Continuous Analysis of Volatile Organic Compounds (VOCs) in the Research Practice

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A small, rapid and sensitive instrument for the continuous analysis of volatile organic compounds (VOCs) was developed and applied to the measurement of VOCs in the research practice of university.

Volatile organic compounds (VOCs) are substantial contributors to the formation of ozone and other photochemical oxidants. Some VOCs have been identified as toxic or mutagenic pollutants at concentrations sometimes found in urban environments.[1] In particular, benzene is an aromatic VOC characterized by the U.S. Environmental Protection Agency as a human carcinogen[2] In Japan, the assessment of the human-health risk due to exposure to ambient VOCs is limited owing to the paucity of available data on VOC levels, since VOC levels are not routinely monitored in many locations throughout Japan.[3,4] In a previous study, the simple analysis of VOCs at low levels in the atmosphere was conducted using passive samplers and the behavior and origins of VOCs in Kyoto City were analyzed.[5]

Furthermore, it is important to elucidate the human-health risk and environmental load due to the occurrence of VOCs in the research practice. The Labor, Safety, and Health Law was applied to the universities in 2004. A portable instrument is necessary for the continuous analysis of chemicals with lower boiling point (bp) than toluene because such chemicals are often used in the research practice. For the continuous analysis of VOCs, non-methane hydrocarbon analyzer, GC with photoionization detector, and GC-MS after collecting VOCs with adsorbent were reported, but these are not portable.[6–8] Although some portable VOCs monitors are commercially available, these were developed for the analysis of VOCs with higher bp than toluene and constituents of VOCs cannot be detected.[9] Then, in this study, a small, rapid, and sensitive instrument for the continuous analysis of VOCs with lower bp than benzene in addition to toluene and xylene was developed and applied to the measurement of VOCs constituents in the research practice of university.

A flow chart of the small instrument (440(W) × 340(H) × 270(D) mm) for the continuous analysis of VOCs is shown in Figure 1. The analytical procedure for VOCs is based on gas chromatography. After gaseous indoor VOCs are pre-concentrated on the adsorbent (I, Tenax TA, 40 mg) at a flow rate of 0.1 L/min and at room temperature (1–10 min) and desorbed by heating at 150 °C, the VOCs desorbed are separated in a packed column [II, SP-1200 + Bentone34(5 + 1.75)% Uniport HP 80/100 mesh, $2\phi \times 2$ m] at 60 °C and detected by two semiconductor gas sensors (D1 and D2). D1 is a sensitive gas sensor for VOCs with lower bp than benzene, while D2 is a sensitive gas sensor for toluene and VOCs with higher bp than toluene. VOCs are detected through the decrease of resistance values of tin oxides of these gas sensors. Compressed air, after eliminating water and VOCs with silica gel and activated carbon, is used as a carrier gas instead of N_2 or He gas at a flow rate of 10–30 mL/min. After the desorption of VOCs, the adsorbent is purged with this compressed air at 150 °C and cooled down for the next measurement. A standard gas (each 0.31 ppm of toluene, *p*-xylene, ethylbenzene, and styrene, N_2 balance, Sumitomo Seika Chemicals Co., Ltd.), and dilution method were used for the calibration of this instrument. Activated carbon tubes for organic gas sampler (20–40 mesh, 50 + 100 mg, Shibata, Tokyo) were used as an active sampler for the determination of VOCs by using a pump at a flow rate of 0.1 L/min. Gas-tube samplers (Shibata, Tokyo) packed with activated carbon (20–40 mesh, 200 mg) were used as a passive sampler for the determination of VOCs. After the VOCs adsorbed on the samplers were extracted into 1 mL of CS_2 in a septum vial, 1 μL of the extracted sample was injected and measured by FID-GC or GC-MS.

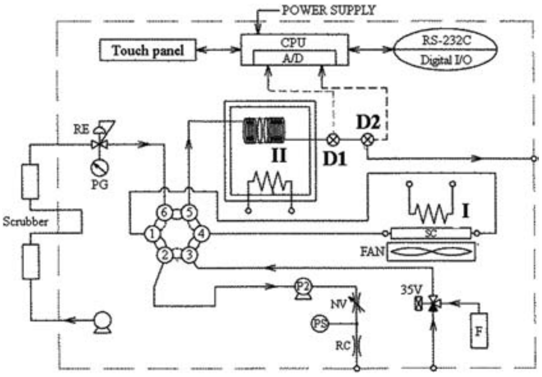

Figure 1. Flow chart of small instrument for the continuous analysis of VOCs.

Volatile organic compounds, such as toluene, xylene, benzene, ethyl acetate, alcohols, and *n*-hexane, can be continuously measured once every 30 min with this small instrument. However, chlorinated organic compounds such as chloroform cannot be detected. The retention time for benzene and toluene was 3.3 min and 6.5 min, respectively. The detection limits of VOCs were 10 $\mu g/m^3$. The relative standard deviation of benzene at the concentration of 200 $\mu g/m^3$ was less than 5% ($n = 5$). The sensitivities of VOCs by the present method were higher than those by the conventional method (FID-GC or GC-MS after adsorption of VOCs with activated carbon). This instrument can then be applied to the continuous measurement of VOCs in the research

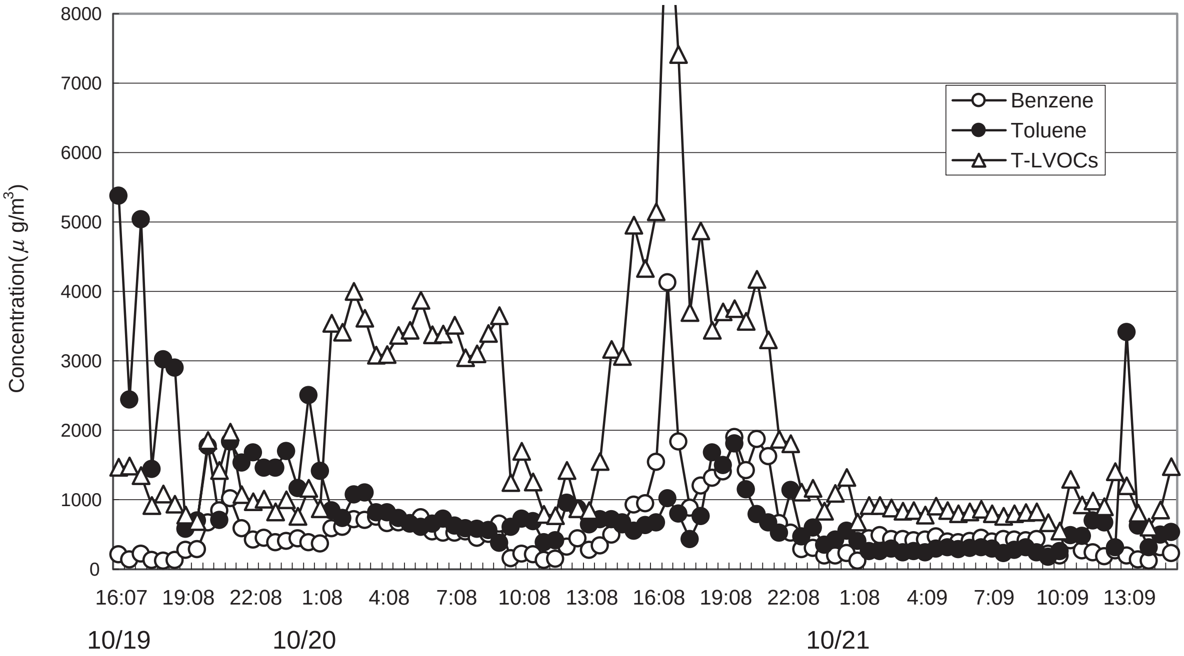

Figure 2. Temporal changes in the VOC concentrations in a laboratory for organic chemistry.

practice of university.

The concentrations of VOCs were measured in several laboratories and in the disposal plant for organic-liquid wastes. Temporal changes in the VOC concentrations in a laboratory for organic chemistry from October 19 to 21, 2004 are shown in Figure 2. T-LVOCs is shown as the total concentration of VOCs with lower bp than benzene. Benzene and T-LVOCs were detected with D1 sensor, while toluene was detected with D2 sensor. Clear peaks of toluene were detected in the procedure of column chromatography by using toluene in the experimental room. The concentrations of VOCs with lower bp than benzene were high in the second daytime because of the use of benzene and ethers. Moreover, the VOC concentrations on the first night were higher than those in the daytime and were almost constant, but those on the second night were very low. The concentrations of benzene, toluene, and xylene were also conventionally measured at 13:30–14:00 on the second and third days. These VOCs were undetected by the conventional method, while 0.1–0.2 ppm of benzene and 0.2–0.3 ppm of toluene were determined by the present method. On the other hand, during October 19 and 29, 2004, high VOC concentrations were measured in the process of transporting organic-liquid wastes in a polyethylene container to a tank in the disposal plant for organic-liquid wastes. The concentrations of benzene and toluene measured by the conventional method at 11:00 on October 29 were 0.8 ppm and 0.2 ppm, which were consistent with the results by the present method. Furthermore, it was found that VOC concentrations also increased after closing the room at night and were almost constant before opening the room the next morning. The concentrations of VOCs were also measured by passive samplers, and compared with those by this instrument. These results suggest that gaseous VOCs may occur while performing experiments and in the evenings and holidays, when chemicals are not used.

From these results, it was found that the developed instrument is very effective for the continuous analysis of VOCs at comparatively low levels in the research practice and then it may be applied to the risk assessment and management of chemicals.

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