Detection of odorants in town gas by portable GC using semiconductor gas sensor

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Abstract

A semiconductor gas sensor is extremely sensitive to the odorants contained in town gas, such as THT (tetrahydrothiophene), DMS (dimethyl sulfide), TBM (tertiary-butyl mercaptan) and cyclohexene. We developed a new type of gas chromatograph (GC) called the XG-100 that uses a semiconductor gas sensor to measure these odorants. The GC is designed to use in identifying whether the gas detected by a detector is the result of leakage from underground pipelines that supply town gas or is naturally occurring gas. The GC can selectively detect very low concentrations of the odorants. For example, it can detect THT at a level of 10 ppb without sample enrichment. The GC uses ambient air as the carrier gas so there is no need for highly pressured cylinder gas of N2, He or H2, which are indispensable for normal GC systems. The GC weighs only 10 kg, is small in size (240×190×330 mm (W×H×D)), and can be used as a portable GC.

1. Introduction

Semiconductor gas sensors are extremely sensitive to various gases and they are used in detectors in gas chromatograph. New Cosmos have produced a new gas chromatograph (GC) in which a semiconductor gas sensor is mounted in order to detect odorants. The target odorants are THT (tetrahydrothiophene), DMS (dimethylsulfide), TBM (tertiary-butyl mercaptan), and cyclohexene. Odorants from those that have been used for a long time to ones whose usage started recently are covered and orodants used not only in Japan, but also odorants used around the world can be detected. We have made it possible to carry this device which detects low concentrations of odorant onsite so that it can be used during maintenance of underground gas pipelines. Combustible gas (ex. methane) is also generated by the fermentation of organic materials. When a combustible gas detector is activated, it is difficult to determine if the gas originates from a leak in a buried pipeline. However, if low concentrations of odorant can be detected, the source of the leak can be identified more accurately.

To enable taking measurements onsite, our GC has been made compact and it operates with a low power consumption. Also, highly accurate measurement of odorants is possible with very simple operating procedures. The concentration of odorants in town gas is extremely low. Even in a 100% concentration of the combustible gas in town gas, there is only approximately 5 to 10 ppm of odorant. Previously it was difficult to directly detect diluted odorant components, and sample gas enrichment was required for analysis. However, the semiconductor sensor mounted in our GC is extremely sensitive and even with a small amount of sample gas, analysis at a sufficiently high accuracy is possible by directly injecting odorant at a ppb level concentration into the GC.

2. Portable GC system

The GC is small in size (240×190×330 mm (W×H×D)) and lightweight (10 kg) so that it can be carried to the measurement site. (See Photo 1.) The GC consists of a pump, a mass flow controller, an air filter, a temperature control part, a gas introduction part to insert the sample gas, a separation column, and the detector. For the carrier gas, air that has been cleaned by the filter is used. In the detectors, high-sensitivity sensors that have been designed to have high selectivity for the odorants have been used for accurate detection of the odorants after column separation. Instead of capillary columns, packed columns have been used. Sample gas enrichment is not required and detection is possible by directly inserting only 10 ml of sample gas into the gas introduction part. The detected odorant output is automatically transferred to a computer where special software quantifies the concentrations of each odorant. Odorant analysis with the GC-MS/FID that is used for standard analytical methods requires gas collection, enrichment, catalytic extraction, thermal desorption, or other time-consuming or complex operations, but these are not necessary with our GC.

Figure 2 shows the gas sensitivity characteristics of the high-sensitivity semiconductor sensor that is used in the detector in our GC. This sensor, which is designed to be highly sensitive to aromatic carbon gases, can detect odorants with low concentrations that could not be detected with previous sensors. By adding several catalysts to the base material of tungsten oxide, an extremely high sensitivity to odorants was achieved along with separation of combustible gases and other gases. The output signal can be accessed with a relatively simple electrical circuit, and an extremely compact device configuration was achieved.

The column that is used depends on the type of odorant. The column to detect THT and cyclohexene uses a packing material that effectively separates organic solvents. The column to detect TBM and DMS uses a packing material that effectively separates sulfur-compounds. In this way, it is necessary to change the packing material according to the target odorant.

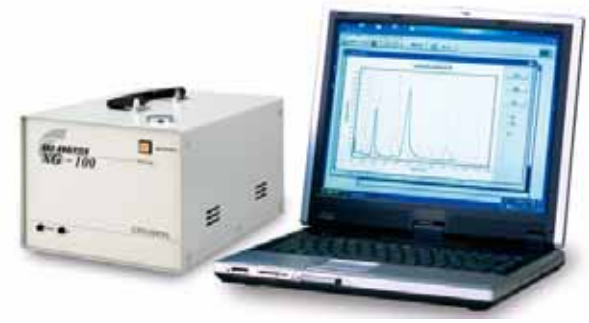

Photo 1 Appearance of XG-100

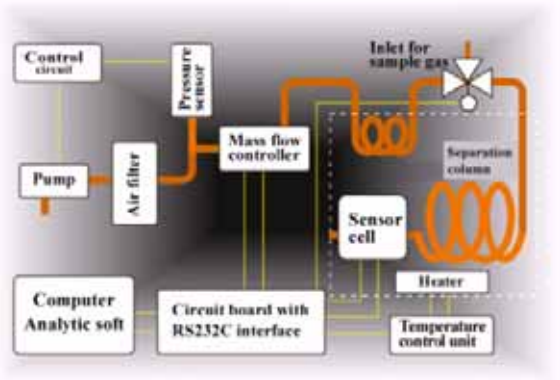

Figure 1 Schematic configuration of XG-100 for detecting odorants.

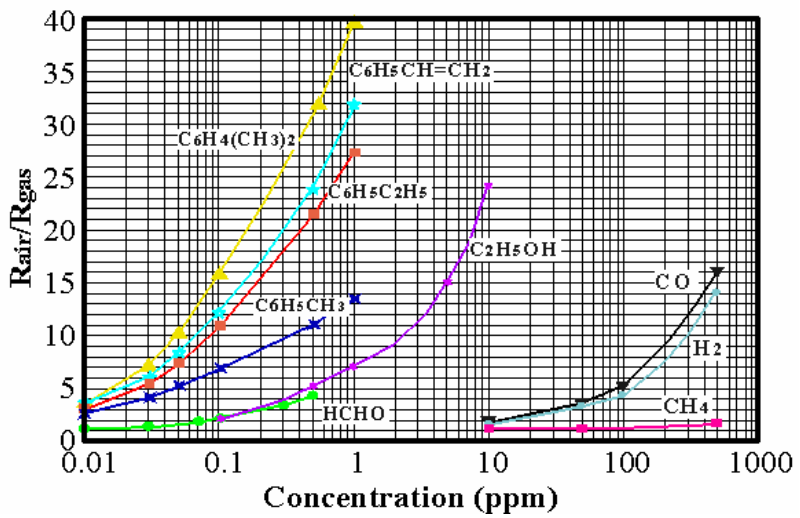

Figure 2 Sensitivities of the semiconductor gas sensor.

3. Detection of odorants

Figure 3 shows an application for measuring low concentrations of THT. By using our GC, THT can be detected at a concentration of 10 ppb. Some gas companies in Japan odorize 100% methane gas with approximately 5 ppm of THT before supplying the gas. The presence of THT is the only way to determine if the gas is from a gas leak in an underground pipeline. Our GC is already in use in devices to check for gas leaks.

Figure 4 shows an application for measuring low concentrations of cyclohexene. By using our GC, cyclohexene can be detected at a concentration of 10 ppb. The use of cyclohexene that does not contain sulfur compounds is increasing among gas companies, and there is a pressing need for detection of this type of odorant. At present, we are working to improve the semiconductor sensors that are used in the detectors so that even lower concentrations of this new type of odorant can be detected.

Figure 5 shows an application for measuring TBM and DMS. In contrast to the above two examples, the lower limits for detection level of TBM and DMS are several tens of ppb. The retention time for these components is 200 s for TBM and 470 s for DMS. TBM and DMS are currently the most common odorants used in Japan. We want to enable detection of even lower concentrations to popularize our GCs.

As shown here, if for instance, the odorant concentration in 100% of the supplied gas were 5 ppm of THT, and the odorant were not adsorbed by the ground or other substances, leak determination would be possible for a leakage gas concentration of approximately 2,000 ppm. As we have described, if a response to combustible gas was confirmed onsite, highly accurate determination of the source of the leak would be possible onsite.

As shown above, there are examples of detecting low concentrations of odorants with high-sensitivity sensors. On the other hand, another type of semiconductor gas sensors can be used for determination of concentrations of odorant at the ppm level in supplied gas. In this case it is necessary only to replace the semiconductor sensor mounted in the detector with a sensor designed for ppm level detection.

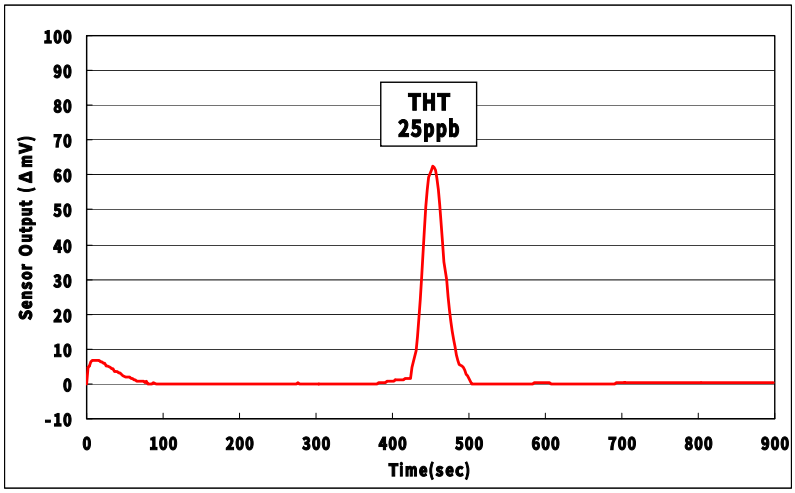

Figure 3 Gas chromatogram by XG-100 for detecting THT (tetrahydrothiophene) of 25ppb.

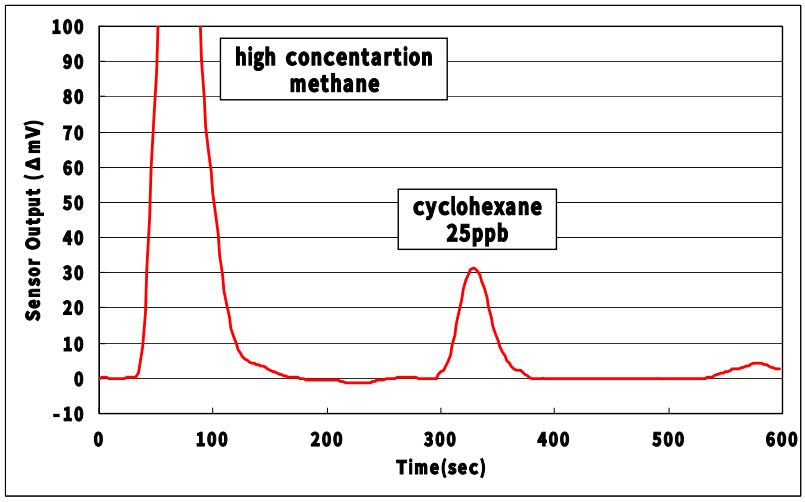

Figure 4 Gas chromatogram by XG-100 for detecting cyclohexane of 25ppb.

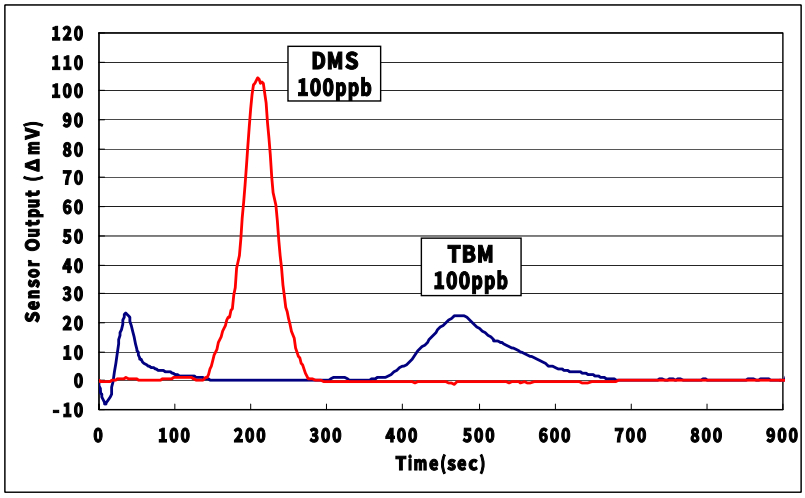

Figure 5 Gas chromatogram by XG-100 for detecting DMS (dimethylsulfide), TBM (tertiary-butyl mercaptan)

4. Conclusion

We have developed a portable gas chromatograph in which a semiconductor gas sensor is mounted in the detector in order to detect odorants in town gas. We have confirmed that this GC can be used to detect between 10 ppb and several tens of ppb of THT (tetrahydrothiophene), DMS (dimethyl sulfide), TBM (tertiary-butyl mercaptan), cyclohexene, without sample enrichment. By using this type of GC, which can be carried onsite to detect low concentrations of odorants, it is expected that more accurate detection of gas leaks will be possible. Furthermore, we are developing portable analytical devices that can detect lower concentrations of odorants, which will present a large potential in gas safety in the future. Also, if the detector in a GC is replaced with a detector for detection of ppm level concentrations of odorants, it is possible to use the GC for odorant concentration control in supplied gas.