

Sensitivity and Response Time of a Quartz Crystal Microbalance Gas Sensor

Gen Matsuno

Environmental and Analytical Products Division, Yokogawa Electric Corporation.
2-9-32 Nakacho, Musashino-shi, Tokyo 180-8750, Japan

(Received June 25, 1999; accepted October 12, 1999)

Key words: quartz crystal microbalance, odor sensor, gas sensor, sensitivity, response time, hydrocarbon

The sensitivity and response time of a quartz crystal microbalance (QCM) gas sensor have been measured for several hydrocarbons with relatively high boiling points (sVOCs). It is shown that both the sensitivity and the response time depend strongly on the boiling point; substances with high boiling points show high sensitivities and long time constants. A theoretical approximation of the sensitivity is also made using thermodynamics, which shows good correlation with the experimental results. The response time is shown to depend highly upon diffusion in the gas phase and is greatly improved by high gas flow.

1. Introduction

Quartz crystal microbalance (QCM) gas/odor sensors have been studied by many researchers.⁽¹⁻⁷⁾ Odor recognition systems, or electronic noses, in which multichannel sensors are used to obtain “fingerprints” of samples have often been studied.^(4,6,7) In contrast, in this study we evaluate environmental measurement systems using QCM sensors.

While the concentration range of the odorants measured with electronic noses is rather high (often near saturation), environmental samples often have very low concentrations of analytes. Therefore, sensitivity is a very important factor in the design of environmental measurement systems.

Another feature of environmental samples is that they usually contain numerous unknown components. Preparing a table of sensitivities for typical substances is not sufficient in many cases. Instead, establishing a method of estimating the sensitivity for a

certain substance is desirable. The method is still useful even if it only gives approximate values. One of the two objectives of our work is to develop such a method through both experimental and theoretical approaches.

On the other hand, response time, or the transient response of QCM sensors, has been studied by several researchers mainly to increase the number of fingerprint variables for electronic noses.^(6,7) In the current study the authors noticed a relationship between the time constant and the diffusion of odorant molecules in a membrane and demonstrated that the response is determined by the diffusion coefficient. However, this may not be true for sensors (membrane-odorant combinations) with very high sensitivities because the diffusion of odorant molecules in the gas phase is thought to have greater influence. When the sensitivity or the distribution coefficient of the membrane is very high, the supply of odorant molecules from the gas phase cannot compensate for the loss at the surface caused by diffusion (absorption) into the membrane.

The second objective of our work is to measure the response time of some substances and to evaluate the influence of gas-phase diffusion.

2. Materials and Methods

2.1 Sensor

We used a QCM gas sensor manufactured by Yokogawa Electric Corporation (K9437EA). The sensor consisted of an AT-cut quartz crystal resonator with a polyvinyl chloride (PVC)-based membrane⁽³⁾ on both sides. The resonant frequency of the bare resonator and that of the sensor with the membrane were 10 MHz and 9,967 kHz respectively, which indicates that the frequency shift caused by the membrane was 33 kHz. The average molecular weight of the membrane components was approximately 1,200.

2.2 Gas substances

The gases we tested were: normal-chain saturated hydrocarbons (octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane) and aromatic hydrocarbons (1,2,4-trimethylbenzene, naphthalene, 1-methylnaphthalene, 1,2-dimethylnaphthalene). All the reagents (gases) were purchased from Wako Pure Chemical Industries, Ltd. or Tokyo Chemical Industry Co., Ltd. in the purest available grade.

2.3 Measurement system

The system used for measuring the sensor response (sensitivity and response time) for each gas is shown in Fig. 1.

Air was supplied from a gas cylinder to two flowmeters with needle valves and a mass flow controller. One of the two flowmeters (flowmeter 1) was used for zero gas, and the other (flowmeter 2) for dilution gas. Both of the flowmeters were adjusted to 200 ml/min. The output of the mass flow controller was connected to a small (ca. 5 ml) vial. About 1 ml of a sample (liquid) and a small piece of cotton were placed in the vial. The vial was used to create a saturated vapor of a sample, and the cotton was used to increase the air-

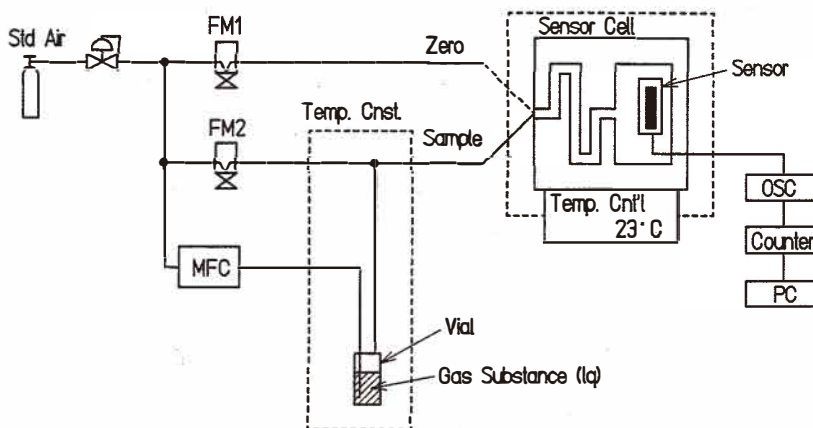


Fig. 1. Sensor response measurement system. The sample concentration was calculated from the dilution ratio of the saturated gas. The switching of zero gas and sample was made manually by changing the tubes.

sample contact area. The output gas from the vial was mixed with the dilution gas from flowmeter 2. The vial and the tube in which saturated gas was passed were placed in a constant temperature chamber. All the tubes used were made of teflon or stainless steel.

The sensor cell was made of an aluminum block ($120 \times 120 \times 31$ mm), the temperature of which was controlled at 23.0°C by an electronic cooling device (Peltier device). In the block, a narrow passage approximately 120 mm long was made as a heat exchanger to maintain the sample gas temperature equal to that of the block and the sensor. The passage led to a small chamber with a volume of approximately 10 ml, in which a sensor was set. The block was covered with a heat insulator.

The sensor was connected to an oscillator circuit outside the cell. The output of the oscillator was measured by a counter (TC110; Yokogawa Electric Corporation) with a frequency resolution of 0.1 Hz. The result was collected with a personal computer at three-second intervals via a GP-IB interface.

In the second experiment, a different sensor cell was used. This cell had a chamber between the heat exchanger and the main chamber, and another sensor (of the same type) was placed in the new chamber. The sectional area of the new chamber was designed to be as small as possible in order to allow the application of the fastest air flow velocity to the sensor.

2.4 Method

A. Experiment 1

Flowmeters 1 and 2 were set at 200 ml/min. The mass flow controller was set at a value between 1 and 5 ml/min, and the constant temperature chamber was set at either 23 or 40°C . The values used for each sample are presented in Table 1 along with the results.

Table 1
Results of Experiment 1. The sensitivity and time constant obtained for each substance.

	Molecular weight	Boiling point [°C]	Molar volume [ml/mol]	Vial temp [°C]	Satu. vapor pressure [atm]	Vial flow [ml/min]	Sample concentration [ppm]	Max. freq. shift [Hz]	Max. freq. [Hz]	Sensitivity [Hz/ppm]	Sensitivity /M.W. [Hz mol/ppm g][s]	Time constant
octane	114	125.6	162.2	23	1.64E-02	3	2.46E+02	38.3	1.55E-01	1.36E-03	2	
nonane	128	149.5	177.3	23	4.93E-03	5	1.23E+02	44.0	3.57E-01	2.79E-03	3	
decane	142	174.0	194.5	23	1.48E-03	3	2.22E+01	29.3	1.32E+00	9.31E-03	5	
undecane	156	195.9	209.3	23	4.41E-04	5	1.10E+01	36.0	3.27E+00	2.09E-02	6	
dodecane	170	214.5	227.0	23	1.27E-04	3	1.90E+00	33.6	1.77E+01	1.04E-01	13	
tridecane	184	234.0	238.4	23	4.59E-05	5	1.15E+00	26.5	2.31E+01	1.25E-01	36	
tetradecane	198	252.5	259.5	23	1.00E-05	3	1.50E-01	26.3	1.75E+02	8.83E-01	94	
pentadecane	212	270.5	273.2	23	2.71E-06	5	6.77E-02	35.0	5.17E+02	2.44E+00	295	
hexadecane	226	286.3	291.3	23	6.82E-07	5	1.71E-02	25.0	1.47E+03	6.49E+00	738	
heptadecane	240	301.9	308.5	23	1.96E-07	5	4.90E-03	26.0	5.31E+03	2.21E+01	2376	
octadecane	254	316.3	326.9	40	5.75E-07	5	1.44E-02	153.0	1.07E+04	4.19E+01	8470	
1,2,4-trimethylbenzene	120	169.0	137.2	23	2.34E-03	2	2.34E+01	63.0	2.70E+00	2.24E-02	6	
naphthalene	128	217.9	128.6	23	2.63E-04	2	2.63E+00	24.4	9.28E+00	7.24E-02	35	
1-methylnaphthalene	142	244.7	138.7	23	5.95E-05	2	5.95E-01	80.0	1.34E+02	9.45E-01	130	
1,2-dimethylnaphthalene	156	266.3	138.7	23	6.87E-06	2	6.87E-02	88.0	1.28E+03	8.19E+00	586	

After putting a sample into a vial, we waited for more than 30 min before measuring to stabilize the concentration in the vial.

First, the zero gas was supplied to the sensor cell for at least one hour to stabilize the baseline of the sensor. (It takes a certain amount of time to purge the absorbed substances from the environment.) Then the sample gas was induced by manually changing the tubes connected to the cell. When the sensor output stabilized at a certain level, the tubes were changed again and the zero gas was supplied until the sensor output returned to the baseline. Thus, a step response was obtained for each sample.

To avoid contamination, one vial was used exclusively for each substance. The tubes and joints were washed with acetone after a measurement, and the baseline of the sensor was tested prior to the next measurement. The tubes and joints were replaced with new ones when necessary.

B. Experiment 2

The measurement procedure was the same as that for Experiment 1 except that the cell with two sensors was used.

3. Results and Discussion

Examples of the step responses obtained in Experiment 1 are shown in Fig. 2. The shapes of the response curves were well approximated by exponential functions, or first-order lag ($A(1 - e^{-\frac{t}{\tau}})$). This indicates that it is possible to use a static response value (maximum frequency shift) to represent the sensitivity of the sensor and time constants for the response speed.

Table 1 is the summary of the results of Experiment 1. The sensitivity to each substance was calculated from the maximum frequency shift of the response and the concentration of the sample gas. The concentration was calculated from the dilution ratio and the saturated vapor pressure, assuming the output gas from the vial was completely saturated. The saturated vapor pressure was calculated using Antoine's equation and Antoine's constants.⁽⁹⁾ The time constant for each substance was read from the response curve; the time when the sensor output reached 63.2% of the maximum output was taken to be the time constant.

Figure 3 is the plot of the sensitivity shown in Table 1 vs the boiling point. The sensitivity has a very strong correlation with the boiling point. This tendency had already been noticed by King, mainly for substances with relatively low boiling points.⁽¹⁾ Figure 3 shows that it is still valid for substances with high boiling points. King explained this tendency using the theory of gas chromatography, relating the sensor sensitivity to the retention volume of the membrane. Because the retention volume in King's theory was based on experimental measurements, experiments were necessary to calculate the theoretical value of the sensitivity. In this study, we made a crude approximation of sensitivity without using experimental values.

A QCM gas sensor consists of an AT-cut quartz crystal resonator with a gas-sensitive membrane on its surface(s). It detects the mass change of the membrane induced by the

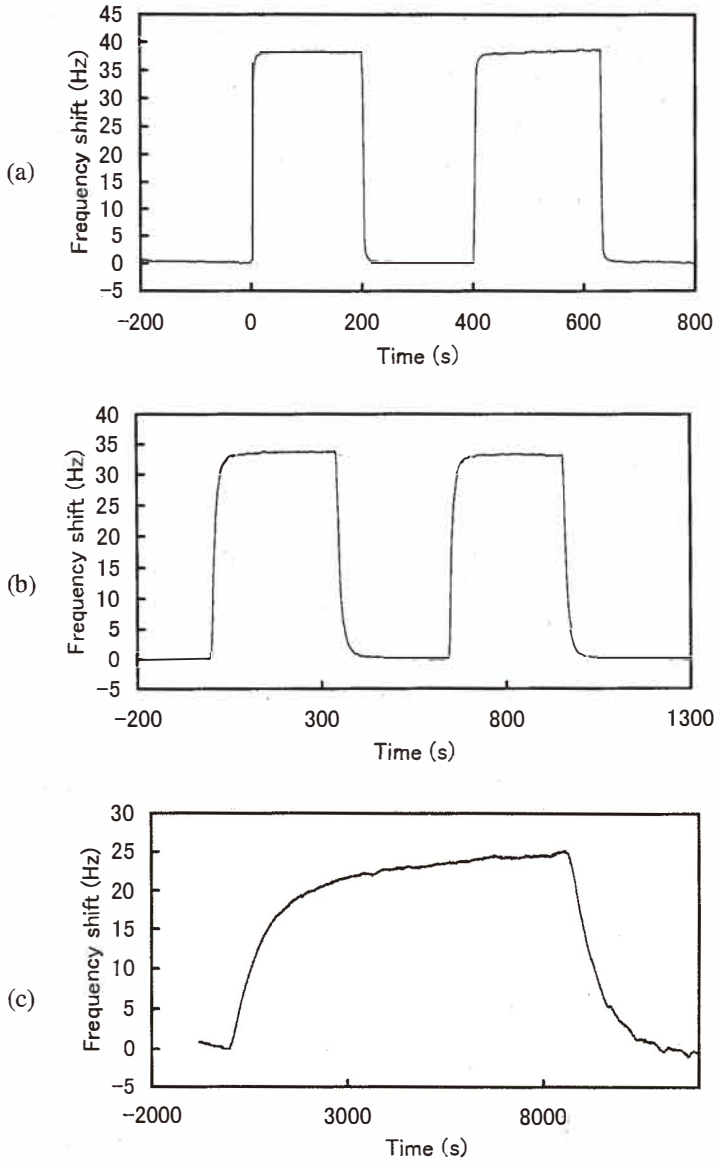


Fig. 2. Examples of sensor response: (a) octane, (b) dodecane, (c) hexadecane. The sensor responses can be treated as first-order lag.

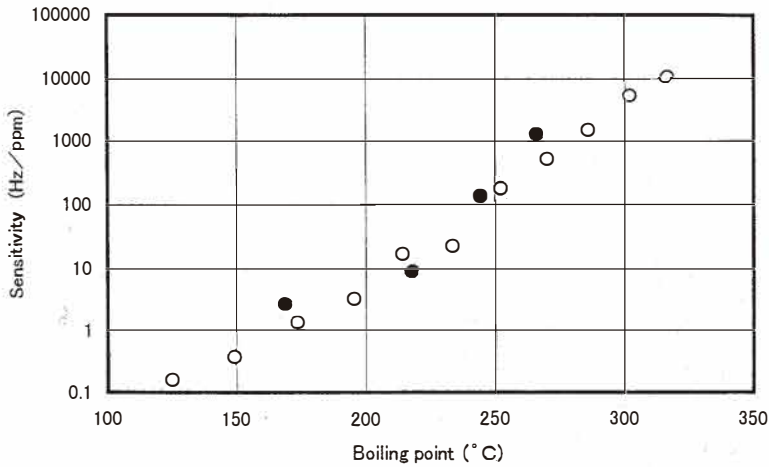


Fig. 3. Sensitivity and boiling point. ○: Normal-chain saturated hydrocarbons, ●: aromatic hydrocarbons. There is a strong correlation. The sensitivity increases with the boiling point.

sorption of gas molecules as a resonant frequency shift of the quartz crystal resonator. The sensor output Δf [Hz] is given by the following equation,⁽¹⁾ where m [kg] is the membrane mass, Δf_m [Hz] is the resonant frequency shift due to the mass of the membrane itself, and Δm [kg] is the mass of the ab(ad)sorbed substance.

$$\Delta f = \Delta f_m \frac{\Delta m}{m} \quad (1)$$

Assuming that gas sorption to the membrane can be treated as a gas-liquid equilibrium in which the gas dissolves in the membrane (solvent), its equilibrium constant K_x is defined by eq. (2) under isothermal and isobaric conditions. In eq. (2), it is assumed that the gas is ideal in the gas phase and forms an ideal solution in the membrane.

$$K_x = \frac{x}{p} \quad (2)$$

The terms x and p [atm] are the mole fraction of the gas in the membrane and the partial pressure of the gas in the gas phase, respectively. The term K_x is equivalent to the distribution coefficient between the gas phase and the membrane, or the Henry's law constant.

When the sorption mass is small, there is a relation between Δm and x :

$$\Delta m = \frac{M}{M_0} m \cdot x, \quad (3)$$

in which M is the molecular weight of the gas and Mo is the average molecular weight of the solvent, or of the membrane. Equations (1)–(3) lead to eq. (4).

$$\frac{\Delta f}{p} = \frac{\Delta f_m}{Mo} \cdot K_x \cdot M \quad (4)$$

Equation (4) shows that the sensor output is directly proportional to the concentration of the substance in the gas phase. When adsorption onto the membrane surface is dominant (*e.g.*, Langmuir adsorption) or the concentration is too high to be treated with Henry's law, eq. (2), and consequently eq. (4), are not effective. As for the PVC-based membrane which we used, it was shown that sensor output was linear to gas concentration.⁽²⁾

It is known that the equilibrium constant K_x can be described by the following equation:

$$K_x = \exp\left(-\frac{\Delta G^\circ}{RT}\right), \quad (5)$$

in which R [J/mol·K] is the gas constant, T [K] is the temperature and ΔG° [J/mol] is the standard Gibbs energy change for the sorption reaction of a gas into the membrane, or the Gibbs energy change when 1 [mol] of gas dissolves in the membrane under standard conditions ($x = 1$, $p = 1$ [atm], $T = \text{const.}$: ca. 23°C). The terms ΔG° , standard enthalpy change ΔH° and standard entropy change ΔS° are related by $\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ$. Substituting this into eq. (5) leads to eq. (6):

$$K_x = \exp\left(-\frac{\Delta H^\circ}{RT}\right) \cdot \exp\frac{\Delta S^\circ}{R}. \quad (6)$$

The following four equations are assumptions for various organic components as gases.

$$\Delta S^\circ = -\Delta S_v^\circ \quad (7a)$$

$$\Delta H^\circ = -HS_v^\circ \quad (7b)$$

$$\Delta S_v^\circ = 88 \text{ [J/mol·K]} \quad (8a)$$

$$\Delta H_v^\circ = 88T_b \text{ [J/mol]} \quad (8b)$$

The terms ΔH_v° , ΔS_v° and T_b are the heat of vaporization, the entropy change of vaporization and the boiling point of the gas, respectively. Equations (7a) and (7b) are equivalent to the assumption that the membrane is an ideal solution. Equations (8a) and (8b) are Trouton's rule, which is effective for almost all substances except associated molecules. Trouton's rule gives ΔH_v° and ΔS_v° at the boiling point. In eqs. (8a) and (8b), the temperature dependence of ΔH_v° and ΔS_v° is assumed to be negligible. Equations (4),

(6), (7) and (8) lead to the following theoretical equation for the sensor sensitivity.

$$\log\left(\frac{\Delta f}{p} \cdot \frac{1}{M}\right) = \frac{88 \cdot \log e}{RT} T_b + \log\left\{\frac{\Delta f_m}{M_o} \cdot \exp\left(-\frac{88}{R}\right)\right\} \quad (9)$$

The left side of eq. (9) is the sensor sensitivity and the right side is a linear function of the boiling point under isothermal conditions. The experimental results and the theoretical values obtained by eq. (9) are replotted in Fig.4.

In the region of low boiling points, the experimental values correlate well with the theoretical values. The sensitivity for substances with relatively high boiling points still good correlates but is somewhat higher than the theoretical values. There are two reasons for this gap: (a) We ignored the influence of temperature in eq. (8). The values of ΔH_v^o and ΔS_v^o obtained by Trouton's rule are values at the boiling point, not at room temperature. It is expected that the difference is greater for high-boiling-point substances because the temperature difference between room temperature and the boiling point is larger. (b) We ignored the influence of the interaction between membrane molecules and gas molecules.

In spite of the gap in the high-boiling-point region, the theoretical values correlate well with the experimental results and are still useful to consider overall tendencies and to estimate an approximate value of sensitivity for a new substance. The correction of the temperature effect is very complicated, but it is certain that the theoretical value increases (approaches the experimental value) in the high-boiling-point region.

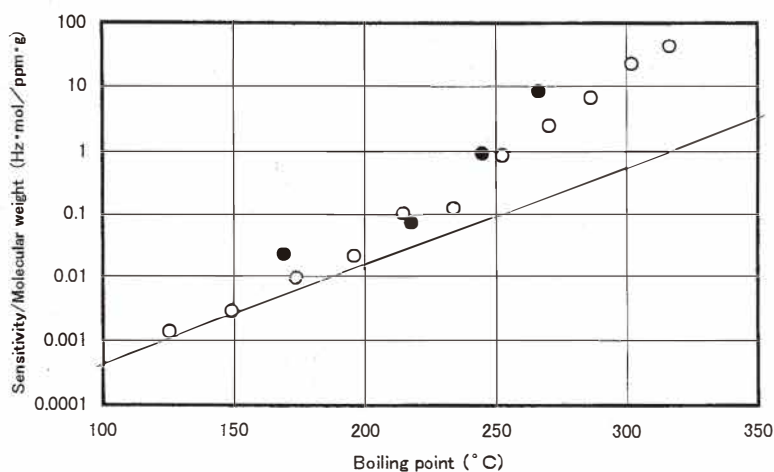


Fig. 4. Sensitivity and boiling point (replot). ○: Normal-chain saturated hydrocarbons, ●: aromatic hydrocarbons, —: theoretical value. Experimental results show a good coincidence with the theoretical values, particularly in the low-boiling-point region.

As for the response time, we expected at first that gas-phase diffusion in the membrane determined the time constant, as this had been reported by other researchers.^(5,7,8) Following this, it was expected that the time constants were related to molecular size. In other words, the smaller the molecules, the easier they diffuse into the membrane (the free volume theory of diffusion).

Figure 5(a) shows the time constant vs molecular volume. There was no relation between the two parameters unless the substances belonged to the same group, such as normal-chain saturated hydrocarbons. Thus, the hypothesis mentioned above was rejected.

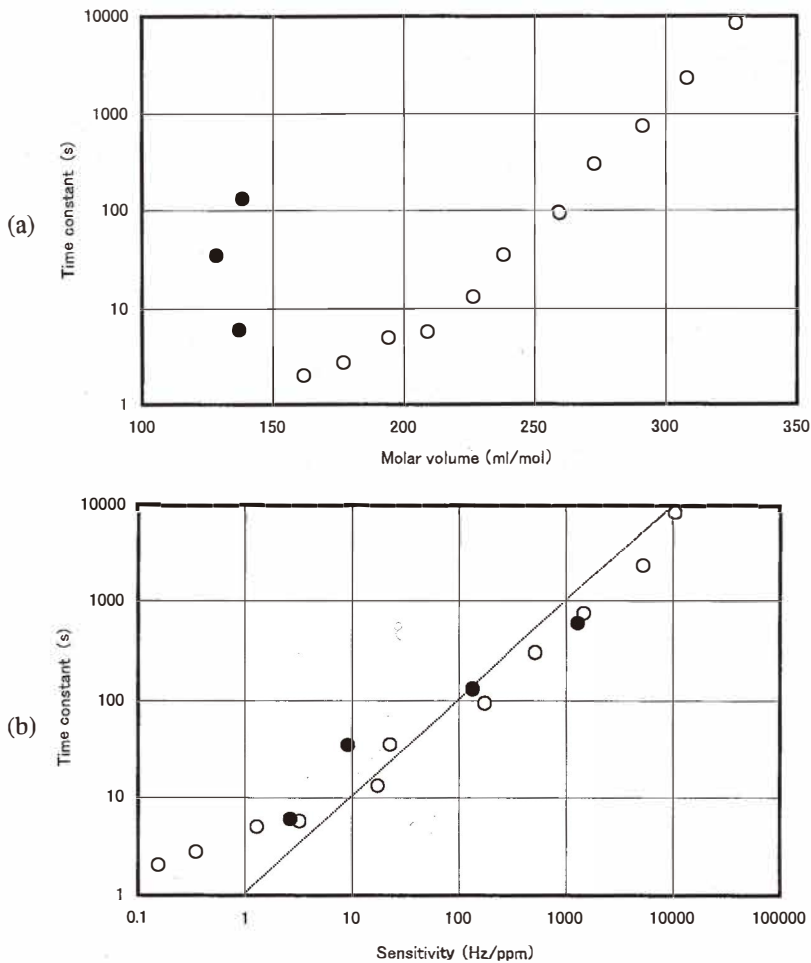


Fig. 5. What determines time constant? (a) Time constant and molecular volume. \circ : Normal-chain saturated hydrocarbons, \bullet : aromatic hydrocarbons. If the diffusion in the membrane were dominant, these two factors should correlate well. (b) Time constant and sensitivity. \circ : Normal-chain saturated hydrocarbons, \bullet : aromatic hydrocarbons. The dependence of the sensitivity means that gas-phase diffusion, or the supply of gas molecules, is the dominant factor influencing the response time.

Figure 5(b) illustrates the time constant vs sensitivity. These two factors correlate very strongly. This suggests that the dominant factor influencing the time constant is diffusion in the gas phase, or the supply of the gas molecules at the surface of the membrane. If this is true, the time constant should be influenced greatly by the flow velocity of the sample at the surface of the membrane. To confirm this, we carried out Experiment 2.

Table 2 is the summary of data from Experiment 2. Sensors 1 and 2 in the table were placed in the main chamber (ca. 10 ml) and the extra chamber (sectional area: ca. 8 mm²), respectively. The columns are the same as in Table 1. The sensitivities and the time constants shown in Table 2 are plotted in Fig. 6. As shown in Table 2 and Fig. 6, the sensitivities of Sensors 1 and 2 are almost identical. This indicates that the sensitivity, or the sorption equilibrium between the gas phase and the membrane, is independent of the flow velocity. In contrast, the time constants of Sensor 1 (high flow velocity) were approximately five times greater than those of Sensor 2. This means that gas-phase diffusion has significant effect on the response time of the sensor. The adsorption/desorption equilibrium on the inner surface of the gas passage between the sample gas inlet and the sensor cell chamber of the sensor cell block influences the response time as well, because it is another factor which affects the supply of gas molecules onto the membrane.

The reasons why we obtained different results concerning the factors influencing the sensor response time compared to other studies are suggested to be as follows:

1. The substances tested in these experiments were only slightly volatile and had relatively high boiling points. The sensor sensitivity, or the distribution coefficient for those substances, was high, which means that the gas concentration can easily decrease

Table 2

Results of Experiment 2. Sensor 1: low flow velocity, Sensor 2: high flow velocity.

	Boiling point [°C]	Vial temp. [°C]	Satu. vapor pressure [atm]	Vial flow [ml/min]	Sample concentration [ppm]	Max. freq. concentration shift [Hz]	Sensitivity [Hz/ppm]	Time constant [s]
Sensor 1								
dodecane	214.5	40	5.24E-04	5	1.31E+01	141.3	1.08E+01	37
tetradecane	252.5	40	5.61E-05	5	1.40E+00	130.7	9.31E+01	217
hexadecane	286.3	40	5.44E-06	1	2.72E-02	31.0	1.14E+03	2179
naphthalene	217.9	40	9.15E-04	1	4.58E+00	81.7	1.79E+01	81
1-methylnaphthalene	244.7	40	2.40E-04	1	1.20E+00	192.9	1.60E+02	288
1,2-dimethylnaphthalene	266.3	40	3.84E-05	1	1.92E-01	157.0	8.18E+02	1116
Sensor 2								
dodecane	214.5	40	5.24E-04	5	1.31E+01	141.6	1.08E+01	7
tetradecane	252.5	40	5.61E-05	5	1.40E+00	128.5	9.16E+01	40
hexadecane	286.3	40	5.44E-06	1	2.72E-02	37.0	1.36E+03	303
naphthalene	217.9	40	9.15E-04	1	4.58E+00	85.6	1.87E+01	17
1-methylnaphthalene	244.7	40	2.40E-04	1	1.20E+00	200.7	1.67E+02	83
1,2-dimethylnaphthalene	266.3	40	3.84E-05	1	1.92E-00	165.0	8.60E+02	233

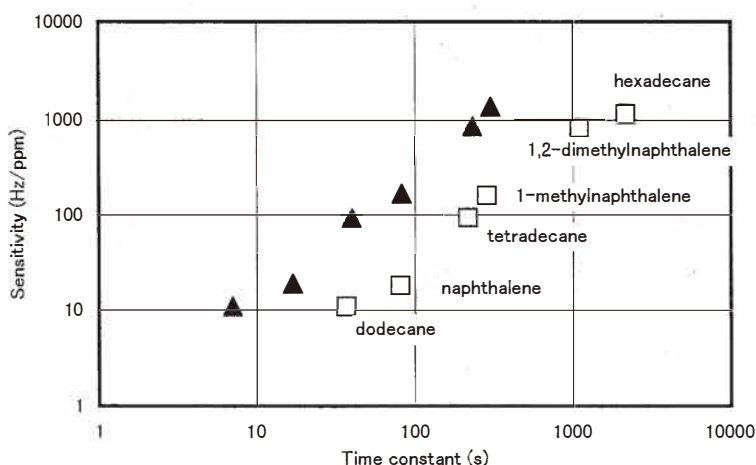


Fig. 6. Influence of flow velocity. □ Sensor 1: low flow velocity, ▲ Sensor 2: high flow velocity. Flow velocity does not influence the sensitivity but does influence the response time. This means gas-phase diffusion is the dominant factor for the response time.

with sorption on the membrane or the passage surface. In other studies, organic solvents such as acetone and toluene were usually used as gas samples.

2. Diffusion in the membrane was very fast because the membrane was very thin (ca. 1 μm) and coarse.

Concerning the effect of the flow velocity on the response time, only the qualitative tendency was examined using the two flow velocities in this study. We plan to make a more quantitative analysis in the near future.

We hope many useful applications can be developed for this sensor. For example, taking the difference between the two sensors in Experiment 2, it is possible to measure only high-boiling-point substances, because the delay between the two sensors for low-boiling-point substances is negligible. This discussion will be extended in future papers.

References

- 1 W. H. King, Jr.: *Analytical Chemistry* **36** (1964) 1735.
- 2 Y. Okahata and O. Shimizu: *Langmuir* **3** (1987) 1171.
- 3 G. Matsuno, D. Yamazaki, E. Ogita, K. Mikuriya and T. Ueda: *IEEE Transactions on Instrumentation and Measurement* **44** (1995) 739.
- 4 T. Nakamoto, A. Fukuda, T. Moriizumi and Y. Asakura: *Sensors and Actuators B* **3** (1991) 221
- 5 S. Munoz, T. Nakamoto and T. Moriizumi: *IEEJ, CS-98-42* (1998) p. 29.
- 6 A. Iguchi, T. Nakamoto and T. Moriizumi: *Tech. Dig. Sens. Symp*, 16th (1998) p. 139.
- 7 I. Sugimoto, M. Nakamura and H. Kuwano: *Sensors and Actuators B* **10** (1993) 117.
- 8 H. Tong and K. Saenger: *Society of Plastics Engineers Annual Technical Conference 46th* (1988) p. 1000.
- 9 The Chemical Society of Japan: *Kagaku Binran* (Maruzen Co., Ltd., Tokyo, 1993) Chap. 8.