Portable Aromatic VOC Gas Sensor for Onsite Continuous Air Monitoring with 10-ppb Benzene Detection Capability

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Abstract

We have developed a portable gas sensor using microfluidic devices (concentration and detection cells) for detecting and identifying gaseous aromatic volatile organic compounds (VOCs), such as benzene, toluene, xylene, styrene, and ethylbenzene. To improve the sensor's sensitivity, we introduced techniques for the precise control of gas transfer from the concentration cell to the detection cell and optimized the spectrum measurement conditions. We achieved a detection level of 10 ppb for benzene gas as an example of aromatic VOC detection in a sampling time of 50 minutes. The calibration curve showed good linearity in the range of 10–100 ppb of benzene. We also carried out gas-monitoring experiments in a garage. The results show the applicability of our aromatic VOC sensor for field monitoring.

1. Introduction

Airborne benzene, toluene, xylene, styrene, and ethylbenzene[*1] are aromatic volatile organic compounds (VOCs) of significant health concern due to their toxicity and mutagenic or carcinogenic properties, even at concentrations of a few parts per billion (ppb). Benzene is a well-known human carcinogen for all routes of exposure and it is a risk factor for aplastic anemia, leukemia, and lymphomas [1], while toluene, xylene, styrene, and ethylbenzene are suspected of playing a major role in sick house and sick building syndromes. In Japan, regulations limit benzene concentration to 3 $\mu g/m^3$ (1.0 ppb) [2]. The guidelines for the indoor upper concentration limits of toluene, xylene, styrene, and ethylbenzene are 260, 870, 220, and 3800 $\mu g/m^3$ (70, 200, 50, and 880 ppb), respectively. The regulations for these aromatic VOCs in Japan, the USA, and the EU are summarized in **Table 1** [3].

The amounts of these aromatic VOCs emitted into the air per year in Japan are listed in **Table 2** [4]. The emission sources are categorized into three groups: point sources (major industrial facilities, such as chemical plants, steel mills, oil refineries, power plants, and hazardous waste incinerators), area sources (small pollution sources, such as drycleaners, gas stations, and auto body paint shops), and mobile sources (exhaust gas from cars, trucks, buses, ships, airplanes, and agricultural and construction equipment).

In Japan, indoor and outdoor concentrations of aromatic VOCs have been reduced sufficiently below the values in the respective guidelines. This success is the result of the self-imposed limits on emissions from point sources and the reduction or replacement of these VOCs in paints, inks, and adhesives and their solvents. However, further reductions are required, because it is now clear that VOCs are sources of suspended particulate matter and photochemical oxidant. The Air Pollution Control Law was revised in 2005 and will be enforced from April 2006. The revised law requires major industrial facilities to measure VOC concentrations and keep them below the permissible level.

For airborne benzene, the main source is exhaust gas from cars. In Japan, the Air Pollution Control

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[*1] Benzene, toluene, and xylene are referred to as BTX; benzene, toluene, ethylbenzene, and xylene are referred to as BETX.

Table 1. Major regulations for aromatic VOCs.

	Japan	US (EPA)	EU (WHO)	Max. cont. indoor air (WHO)
Benzene	3 μg/m^3 (1 ppb)	1.3 – 4.5 μg/m^3	1.7 μg/m^3	10 μg/m^3
Toluene	260 μg/m^3 (70 ppb)	400 μg/m^3	260 μg/m^3	200 μg/m^3
Xylene	870 μg/m^3 (200 ppb)	400 μg/m^3	—	100 μg/m^3
Styrene	2200 μg/m^3 (50 ppb)	1000 μg/m^3	260 μg/m^3	20 μg/m^3
Ethylbenzene	3800 μg/m^3 (880 ppb)	1000 μg/m^3	—	100 μg/m^3

Table 2. Statistical data and chemical characteristics of major aromatic VOCs in Japan.
Source: 2003 Pollutant Release and Transfer Register (PRTR) 2003 data.

	Emission amount to air (automobile exhaust gas)	Outdoor concentration (year)	Indoor concentration (year)	Half-life in air	Boiling point (°C)
Benzene	16,500 ton (14,500 ton)	3.4 μg/m^3 (1997) 1.9 μg/m^3 (2003)	—	7–13 day	80.5°C
Toluene	188,100 ton (39,900 ton)	1.1–85 μg/m^3 (1998)	85 μg/m^3 (2001) 15 μg/m^3 (2004)	1–3 day	110.8°C
Xylene	106,700 ton (23,100 ton)	o-xylene: 0.33–9.5 μg/m^3 (1998) m-xylene + p-xylene: 0.55–35 μg/m^3 (1998)	39 μg/m^3 (2001) 13 μg/m^3 (2004)	0.6–1.2 day	o-xylene: 144°C m-xylene: 139°C p-xylene: 138°C
Styrene	6400 ton (2500 ton)	0.04–2.7 μg/m^3 (1998)	9 μg/m^3 (2001) 0 μg/m^3 (2004)	0.3 day	145.2°C
Ethylbenzene	30,700 ton (6500 ton)	0.09–10 μg/m^3 (1998)	22 μg/m^3 (2001) 4 μg/m^3 (2004)	0.2–1 day	136°C

Law was revised in 1996 and the Environmental Quality Standard level for benzene was set at 3 μg/m^3 in 1997. In January 2000, the permissible upper limit of the benzene concentration in gasoline was lowered to 1 vol.%.

The statistics indicate a gradual reduction in benzene concentration. They show averaged values of measurements taken during limited time periods and at limited locations. It is obvious that the benzene concentration in the air depends on many factors such as traffic density, weather, and surrounding materials that might absorb it. To ensure and maintain a benzene-free environment, we require multi-point, continuous, long-term monitoring.

In this paper, we report the development of a portable aromatic VOC sensor for field monitoring.

2. Performance requirements for field monitoring

The standard method of VOC analysis is gas chromatography[*2] combined with mass spectrometry[*3] because it has several advantages including a parts-per-trillion (ppt) detection limit, high selectivity, and high accuracy (**Fig. 1**). For measuring the total amount of VOCs, the standard methods are flame ionization detection[*4] and catalytic oxidation/non-dispersive infrared detection[*5]. However, these methods require manual air sampling on site and specially

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[*2] Gas chromatography: A technique that can be used to separate volatile organic compounds. The organic compounds are separated due to differences in their partitioning behavior between the mobile gas phase and the stationary phase in the column.

[*3] Mass spectrometry: A technique for separating ions by their mass-to-charge ratios to enable the identification of unknown compounds at very low concentration levels.

[*4] Flame ionization detection: A technique for measuring the total amount of VOCs. The VOCs are decomposed to C$^+$ in a hydrogen flame and the amount of C$^+$, which corresponds to the concentration of all the VOCs, is determined by measuring the electrical current that passes when a potential is applied between two electrodes set facing the flame.

[*5] Catalytic oxidation/non-dispersive infrared detection: A technique for measuring the total amount of combustible vapors based on measuring the infrared absorption of CO$_2$ produced from them.

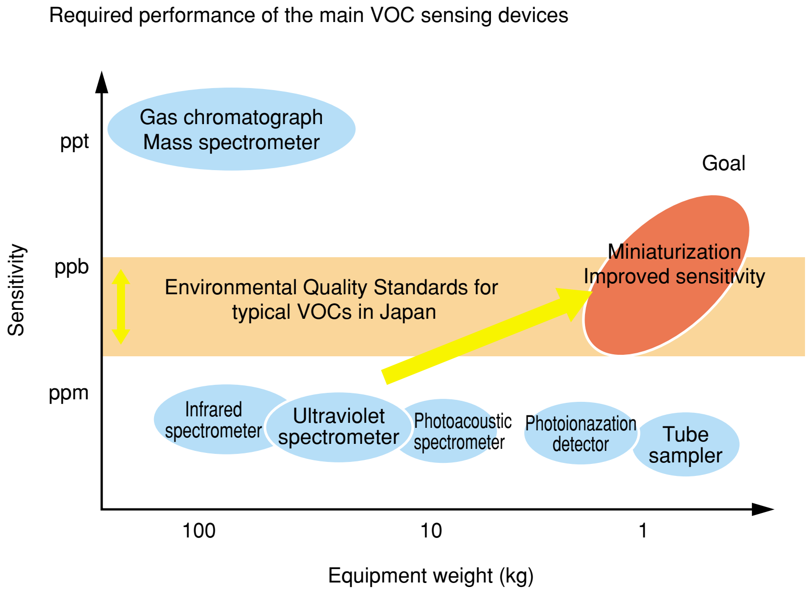

Fig. 1. Relationship between portability and sensitivity of main VOC sensing devices.

Fig. 2. Portable VOC sensor developed by NTT.

trained operators to perform the analysis. These factors lead to a high cost and long analysis time.

Benzene has the highest toxicity among the aromatic VOCs mentioned above. More than 80% of the benzene emitted into the air comes from mobile sources. Benzene is more stable in air (half-life: 7–13 days) than other VOCs, which makes it important to be able to determine the concentration of each compound in the air separately for multi-point onsite field monitoring. A portable system that can detect each VOC species with a low operating cost is therefore required for onsite monitoring.

Ultraviolet (UV) absorption spectroscopy is also used to analyze aromatic hydrocarbons. The characteristic peaks of aromatic hydrocarbons appear in the wavelength region of 200–300 nm, where there is hardly any influence from water or impurities in the air. The optical components used in UV spectrometers are simple and easy to miniaturize. Operation is also simple and easy. However, the sensitivity of UV absorption spectroscopy is not high enough for accurate gas analysis. We have overcome the sensitivity problem and developed a portable system by using microfluidic devices, which should lead to higher throughput, shorter analysis times, reduced sample volumes, *in situ* operation, and reduced manufacturing and operating costs [5].

3. Detection mechanism

A photograph of the portable aromatic VOC gas sensor for field monitoring is shown in **Fig. 2**. The sensor is 33 cm wide, 15.5 cm deep, and 17 cm high. It is controlled through a SCSI interface by a notebook personal computer running Windows 2000. It requires a 100-V power source.

The detection mechanism of the sensor is illustrated in **Fig. 3**. The main components of the sensor are shown in **Fig. 4**. The sensor box contains two microfluidic devices, namely the concentration and detection cells. Each consists of two Pyrex plates and is 3 cm × 1 cm. The adsorbent is mesoporous silicate powder packed into the microchannel of the concentration cell. The sampling gas is introduced into the concentration cell and the powder adsorbs aromatic hydrocarbon molecules in the sampling gas over a certain period of time. Then, the molecules on the adsorbent are desorbed by heating the microchannel to 250°C and maintaining that temperature for several tens of seconds. The heating is performed by a thinfilm platinum heater formed on the outer microchannel wall. The highly concentrated desorbed gas is then introduced to the next cell: the detection cell. Both ends of the channel are sealed with optical fibers, and the channel is aligned between a UV light source and a UV spectrometer (Soma Optics, Fastevert S-2400, 12-bit analog-to-digital converter). The UV absorption spectra of the desorbed gas are measured in the detection cell. The UV spectrum of the sampled gas is analyzed and then decomposed by the least squares method to the standard spectra of individual components, which are stored in the personal computer. The concentration of each aromatic VOC is quantified by its proportionality to the standard spectrum.

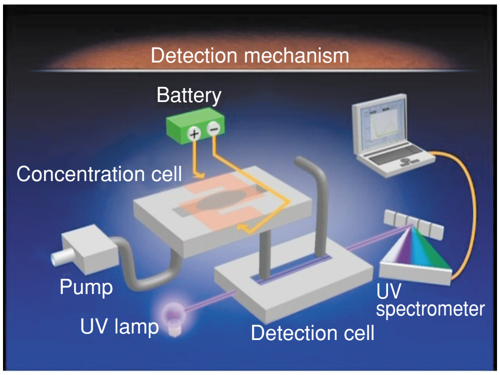

Fig. 3. Detection mechanism of the portable VOC sensor.

4. Sensor improvements

4.1 Nanomaterial for adsorbent

We tested several kinds of glass powder for the adsorbent [6], including commercially available amorphous silicon dioxide powder, as well as mesoporous silicate powder (SBA-16) that we synthesized by the method described in Ref. 7. The cubically ordered SBA-16 was synthesized using triblock copolymer[*6] EO_{100}-PO_{65}-EO_{100} (BASF Corporation: Pluronic F127; $M_w = 12{,}600$) as template agents. This mesoporous silicate powder has much greater adsorption capacity than ordinary glass powders because of its large surface area. We successfully detected 100 ppb of benzene gas using SBA-16 with a preconcentration time of 30 minutes [8].

4.2 Cell structure

We examined several concentration cells with different microchannel structures and heater shapes [9]. The heater was fabricated by the sputter deposition (platinum thickness: 150 nm) and lift-off techniques. The microchannel in our initially developed concentration cell was formed from linear grooves made by dicing. When the amount of adsorbent in the

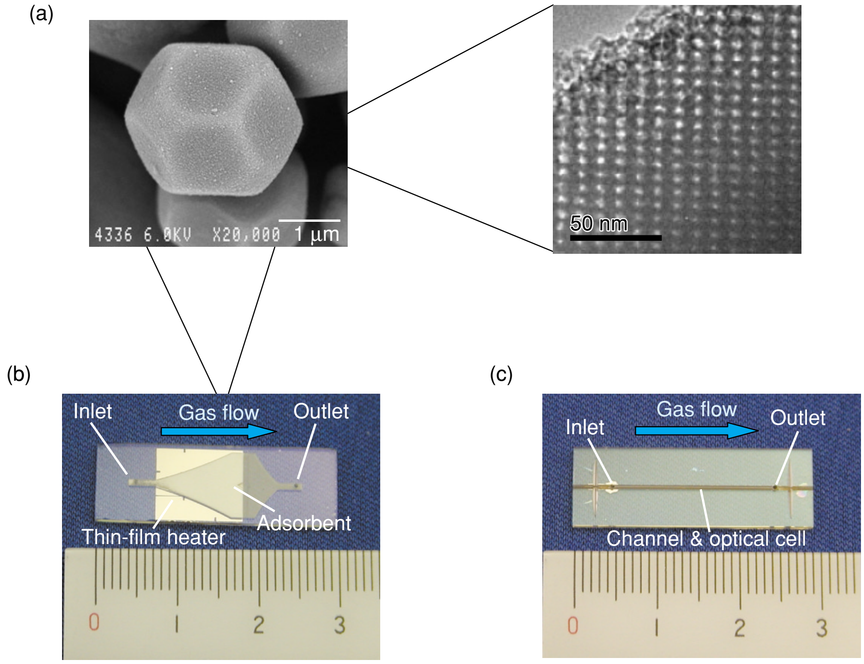

Fig. 4. Main components of microfluidic device: (a) mesoporous silicate powder SBA-16, (b) concentration cell, and (c) detection cell.

[*6] Copolymer: A polymer resulting from the polymerization reaction of two chemically different monomers.

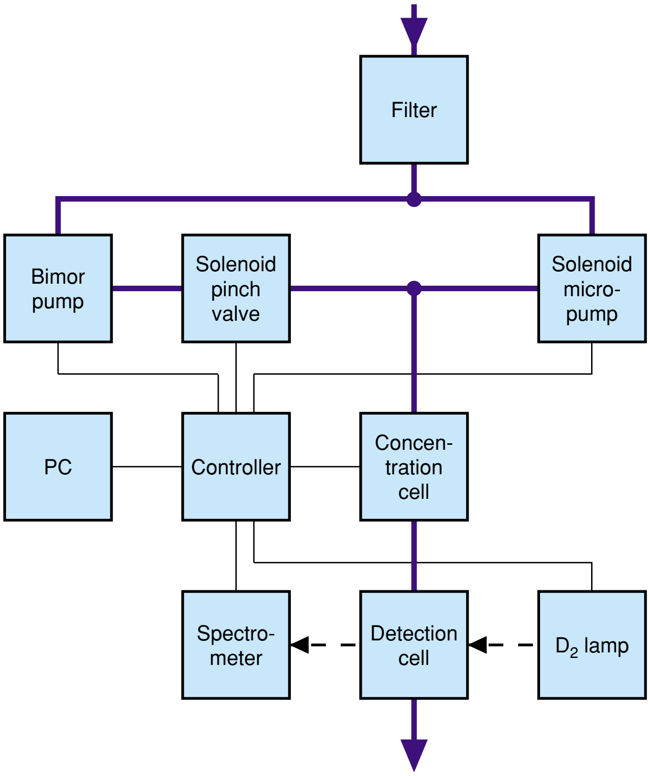

Fig. 5. Block diagram.

microchannel was increased to increase the total amount of adsorbate, it was difficult to obtain a sufficient gas flow rate because the flow resistance was greater. Therefore, we used sand blasting to fabricate a microchannel with a large adsorbent capacity while maintaining a high flow rate. The channel width was gradually changed, so that the widths at the inlet and outlet were minimum but that at the adsorbent-stopper was maximum. Using this concentration cell filled with SBA-16, we achieved 50-ppb benzene gas detection with a preconcentration time of 50 minutes.

The detection cell was also improved. In the first detection cell we developed, two short optical fibers were arranged inline in a groove in a glass plate with a separation distance of 2 cm. The light intensity was greatly decreased after traveling this distance because of the low efficiency of the waveguide in the microchannel. After we coated the inside of the cell's microchannel with a reflective layer of platinum to improve the waveguide efficiency [10], the signal-to-noise ratio (SNR) was increased by increasing the accumulation number by shortening the exposure time. Using this concentration cell filled with SBA-16 and this platinum-coated detection cell, we have achieved 25-ppb benzene gas detection with a preconcentration time of 50 minutes.

4.3 Gas transfer system

We modified the gas transfer system to further increase the SNR. The previous system had only one pumping system, which was used to sample the air and transfer the desorbed gas from the concentration cell to the detection cell. It was a piezoelectric bimorph pump (bimor pump, Nitto Kohki Co., Ltd., BPF-465P, 7.2 cm × 7.2 cm × 3.2 cm[*7]). A Teflon tube 7–8 cm long (inner diameter: 0.5 mm) was used to connect the two cells. The flow rate observed at the outlet of the detection cell was typically 4–6 ml/min when the pump was operated with 100-V AC (50 Hz) using the concentration cell filled with SBA-16. When the desorbed gas is transferred between the cells with this flow rate, the optical measurement must be finished within only a few seconds, which is how long the desorb gas is present in the detection cell. This limitation on measuring time prevents noise reduction by increasing the accumulation number. On the other hand, high-flow-rate sampling using the bimor pump was effective in increasing the signal because of the large amount of adsorbate.

We added two components to the gas line. A block diagram of the modified portable sensor is shown in **Fig. 5**. The bold lines show the gas line and broken

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[*7] http://www.nitto-europe.com/pumps/bimor/index.html

lines show the light path. The major components are controlled electrically (thin lines). A solenoid pinch valve (Bio-chem Valve Inc., 075P2N024-02S) was placed between the concentration cell and the bimor pump, and a solenoid micropump (Bio-chem Valve Inc., 090SP24-8) between the concentration cell and the filter. The solenoid micropump dispenses 8 µl per solenoid actuation. Several actuations can transfer the highly concentrated desorbed gas from the concentration cell to the detection cell and keep it inside, even if pressure caused by the bimor pump remains in the gas line, because the solenoid pinch valve closes the path from the bimor pump. The main components work as follows. In the preconcentration period, the bimor pump takes in an air sample and transfers it to the concentration cell through the pinch valve, which is normally open. The background and reference spectra are measured during the preconcentration period. Next, for the spectra measurement, the bimor pump stops and the pinch valve is closed. The heater turns on and the solenoid micropump starts working. After several solenoid actuations (0.5-s intervals), the spectrum of the desorbed gas is measured with a large accumulation number (typically 1000 × 10-ms exposure time). After spectrum measurement, the bimor pump starts again and the solenoid pinch valve opens to cool the cell and purge the gas lines with fresh air. Typically, we set the preconcentration time to 50 minutes and one experiment takes one hour.

5. Detection limit

Spectra of benzene at 20, 10, and 5 ppb measured using the modified system are shown by curves (a), (b), and (c) in **Fig. 6**, respectively. Curve (d) in Fig. 6 is a spectrum of 10-ppb benzene measured with the previous system where the intensity is scaled to have the same noise amplitude as curves (a)-(c). In the previous system, it was difficult to reduce the noise amplitude by increasing the accumulation because the desorbed gas immediately passed though the detection cell. On the other hand, with the improved system, 10-ppb benzene was measured with an adequate SNR (>3). This shows that the system can be used for quantitative analysis of benzene.

The calibration curves for both systems are shown in **Fig. 7**. The detection limit of the modified system

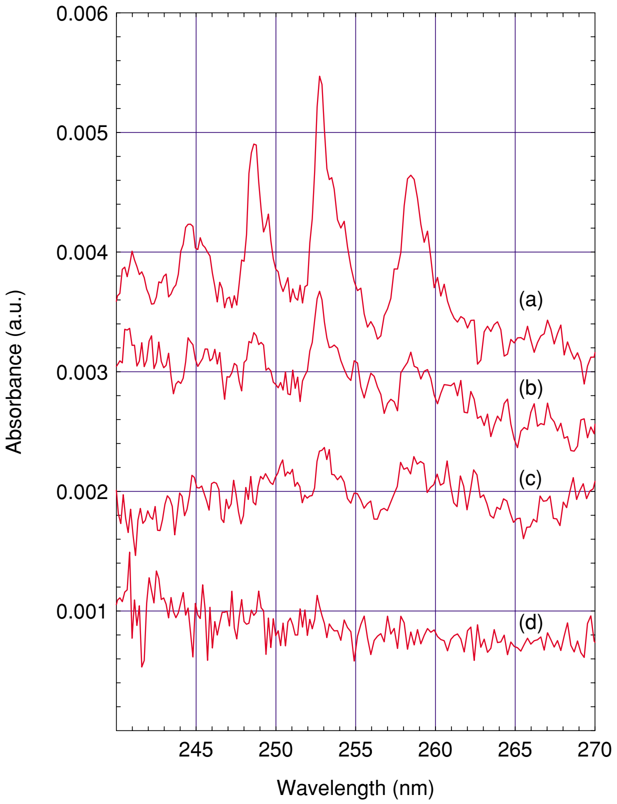

Fig. 6. Absorption spectra of benzene: (a) 20 ppb, (b)10 ppb, (c) 5 ppb, and (d) 10 ppb (measured with the previous system).

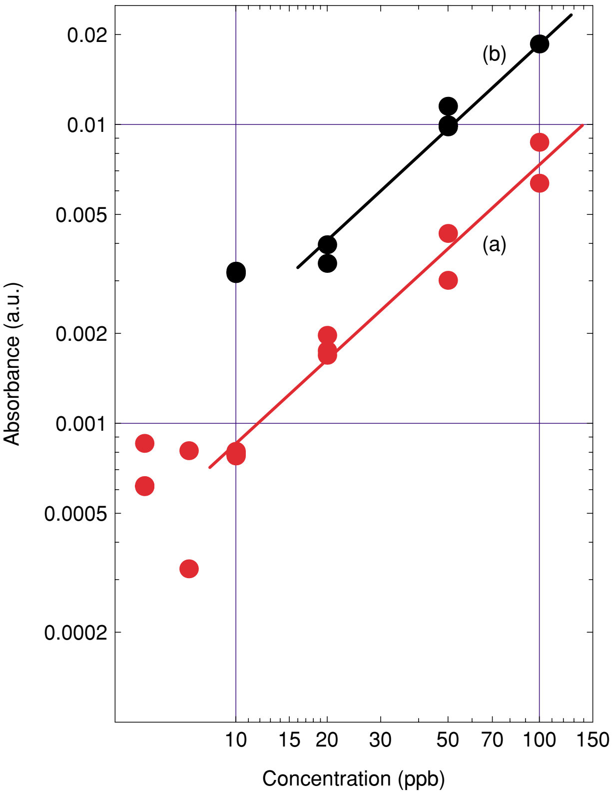

Fig. 7. Calibration curves for benzene detection: (a) improved system and (b) previous system.

is 10 ppb. A linear relationship was obtained between the benzene concentration and absorbance in the range of 10–100 ppb for the modified system. We could also detect 5-ppb benzene qualitatively as shown in Fig. 6(c).

This system can operate continuously for long periods without maintenance, which is very advantageous for application in the field. We have conducted a one-month experiment to investigate its reliability and durability. The absorbance change in a 10-ppb benzene equivalent experiment (5-minute preconcentration of 100-ppb benzene) is shown in **Fig. 8**. The average absorbance was 0.242 × 10^{-2}, and the standard deviation was 0.989 × 10^{-4}.

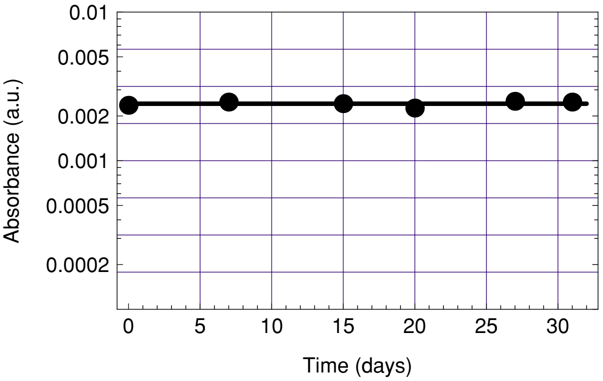

Fig. 8. Reliability and durability test.

6. Test using a real sample

The portable VOC sensor was tested on a real sample in preparation for field deployment. The sensor was placed in a residential garage containing a Japanese car with its engine running and the garage door was left open. Curve (a) in **Fig. 9** shows the raw data for a 50-minute sampling. Many characteristic peaks from aromatic VOCs can be observed along the large tilted baseline (curve (b)). The origin of this baseline is unknown at this point. We removed the baseline manually and conducted further analysis using the subtracted spectrum (curve (c)). There were no large characteristic peaks around 270–275 nm, indicating that xylene concentrations were not significant. Then the subtracted spectrum was decomposed into toluene and benzene (curves (e) and (f), respectively). The composition of curves (e) and (f) corresponds to curve (d), which agrees well with the measured spectrum shown by curve (c). The concentrations of benzene and toluene in the gas sampled at the garage were estimated to be 23 and 250 ppb, respectively, by referring to previously measured standard spectra.

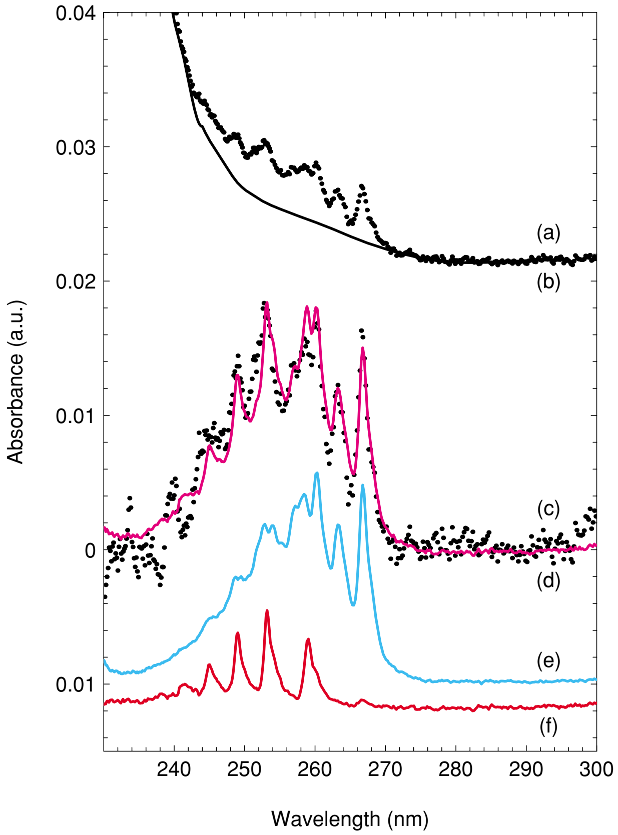

Fig. 9. Measurement of garage air: (a) raw spectrum, (b) baseline, (c) baseline subtracted spectrum, (d) simulation spectrum, (e) toluene component, and (f) benzene component.

7. Conclusion

We have optimized several operating conditions of the portable aromatic VOC gas sensor to lower its detection limit. We achieved 10-ppb benzene gas detection with good linearity in a low concentration range (10–100 ppb). This was accomplished by effectively reducing the noise amplitude through precise gas transfer control for increased spectrum accumulation. We tested this system on air in a residential garage. The sensor indicated that the air in the garage contained high levels of benzene and toluene. With further improvements, the sensor is expected to approach and exceed the detection values specified in governmental guidelines and be applied to field monitoring.

References

[1] See for example: “Carcinogenic Effects of Benzene: An Update,

1998," EPA/60/P-97/001F; U.S. Environmental Protection Agency, U.S. Government Printing Office: Washington, DC, 1998.

[2] "Environmental Quality Standards in Japan—Air Quality," Environmental Quality Standards of Benzene, Trichloroethylene and Tetrachloroethylene, 1997, http://www.env.go.jp/en/lar/regulation/aq.html; Ministry of the Environment.

[3] Technology Transfer Network Air Toxics Website: U.S. Environmental Protection Agency. See for example: http://www.epa.gov/ttnatw01/hlthef/benzene.html

[4] Fact sheets for chemical substances: Ministry of the Environment, http://www.env.go.jp/chemi/communication/factsheet.html (in Japanese); Monitoring results of hazard air pollutants: Ministry of the Environment, http://www.env.go.jp/air/osen/monitoring/index.html (in Japanese); News releases and speeches: Ministry of the Environment, http://www.env.go.jp/en/news/index.html, http://www.env.go.jp/chemi/kurohon/http2002/siryo2.html (in Japanese); Survey results of chemical substances indoor air (2004): Ministry of Land, Infrastructure and Transport, http://www.mlit.go.jp/kisha/kisha05/07/070510_.html (in Japanese).

[5] Y. Ueno, T. Horiuchi, T. Morimoto, and O. Niwa, "Microfluidic device for airborne BTEX detection," Anal. Chem. 73, 4688, 2001.

[6] Y. Ueno, T. Horiuchi, M. Tomita, O. Niwa, H. Zhou, T. Yamada, and I. Honma, "Separate detection of BTX mixture gas by a microfluidic device using a function of nanosized pores of mesoporous silica adsorbent," Anal. Chem. 74(20), 5257, 2002.

[7] D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, "Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures," J. Am. Chem. Soc., 120, 6024, 1998.

[8] Y. Ueno, A. Tate, O. Niwa, H. Zhou, T. Yamada, and I. Honma, "High benzene selectivity of mesoporous silicate for BTX gas sensing microfluidic devices," Anal. Bioanal. Chem. 382, 804, 2005.

[9] Y. Ueno, T. Horiuchi, and O. Niwa, "Air-Cooled Cold Trap Channel Integrated in a Microfluidic Device for Monitoring Airborne BTEX with an Improved Detection Limit," Anal. Chem. 74(7), 1712, 2002.

[10] S. Camou, Y. Ueno, A. Tate, and O. Niwa, "Absorption detection on glass microchip with reflective layer coating for portable BTX measurements," Micro Total Analysis Systems 2004. 2, 455, 2004.

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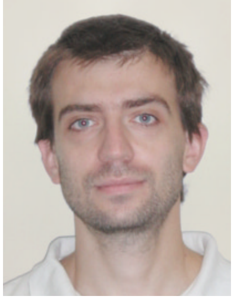

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