MEASUREMENT OF VENTILATION RATE USING TRACER-GAS-DECAY METHOD WITH ISOBUTENE AND PHOTO IONIZATION DETECTOR

イソブテンとPIDを用いるトレーサーガス減衰法による換気回数の測定

Masahiro Hori* and Tadashi Mizoguchi**

換気回数の測定, 低地球温暖化係数トレーサーガス, 光イオン化検出器, イソブテン

1. Introduction

We saved energy to consume in buildings to decrease both the cost and the environmental load. One of the environmental load is emission of global warming gases such as carbon dioxide(CO₂). These gases bring about their global warming phenomenon because of the absorption of infrared rays emitted from the glove’s surface. On the other hand we have used carbon dioxides or sulfur hexafluoride as tracer gases to measure ventilation rates in buildings[1,2]. The sulfur hexafluoride has a high global warming potential(GWP). Today we are required to decrease emissions of both carbon dioxides and sulfur hexafluoride In tracer gases decay method for measurement of ventilation rates, a large amount of carbon dioxide is emitted at one time, and sulfur hexafluoride that is used in concentrations less than one hundredth of carbon dioxide is 23900 in GWP. In recent years nitrous oxide(N₂O) of 310 in GWP was proposed in ISO[3] as a tracer gas, and is used at a concentration of 50ppm. The product of the GWP and the operating concentration is significantly smaller than that of sulfur hexafluoride, while it is significantly larger than that of carbon dioxide used at approximately 2000 to 5000 ppm. On the other hand, carbon monoxide can be regarded as one of the tracer gases because its concentration level is less than 1ppm, except for smoking rooms and rooms in which combustion gas is directly emitted; for example, it was once applied to measurement in ice skating arenas[4]. However, it is hardly used nowadays to measure ventilation rates, it newly appears to be acutely harmful. Therefore, in this study, isobutene was proposed as a low-environment-load tracer gas instead of the above-mentioned gases. Its concentration was monitored with Photo Ionization Detector (PID).

Performance characteristics of this system were examined to create the procedures and the conditions for the measurement of the ventilation rate.

2. Material and Method

Isobutene(1-butene) liquidized gas in a 3 kg cylinder available on the market was used. The PID monitor used is a VOC monitor, PGM-7240 type made by RAE Systems Inc. A 10.6eV lamp was used for the monitor. While the zero was adjusted by clean air through a column packed with active carbon, PID monitors were calibrated with standard isobutene gas of 10 ppm. The outputs were normalized by isobutene and shown by ppm.

Sulfur hexafluoride was monitored by photo-acoustic Type 1302 of B & K Inc.(PAS). They have the function of a data logger and the outputs were recorded every minute. VOCs in an object room were collected with a charcoal tube and analyzed with CS₂ extraction and GC-MS. The ventilation rate was measured using the following procedures: the tracer gases were discharged from the respective cylinder into in an object room, and the air of the room was stirred with two fans. The output of the monitor was monitored during the measurement. The ventilation rate (VR) was calculated by the following formula.

\[
VR (N)= \left\{ \ln \left( C_{0} \right) - \ln \left( C_{t} \right) \right\} / t_{1} \cdots (1)
\]
Where $C_0$: Concentration at the starting time of time 0 when the rate of decease of tracer gas concentration in the room has observed to become approximately constant at $t_1$: Concentration at time when time $t_1$ (h) elapses; $C_0$ and $C_{t_1}$ is the reading of the monitor.

Reactivity of isobutene with ozone was examined by a chamber test as follows: the glass air chamber of 20L in volume has a fan for stirring and an ultra violet (UV) lamp for ozone generation. The concentrations of both isobutene and ozone in the chamber were monitored with the PID monitor and an ozone monitor on UV absorption. The lamp was stopped when ozone reached 1ppm, then 2% isobutene of 100 ml was injected into the chamber with a glass syringe. After the gases were mixed, VOCs of 1ml in the chamber were determined by a gas chromatograph.

3. Results and Discussion

3.1. Comparison of isobutene and sulfur hexa-fluoride

Both isobutene and sulfur hexafluoride was scattered in such a way that the concentrations were approximately 100ppm in a residence which is 37 m² in floor area and has full-time ventilation. The concentrations were simultaneously monitored at one point. Time courses of the outputs from the monitors are shown in Figure 1. Sulfur hexafluoride does not interfere with the measurement of isobutene by PID, and the influence of isobutene to PAS for sulfur hexafluoride is negligible. The result shows that VR measured with isobutene and PID agrees with that done with hexafluoride and PAS, and that the VR was 1.0/h.

3.2. PID output levels in buildings and concentrations of isobutene scattered in operation

Figure 2 (Upper) shows an example of the time course of the PID outputs in measurement of VR. The outputs of PID before the scattering of isobutene are called “the background” in this study. The PID also detects some species of VOCs emitted in indoor air, though isobutene as a tracer gas is one of the most sensitive gases in a PID monitor. Both the species and concentration of the VOCs governs the level of the background. On the other hand, the outputs after the scattering of isobutene are required to be at least approximately ten times the background level to be able to suppress influence of the background fluctuation in approximately 10 %. If the background concentration is stable, it is able to measure with the outputs (concentration) after the scattering less than ten times of concentration. The operating outputs are given by the concentrations of scattered isobutene, and selected according to the background outputs.

The background outputs were surveyed in both summer and winter in some new buildings. They were RC-type apartment houses of 1 DK and 3 LDK type with flooring finish. One of them had mechanical ventilation and the other passive ventilation. The level of PID outputs in new buildings in summer and winter in Japan were 3.8 to 9.9 ppm and 0.1 to 3.0 ppm, respectively, and 2.8 ppm in average (n=15). On the other side the level of PAS outputs were 0.02 to 0.18 ppm, and 0.1ppm in average (n=15).

This result shows that we are able to apply isobutene to measure VR with the concentrations of 10 to 100 ppm in operating outputs. The total of VOCs that were measured in parallel in the survey were 0.5 to 5 mg/m³, and a-pinene governed the background outputs. A-pinene had the largest relative coefficient between the outputs and the concentrations in those of the VOCs, and PID is sensitive to a-pinene. Outputs for outdoor air were 0.04 to 0.05 ppm and negligibly small shown in Figure 2(Upper and Lower). While the zero was adjusted by clean air through a column packed with active carbon.
in the measurement, it is not necessary to carry out zero point adjustment of PID in amount-of-ventilation measurement. A simple and inexpensive semiconductor gas sensor is also used as a total VOC monitor for indoor air. The monitor was also applied simultaneously to compare with PID. The result in Figure 2 (Lower) shows that the change rate of the concentration is less than that of PID because the low selectivity for isobutene. The background output was also measured by PAS monitor for sulfur hexafluoride. The outputs were 0.02 to 0.2 ppm and 0.1 ppm in average. This shows that PAS monitor also is interfered by VOCs and to be operated in 0.2 to 2 ppm.

3.3. The reaction of isobutene in environmental air

Isobutene is unstable in indoor and outdoor air because of the double-bond compound. The reactivity, especially, with ozone is 0.02ppm⁻¹ min⁻¹ in a rate constant at 25 °C. Time courses of the PID output and ozone concentration after mixing ozone of 1 ppm with isobutene of 100 ppm in the chamber experiment is shown in Figure 3. After a time elapse of 10 minutes ozone was not detected, and the output was reduced for 10 minutes. The result shows that isobutene reacts rapidly with ozone for a few minutes, changing to isobutene oxide for a maximum of 10 minutes. On the other hand, concentration levels of ozone in indoor air are usually less than 0.01 ppm, except for areas with a source nearby such as a PPC machine or an air cleaner with a discharger. Therefore it is regarded that influence of the reaction to the measurement is negligibly small. Further, decrease of concentration in 10 to 40 min depends on leak.

3.4. Measurement procedures

The ventilation rate was measured in residences with and without mechanical ventilation systems, in order to determine the procedures. One of them was a 2LDK, 83 m² in floor area, and did not have a mechanical ventilation system. The other was a 1DK, 37 m² in floor area in which a ventilation system was operated. Both of them had electric fans for stirring operating inside. Sampling at multi points to inform average air life in a space is desirable, but the simple method of one point sampling was performed in this study. The procedures were as follows: exterior doors and windows were shut. Closets, shelves and interior doors were opened, and the fans were operated before measuring. If the residence had a mechanical ventilation system, it was started a few hours beforehand. Output of PID for background in the residence was measured.

An operator scattered isobutene gas little by little from a mini cylinder around the rooms while reading outputs until the output showed five to ten times their background level.

The operator went out of the room. The output was recorded with a data logger. The PID was also available with a lead pipe outside of the residence.

The output was monitored for one hour or more. The time course of the outputs in the residence without a mechanical ventilation system is shown in Figure 4. The result shows that a stationary state was reached in the reduction of output when 20 minutes or more had elapsed. In contrast, the time course of outputs in the residence with a mechanical ventilation system is shown in Figure 1. It is estimated that a stationary state was reached in the reduction of output when approximately 10 minutes had elapsed.

3.5. Comparison of measurement systems

Monitors on semiconductor gas sensors and FID (hydrogen ionization detector) have high sensitivity for isobutene, but they are insufficient in the selectivity of isobutene because of the presence of many kinds of VOCs in indoor air and because of the level of TVOC. On the other hand PID is sensitive for unsaturated compounds, and it satisfies both the sensitivity and the selectivity. Carbon monoxide is monitored with an electrochemical sensor in potential control electrolysis. Carbon dioxide is monitored using IR absorption. The cost of the PID monitor is more than that of monitors on semiconductor gas sensors and FID, and one fifth than that of the PAS. An electrochemical sensor for carbon monoxide is lower in price than the other monitor, and IR for carbon dioxide is the most stable monitor. PAS also is interfered by co-existing VOC to indicate 0.18 ppm or less of indoor air. Therefore the operating concentration is around 2ppm.

The properties of isobutene are as follows: 57 in mol weight; 1.96 in gas space gravity; 1.6 to 10 % in explosion range. Isobutene scattered from a cylinder is diluted at ten thousandths by stirring. The concentrations after diluting is 10 to 100 ppm, and sufficiently low, compared with lower limits of explosion. Isobutene is an odorous gas and its toxicity is estimated to be less than that of CO but more than that of SF₆.⁶ though its maximum
allowance concentration is not yet provided. On the other hand the toxicity of production from isobutene and ozone is negligibly small because of the low concentration in indoor air. The environment load for photochemical pollution in summer is negligible in the local area, although it is temporary. The GWP of carbon dioxide, Sulfur hexafluoride and nitrous oxide are, respectively, 1, 23,900 and 310. On the other hand GWP of carbon monoxide and isobutene is unknown, but is estimated as 1 and 4, respectively, because their compounds finally become carbon dioxide in the global atmosphere.

It is possible to estimate the load of tracer gases in the environment by the product of GWP and the operating concentration. The result is shown in Table 1. The ventilation rate measurement system of gas and a monitor is to be evaluated relatively. An example of the overall evaluation of five types of systems is shown in Table 2. The low evaluation of carbon dioxide comes from consuming large amounts of it. Carbon monoxide is less than the other gases in GWP, but high in toxicity and not perceived because it is odorless gas. On the other hand isobutene is negative in mutation test and its acute toxicity is 620g/m³/4h for rat in LD50 (Inhalation). It is less than CO in toxicity and perceived to be more than 10ppm. Therefore isobutene can be handled more safely in rooms.

4. Conclusion

The system of isobutene and PID for ventilation rate measurement was proposed and the procedure for the measurement system was established. However, no system for the measurement of the ventilation rate by concentration-decay method is perfect. There is a great difference between the four systems using gas and a monitor. When the evaluation points are changed, the ranking of the systems changes. The system of isobutene and PID was rated high from the viewpoints of GWP and risk of acute toxicity.

References

1. JIS A1406, Measurement method for indoor ventilation (Carbon dioxide method).
8. Yoshio NAGATA and Norifumi TAKEUCHI, JESC Report 17, p77,1990

<table>
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<th>Tracer gas</th>
<th>GWP</th>
<th>Operation concentration</th>
<th>Load to environment</th>
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<td>SF₆</td>
<td>23,900</td>
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<td>CO₂</td>
<td>1</td>
<td>3,000-5,000ppm</td>
<td>3,000-5,000</td>
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<td>N₂O</td>
<td>310</td>
<td>50ppm</td>
<td>15,500</td>
</tr>
<tr>
<td>CO</td>
<td>(1)</td>
<td>50ppm</td>
<td>50</td>
</tr>
<tr>
<td>Isobutene</td>
<td>(4)</td>
<td>5-100ppm</td>
<td>20-400</td>
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*Load to environment is estimated by the product of GWP and operating concentration

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<td>Performance</td>
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<td>N₂O</td>
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Evaluation: Blank Extremely low * Low ** Middle *** Good **** Superior

Table 1. GWP and operating concentration of tracer gases

Table 2. Example of relative evaluation of 5 types of systems for ventilation rate measurement
和文要約
トレーサーガス濃度測定法による換気回数の測定において、トレーサーガスとして温室効果ガスの二酸化炭素又は六フッ化硫黄が用いられていた。筆者らは低環境負荷ガスとしてイソプテンを提案し、そのトレーサーガスとしての評価を検出器含めて他の4種類のシステムと比較検討するとともに、光イオン化検出器（PID, UVレベル10.6eV）をイソプテンモニターとして適用する際の条件を、実測例をもとに検討した。

材料と方法：
とりあげたガスとそのガス濃度モニターは次の通りである。六フッ化硫黄（光圧送式検出器：PAS）、亜酸化窒素（赤外線吸収法）、一酸化炭素（定電位電解法）、二酸化炭素（赤外線吸収法）、およびイソプテン（PID）の5種類である。イソプテンはPIDのほかに半導体モニターを用いた。

結果と考察：
イソプテンと六フッ化硫黄を同時に散布して並行測定を行い、濃度減衰から換気回数を求めた結果、両者は1.0回/hで一致した。次に、イソプテンのモニターとしてPIDと半導体のモニターを用い、室内濃度とイソプテン散布後の濃度の経時変化をみたところ、指示濃度の変化はPIDの方が半導体よりも大きい（約2倍）結果が得られた。これにより、どのモニターもトルエンなどのVOCの影響を受けるが、PIDが半導体よりも二重結合化合物のイソプテンをより選択的に検出したためであり、室内におけるイソプテンモニターとして優れていることを示している。

トレーサーガスはPIDの指示値でバックグラウンド濃度の10倍程度になるように散布すればよいので、イソプテンの散布濃度を決定するために15の新築の建築物でPIDのバックグラウンド値を調査し、同時にVOC成分濃度とTVOCを測定した。PID指示値はTVOC濃度との相関もあり、1mg/m³以下ではほとんど影響がなかったが、成分ではα-ビニールの影響が支配的であった。指示値は夏季3.8～9.9 ppm、冬季0.1～3ppm平均で2.8ppmであったことからイソプテン濃度は10～100ppmで選べる。一方、チャンバー試験でイソプテンとオゾンとの反応性が確認され、通常の室内オゾン濃度0.1ppm以下と低いので無視できる。

5種類のガスとモニターのシステムについて環境負荷・毒性・性能（使い易さ・コストの観点から相対評価を行った。個々の比較をすると、二酸化炭素は亜酸化窒素や六フッ化硫黄に比べ地球温暖化に対する環境負荷は小さいが、1回に必要な消費量が多く使いにくい。一酸化炭素は環境負荷やモニターのコストの点では最も評価されるが、急性毒性の点で問題がある。この点で亜酸化窒素は一酸化炭素に勝るが、許容濃度が低く使用濃度を考慮した時の環境負荷は六フッ化硫黄の1/3以下であるものの二酸化炭素の5倍以上である。この結果、イソプテンは使用濃度と温暖化係数の積で求める環境負荷は最も小さい。一方、モニターを総合的な評価すると定電位電解、赤外吸収、PID、PASの順になるが、赤外吸収とPIDは同等である。イソプテンは可燃性ガスで適度な臭気もあるが、毒性の問題もなく、100ppm以下で使用できるので最も環境負荷が小さい。PIDをモニターとして使用するとこのシステムが総合的に最も優れている。

(2007年8月20日原稿受理、2008年1月9日採用決定)