plugged with glass wool.

The sampler was conditioned once by heating at 220°C for three hours under nitrogen flow to prevent oxidation, and stored capped at both ends with Swagelock Caps and Teflon ferrules. The sampler was used repeatedly without subsequent conditioning, because the thermal desorption step desorbed contaminants, and the sampler was sufficiently cleaned.

*Exposure System (Fig. 2)*

MeI vapor was generated by a diffusion tube method. The diffusion path was made of a glass capillary (0.32 mm i.d., 10 cm length). The temperature of the diffusion tube was kept constant with a water jacket and a temperature controller. The air vapor mixture was diluted with humidified air to the desired concentration, and fed to an exposure chamber. The flow rate of the test air was

![Fig. 1. Sampler.](image-url)

1. Porapak Q, 50/80 mesh 40 mg.  2. Teflon tube 3 mm i.d. and 52 mm length.  3. Stainless steel screen 100 mesh.  4. Glass wool.  5. Swagelock caps.  6. Glass tube 6 mm o.d., 4 mm i.d. and 16 cm length.
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Fig. 2. Exposure System.
The diffusion tube and the exposure chamber were enclosed in separate thermostats.

Fig. 3. Thermal Desorption Cold Trap (TCT) Injector and GC.
A gas chromatograph (HPS890) equipped with a fused silica capillary column (Poraplot Q 0.32 mm i.d., 10 m length), an FID detector, and a TCT (Chrompack) was used to analyze the sample.
between 0.5 and 4.5 L/min.

The exposure chamber was made of a glass jar (Culstir double arms, Shibata Hario Glass, Tokyo) with a Teflon turntable on which maximum of six samplers can be mounted. The rate of rotation of the turntable was variable from 20 to 200 rpm. Wind speed during exposure was calculated from the dimensions and rotation rate of the turntable. The chamber was placed in a thermostat (IN61, Yamato Scientific, Tokyo) to control exposure temperature.

The samplers were set on the turntable after removing the caps at the asampling ends, and exposure was started by switching a 4-way valve. During exposure, a portion of the effluent of the exposure chamber was flown through a gas sampling loop and the concentration of MeI was monitored every 6 to 30 minutes, depending on the exposure time, by a gas chromatograph equipped with a photo ionization detector (PL52, HNU, Newton). An exposure (ppm•h), defined as the MeI concentration multiplied by the sampling time, was calculated from the monitor results. After the exposure, the open end of the sampler was sealed with a Swagelock Cap. The samplers were stored wrapped with aluminum foil to shield light.

Thermal Desorption Cold Trap (TCT) Injector and GC (Fig. 3)

A gas chromatograph (HP5890, Hewlet Packard, PaloAlto) equipped with a TCT (Chrompack, Middleburg), a fused silica capillary column (PoraPlot Q, 0.32 mm i.d., 10 m length, Chrompack), and an FID was used to analyze the sample. The operating conditions are summarized in Table 1.

The procedures of an analysis were as follows:

1. The cold trap was cooled to $-120^\circ$C.

2. The sampler was placed on the desorption heater block, and connected to the carrier gas line. Flow rate was 1.6 ml/min at 100$^\circ$C

3. The temperature of the heater block was raised to 180$^\circ$C and kept there for 8 min. The purge flow (2.5 ml/min) was vented through the magnetic valve.

4. The trap capillary was heated to 150$^\circ$C for 3 min to inject the sample to the capillary column, and the GC run sequence was started. The column oven temperature was programmed to be held for 1 min at 100$^\circ$C then raised at the rate of 5$^\circ$C/min to 145$^\circ$C. The retention time of MeI was 5.2 min.

5. After the run, the temperature of the cold trap was cooled to $-120^\circ$C, and the sampler was replaced with the next one and sealed with caps for reuse.

Grab Sampling

A 20 ml sample of test air was measured and injected into the sampler by 20 ml glass syringe connected to the exposure system through a 3-way valve (Hamilton, Reno). The samples were treated as those exposed to test air.
Breakthrough of the Sampler
The test air was introduced to the sampler that was kept at 25 °C at a flow rate of 24 ml/min, and the concentration of MeI in the effluent air was monitored. The breakthrough volume was defined as the volume of test air introduced before the MeI concentration in the effluent became more than 5% of that in the test air. The relative humidity (R.H.) of the test air was varied from 17 to 80%.

Calibration of Detector
The FID was calibrated by analyzing samples prepared by grab sampling of the standard gas. The standard gas was calibrated by gravimetry of the diffusion tube using an electromagnetic balance (Type 1000, Cahn Instruments Inc., Cerritos).

Adsorption Isotherm
Test air was passed to the diffusive sampler containing 30 mg of Porapak Q at a flow rate of 100 ml/min for more than one hour after the concentration of MeI in the effluent reached that in the test air, to ensure adsorption equilibrium. The concentration of MeI was varied from 0.6 to 12 ppm in repeated experiments. The adsorbed MeI was analyzed by the TCT-GC method described above.

<table>
<thead>
<tr>
<th>Table 1. Settings of TCT, GC, and FID</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>TCT</strong>: Chrompack TCT</td>
</tr>
<tr>
<td>Desorption:</td>
</tr>
<tr>
<td>Temperature of Cold Trap</td>
</tr>
<tr>
<td>Temperature of Sampler heater</td>
</tr>
<tr>
<td>Injection:</td>
</tr>
<tr>
<td>Temperature of Cold Trap</td>
</tr>
<tr>
<td>Temperature of the Sampler Heater</td>
</tr>
<tr>
<td>Pressure of Carrier Gas (He)</td>
</tr>
<tr>
<td><strong>Gas chromatograph</strong>: HP5890</td>
</tr>
<tr>
<td><strong>Column</strong>: PolaPlotQ (Chrompack, Middelburg, 0.32 mm i.d., 10 m length)</td>
</tr>
<tr>
<td>Initial Temperature</td>
</tr>
<tr>
<td>Program Rate</td>
</tr>
<tr>
<td>Final Temperature</td>
</tr>
<tr>
<td><strong>FID</strong>:</td>
</tr>
<tr>
<td>Pressure of Air</td>
</tr>
<tr>
<td>Pressure of Hydrogen</td>
</tr>
<tr>
<td>Flow Rate of Auxiliary He</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

*Calibration for Grab Sampling (Fig. 4)*

The calibration line was obtained by analyzing samples prepared by grab sampling.

The FID peak area counts showed an excellent linear relationship with MeI concentration. The calibration line was expressed as follows:

\[
\text{Peak Area Count} = 369 + 60500 \times \text{Concentration (ppm)} \quad (R^2 = 0.999)
\]

The breakthrough volume was about 850 ml, and was independent of relative humidity. The sample volume of 20 ml was less than 1/40 of the breakthrough volume, therefore, MeI sampled by the grab sampling method was considered to be quantitatively adsorbed by the polymer beads.

*Calibration for Diffusive Sampling (Fig. 5)*

The calibration line for diffusive sampling was obtained by analyzing the samplers exposed to several different concentrations of MeI under the condition of 25 °C, 50% R.H., and wind speed of 10 cm/s. Exposure and the amount of desorbed MeI (ng) showed a linear relationship, expressed as follows:

\[
\text{Amount of MeI (ng)} = -12.2 + 27 \times \text{Exposure (ppm. hour)} \quad (R^2 = 0.998)
\]

The sampling rate, derived from desorbed amount/exposure, was 4.6 ml/h, while the sampling rate calculated as DS/S (D: diffusion constant, S and L; cross section and length of the diffusion path), using D derived by the Hirschfelder formula, was 4.7 ml/h. They agreed well. Therefore, the sampled MeI was retained quantitatively in the sampler.

*Effect of Exposure Temperature (Fig. 6)*

The sampling rate seemed to decrease slightly with increase in the exposure temperature. The difference in the rates at -5 and 35 °C, however, was smaller than the overall reproducibility, which was 8%. Therefore, for practical purposes, the sampling rate was considered independent of the exposure temperature.

Theoretically, sampling rate should be proportional to temperature to the power of 0.5 to 1, as shown in Table 2. Because a fixed volume sample loop of GC at room temperature was used to monitor exposure concentration, the actual exposure concentration differed from the monitored concentration. The ratio of actual concentration at exposure temperature to measured concentration at room temperature was proportional to the reciprocal of the exposure temperature. Therefore, the sampling rate derived in this experiment should be proportional to the absolute temperature to the power of -0.5 to 0. The magnitude of variation
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Fig. 4. Calibration for Grab Sampling.
The calibration line was obtained by analyzing samples prepared by grab sampling.

\[ Y = 369 + 60500X (R^2 = 0.999) \]

Fig. 5. Calibration for Diffusive Sampling.
The calibration line for diffusive sampling was obtained by analyzing the samplers exposed to several different concentrations of Mel under the conditions of 25°, 50% R.H., and sampling period of 6 hours.

\[ Y = -12.2 + 27X (R^2 = 0.998) \]
Fig. 6. Effect of Temperature on Sampling Rate.

The sampling rates were plotted against the exposure temperatures. The line shows linear regression and the bars indicate standard deviation.

**Table 2. Temperature Dependence of Sampling Rate**

\[ Y = 4.3 + 0.0066X (R^2 = 0.083) \]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mel Concentration</td>
<td>1.7-2.4 ppm</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>48-55%</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>10 cm/min</td>
</tr>
<tr>
<td>Sampling Time</td>
<td>6 hours</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
F &= \frac{DSC}{L} \\
C &= \frac{P}{RT} \\
D &= D_o \left(\frac{T}{T_o}\right)^n \frac{P_t}{P} \\
F &= \frac{S}{L} \frac{D_o P_t}{R} \frac{T^{-1}}{P_t} = \frac{S}{L} \frac{D_o P_t}{R} \frac{T^{-1}}{P_t} \text{ Conc (ppm)} \\
K(T) &= \frac{S}{L} \frac{D_o P_t}{R} \frac{T^{-1}}{P_t} \\
\end{align*}
\]

where

\[
\begin{align*}
F &: \text{ diffusion rate (mol/time)} \\
D &: \text{ diffusion constant} \\
D_o &: \text{ diffusion constant at standard state} \\
S &: \text{ cross section} \\
L &: \text{ diffusion path length} \\
C &: \text{ concentration (mol/vol)} \\
P &: \text{ total pressure} \\
p &: \text{ partial pressure} \\
T &: \text{ temperature} \\
T_o P_t &: \text{ standard state} \\
\text{Conc} &: \text{ concentration (v/v such as ppm)} \\
m &: \text{ constant between 1.5 to 2} \\
K(T) &: \text{ sampling rate (vol/time)}
\end{align*}
\]
of the sampling rate was 5% when \( m = 1.5 \) (theoretical value of the parameter in formula 3 in Table 2) was assumed, and might not be distinguishable from experimental error.

**Effect of Humidity (Fig. 7)**

The relative response decreased slightly with the increase in relative humidity from 17 to 78%. The change in sampling rate was again negligible. The absence of an effect of humidity might be attributable to the low solubility of MeI in water, the hydrophobic nature of the adsorbent, and the fact that the amount of MeI adsorbed was less than 1 percent of the equilibrium amount.

**Effect of Wind Speed (Fig. 8)**

The sampling rate of MeI increased slightly with the increase in wind speed from 3 to 34 cm/s. The change was, however, negligible. This experiment was carried out within a low range of wind speed, because the effect of wind speed has been considered to be due to insufficient mixing of the air surrounding the sampler, and has been observed at a low wind speed range\(^6\). The ratio of the length to the diameter of the diffusion path of this sampler is 17, and the other wind effect due to the mixing of the air inside the diffusion path, which is reportedly small\(^7\) if the length/diameter is more than 3.5, was assumed to be small.

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**Fig. 7. Effect of Humidity on the Sampling Rate.**

Sampling rate is plotted against exposure humidity. The line shows a linear regression and the bars indicate standard deviation.
Effect of Exposure Concentration Change

The samplers exposed to four ppm of MeI for two hours and subsequently exposed to zero air (concentration of MeI less than 0.01 ppm, i.e., the detection limit of PID) for 4.5 hours retained 97% (c.v. = 4.1%, n = 3) of MeI, compared with the samplers without zero air exposure. Therefore, the rate of back diffusion considered to occur during zero air exposure was assumed to be small.

The adsorption isotherm of MeI at the ppm level was linear, as shown in Fig. 9. The rate of back diffusion is proportional to the equilibrium vapor pressure of MeI at the surface of the adsorbent, and is approximately constant during zero air exposure. Therefore, sample loss due to back diffusion is considered to be less than several percent of the total amount of adsorbed MeI.

Effect of Storage

Two sets of six samplers were exposed to 2.8 ppm of MeI for six hours at a relative humidity of 50%, temperature of 25°C, and wind speed of 10 cm/s. Three samplers were stored at −20°C, and the other three samplers were stored at 25°C, and wrapped with aluminum foil to shield light. After two weeks of storage, the samplers stored at −20 and 25°C retained 103% (c.v. = 8.1%), and 99% (c.v. = 4.5%), respectively, compared with the samples analyzed immediately after the exposure. Therefore, the samples could be stored at least two weeks without degradation, if samplers were sealed and shielded from light.

![Fig. 8. Effect of Wind Speed on Sampling Rate.](image)

Sampling rate is plotted against wind speed. The line shows a linear regression and the bars indicate standard deviation.
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CONCLUSION

A new analytical method for methyl iodide using diffusive sampling or grab sampling and thermal-desorption-GC analysis was presented. The method enables to measure time weighted average concentration of Mel for a long span (two to six hours) or for a very short span (few seconds) at ppm or sub ppm level. The sampling rate was not affected by ambient temperature, relative humidity, or wind speed. The sample could be stored for two weeks.

REFERENCE


Fig. 9. Adsorption Isotherm of Mel on Porapak Q at 25°C.
Test air containing 0.5 to 12 ppm of Mel was passed to a sampler containing 30 mg of Porapak Q. After equilibrium was reached, the sampler was analyzed, and the adsorbed amount of Mel was plotted against concentration.