The application of semiconductor-based odour sensors capable of measuring and evaluating indoor air quality

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ABSTRACT
Now believed to be responsible for anaphylaxis to chemical substances, concentrations of formaldehyde and VOCs emitted by interior finish materials and furniture, is very low in residential spaces. To accurately measure these concentrations, it is necessary to concentrate the air sample during sampling and to employ high-precision analysers such as a GC analyzer to obtain the results. Since these complicated sampling and analytical operations require a high level of expertise, the development of an on-the-spot precise measuring instrument has long been awaited. This study examines the application of two semiconductor-based odour sensors each capable of measuring and evaluating TVOC levels in low concentrations quickly and in a timed sequence. To evaluate the characteristics of each sensor, the results of the measurements were compared with results obtained from high-precision analysers, such as a GC Analyzer and a GC Mass Spectrometer. A relatively good correlation was obtained between the results, indicating the sensors can be used to develop an effective complementary system to enhance the analysers.

INDEX TERMS
Measurement methods; IAQ; Formaldehyde; VOCs; TVOC; Odour sensor; MCS

INTRODUCTION
Mites, fungi and house dust contain allergens that may cause allergic disease. This is a recognized problem in the field of indoor air quality (IAQ). At the same time, volatile organic compounds (VOCs) and formaldehyde (HCHO), released by interior finish materials, fixtures and furniture have been newly recognized as contributing to sick building syndrome and multiple chemical sensitivity (MCS) (Spengler and Sexton, 1983; CEC, 1997).

The equipment conventionally available for analysing HCHO-VOCs, such as the gas chromatograph (GC), the gas chromatograph/mass spectrograph (GC/MS), and the high-performance liquid chromatograph (HPLC), offers excellent accuracy of measurement but has the disadvantage of requiring complex processing, a high level of expertise, and special equipment. It is unsuitable for large numbers of measurements where results are required immediately. A simplified tool for the quick on-site analysis of large numbers of VOCs samples would be an extremely effective means of evaluating an environment and ensuring that necessary measures are taken.

From the several tens of available odour sensors, the author selected two semiconductor-based ones that are capable of detecting TVOC (total VOC) at concentrations of the order of $\mu g/m^3$ while offering easy transfer of measured data to a data logger or other device for storage and analysis. The performance and characteristics of the chosen sensors were evaluated by comparing measurements with data obtained using

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high-precision analysers. Semiconductor sensors operate on the principle that the electrical conductivity of a semiconducting material is proportional to the product of the effective charge, mobility and the density of carriers (Shiozawa *et al.*, 1996; Yamaguchi *et al.*, 1998).

SEMICONDUCTOR-BASED ODOUR SENSORS

Gas Detection Mechanism

In general, the electrical conductivity of a semiconducting material is proportional to the product of the effective charge, mobility and the concentration of carriers. A reducing gas on the surface of a metal oxide, such as tin oxide or zinc oxide, causes a change in the electrical conductivity of the material as a consequence of changes to one or more of these three factors. The performance of an odour sensor varies with manufacturing method and the shape and size of the particles comprising the sensor. Metal oxides contain free (conduction) electrons and exhibit an n-type semiconducting performance. At the surface of the crystalline metal oxide structure, oxygen atoms in the air capture conduction electrons from the structure and are adsorbed into the structure. The adsorbed oxygen builds a potential barrier and obstructs the movement of carriers, causing the electrical resistance of the sensor to increase. When a reducing gas such as a VOC is present, oxidation takes place and the captured electrons return to the crystalline structure of the semiconducting material. The resulting increase in electron density leads to the adsorption and desorption of a reducing gas. To accelerate the reactions, it is important to keep the detecting portion of the sensor at an elevated temperature using a heater or other device.

The change in electrical resistance of the sensor caused by the reducing gas is related to the gas concentration through the following equation:

$$R = KCn \quad (1)$$

where, R is the electrical resistance of the sensor; K and n are constants; and C the concentration of reducing gas.

Gas concentration readings are obtained with a semiconductor-based sensor from resistance measurements using the above equation. The sensor is connected to an electrical circuit such as a bridge, allowing the change in electrical resistance to be picked up as a difference in electrical potential and measured as an electrical output (V). Gas detection sensitivity ($\bullet V$) is given by the following equation,

$$\bullet V = V_t – V_o (2)$$

where V_o is the electrical output in clean air and V_t is the output when the reducing gas is present in the air:

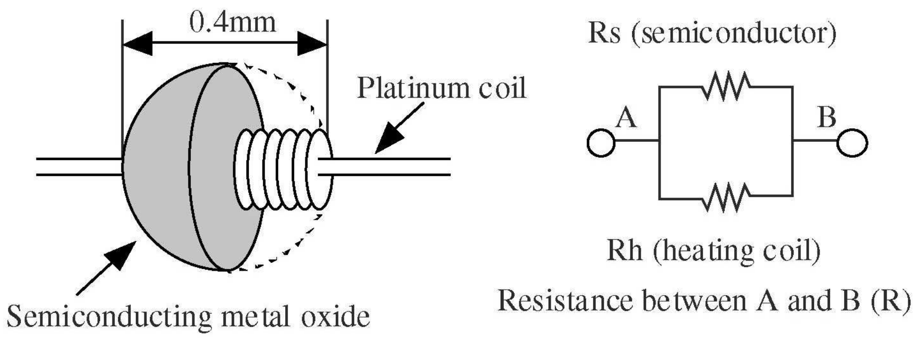
The relationship between $\bullet V$ and gas concentration, C, is given by Eqn (3) in the same manner as Eqn (1):

$$\bullet V = K'Cn' (3)$$

where K' and n' are constants.

Structure and Operational Principle of Semiconductor-Based Odour Sensors

As a typical example of a semiconductor-based odour sensor, a hot-wire semiconductor-based sensor of two-terminal structure is shown in Figure 1. The sensor is spherical, approximately 0.4 mm in diameter,



$$R = \frac{Rh - Rs}{Rh + Rs}$$

Figure 1 Structure of hot-wire semiconductor-based sensor.

with a porous metal oxide sintered onto a precious metal coil with two terminals. The coil serves both as a heater (to elevate the temperature of the semiconducting material) and as one of the resistance-detecting electrodes. Such a sensor is typically arranged as one side of an electrical circuit, such as a bridge. Looking at the structure of the sensor from the viewpoint of an electrical circuit, the resistance of the coil (R_h) and the resistance of the semiconducting material (R_s) appear in parallel in the circuit. When gas molecules are adsorbed onto the surface of the semiconducting metal oxide, its resistance falls, and the overall resistance of the sensor (R) also decreases.

METHOD

A number of temperature/humidity sensors (‘Ondotori’ TR-72S; T&D Corp.) were used to measure changes in temperature and humidity over time. To measure TVOC, 10 l of interior air was drawn by suction into a Tenax tube and analysed with a gas chromatograph (GC-17A; Shimadzu Corp.) using the solid-phase adsorption and heating desorption GC method. For qualitative analysis of VOC components, a gas chromatograph/mass spectrograph (QP-5000; Shimadzu Corporation) was used. The TVOC level was calculated by converting the total amount of VOCs on a toluene basis.

Changes over time in the output from two types of (semiconductor-based) odour sensors were stored in a data logger and output to a personal computer. The two sensor types are described below. The Type S odour sensor is a high-sensitivity metal oxide semiconductor gas sensor with a heating coil. The sensor is specified as reacting to alcohol, toluene, xylene, formaldehyde and acetaldehyde, but the relationship between concentration and sensor reading is not disclosed. Type T6 odour sensors is based on SnO_2 ceramic semiconductors. The correlation between concentration of ethanol and isobutane, as well as ammonium, and sensor reading is suggested for the Type 6 sensor.

RESULTS AND DISCUSSION

Evaluation of Odour Sensors by Measurement of TVOC in a Controlled Chamber

A laboratory test was carried out to study whether odour sensors could be used as a substitute for analysers in measuring the concentration of TVOC emitted by a variety of interior finish materials. Specimens of the finish materials were placed individually in a controlled chamber (1000 × 1000 × 500 mm; 0.5 m^3; Type 304 stainless steel) such that the load factor (LF) matched that in an actual room. The chamber was then ventilated using clean air treated with activated carbon. After ventilation, the air in the chamber was sampled and the TVOC level was monitored.

The correlation between TVOC as measured using the analysers and readings taken with the (Type S) odour sensor was examined. One of the results (see the next section for more details) is given as an example in Figure 2: the correlation for a sample of particle board used as a flooring material. As regards the correlation between TVOC obtained with the analysers and the readings of the Type S odour sensor, the value R^2 of the exponential correlation function is not less than 0.9, indicating that the correlation is good. The sensor is judged to be very useful as a simplified semi-quantitative primary screening tool for evaluating IAQ.

Consideration of Correlation between Type S Sensor Readings and Analyzer Measurements of TVOC in Chamber

The correlation between TVOC levels as measured with the analyzers and the readings of the Type S sensor is examined here. The value of R^2 averages 0.61 for all specimens examined (as shown in the top graph of Figure 3). This low correlation is attributable to different components of VOCs emitted by different types of interior finish materials. Examining the correlation after grouping the materials by type, the value R^2 for Group A increases to 0.85 (as shown in the middle graph of Figure 3). Thus, in using degree of similarity among the VOCs emitted and the ratio of each component's concentration to the total, the better the correlation between the analysers and the sensor readings. For interior finish materials of the same type, a better correlation holds (as shown in the bottom graph of Figure 3).

These test results demonstrate that the odour sensors are useful for measuring TVOC as a simplified semi-quantitative primary screening tool on a laboratory scale.

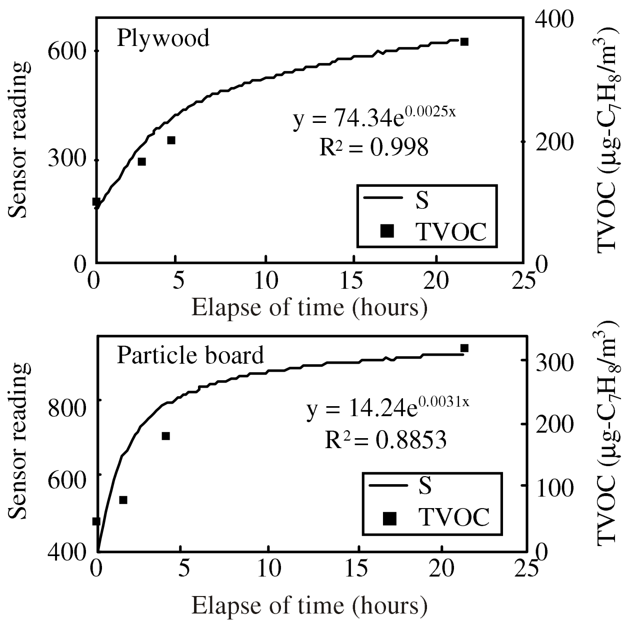


Figure 2 Changes over time in readings of Type S odor sensor and TVOC emissions from interior finish materials.

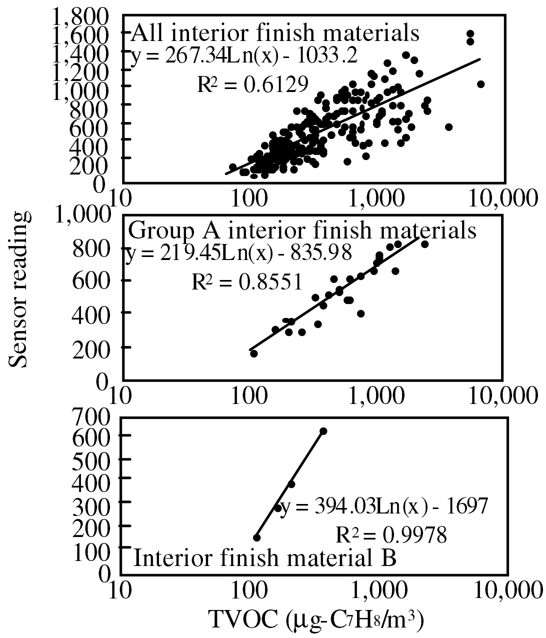


Figure 3 Correlation between TVOC emissions from interior finish materials as measured with analyzers and readings of Type S odor sensor.

Effects of inhibitor gases on odour sensor readings

The operational principle of odour sensors of the types studied here means that readings could become unstable if on-the-spot measurements are taken in locations where environmental conditions, such as temperature and humidity, cannot be controlled. Further, in measuring the quality of air containing two or more VOCs, a sensor may have good sensitivity to some VOCs but not to others.

Semiconductor-based sensors depend for their operation on the oxidation and adsorption of gas molecules on the surface of a semiconductor. Consequently, in using such sensors to measure TVOC, other reducing gases and/or oxidizing gases may interfere with measurement precision. Airborne moisture causes changes in the resistance of semiconductor-based odour sensors, so this must be taken into account when measuring the concentration of TVOC (Yamaguchi *et al*., 1998).

Applicability of Odour Sensors to On-the-Spot Measurements

The laboratory tests suggested that odour sensors might be suitable for detecting chemicals such as VOCs given off by interior finish materials and considered to be an IAQ problem. Actual on-the-spot measurements were made to determine whether such sensors could be used in place of the available analysers in the measurement of interior TVOC levels.

Monitoring was carried out in the western-style Room (with a floor area of about 30 m^2) on the sixth floor of the apartment building immediately after completion. The changes over time in concentration of TVOC were measured. Initially, the room windows were opened for 30 min to introduce outside air and balance the IAQ with that outside. The windows were then closed, and changes in the concentration of TVOC were measured with a GC analyzer while taking readings with a Type T6 sensor. The air change rate in the room was 0.2 times per hour, and the temperature and relative humidity were in the range 15–19°C and 40–60%.

After 2.5 h, the TVOC level increased to 1000 μg-C_7H_8/m^3, and then to more than 1700 and about 3500 μg-C_7H_8/m^3, respectively, at 5 and 21 h, respectively. The concentration of HCHO at 21 h was about 98 μg/m^3. The sensor readings increased as TVOC rose. The process of TVOC in the room reaching equilibrium can be seen in the sensor readings. There was good correlation between the concentration measured by the analyzer and the sensor readings ($y = 23{,}609\ e^{1.0655x}$ and $R^2 = 0.8347$). This demonstrates that a Type T6 odour sensor can be used to monitor TVOC levels (Figure 4).

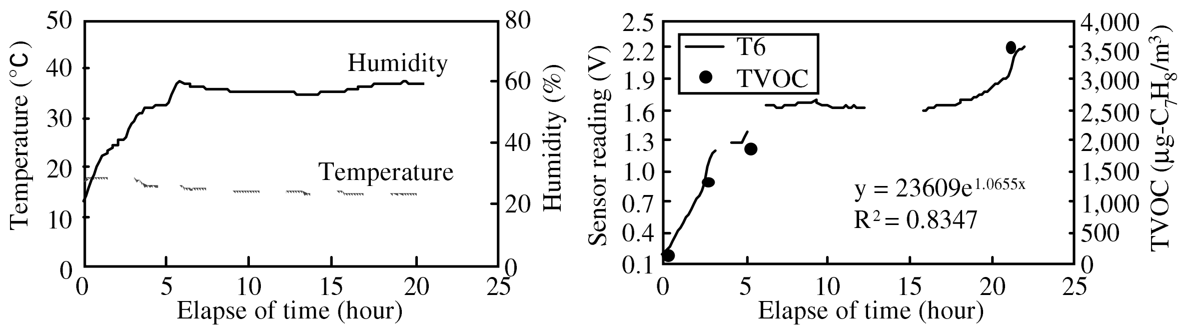


Figure 4 Correlation between interior TVOC level measured by analyzer and Type T6 odor sensor readings.

CONCLUSION AND IMPLICATIONS

The actual TVOC level in a room, however, varies greatly with the type and age of the interior finish materials, the construction method used, the season, the design and airtightness of the room, and interior temperature and humidity. In on-the-spot measurements, HCHO and TVOC concentration have been found to vary from 5 μg/m^3 at the lowest to 286 μg/m^3 at the highest and from 50 to 3600 μg-C_7H_8/m^3, respectively. According to other reports, some rooms have been measured with TVOC, one-order of magnitude higher than the measurements made by the author (Yoshino *et al.*, 2002).

The author has developed a simplified method of measuring chemicals such as VOCs in the room environment at concentrations of the order of μg/m^3 using odour sensors as a substitute for conventional measurement methods, which are very complex. Judging from the results of laboratory tests, odour sensors would ideally have a measurement range from several hundreds of μg-C_7H_8/m^3 to several tens of mg/m^3 for TVOC. However, for practical application, a sensor can be considered adequate as a simplified measurement tool if it can measure TVOC levels from approximately 300 μg/m^3, as given in the WHO guidelines, to an upper limit of several mg/m^3.

The two types of odour sensor selected for testing (Types S and T6) proved satisfactory in terms of performance as a simplified tool for measuring TVOC, and readings could be stored/analysed using a data logger and personal computer. However, this development work aimed at the measurement of chemicals at low concentrations, so the chosen sensors were highly sensitive. Consequently, in some cases, they were affected by inhibitors and moisture. Despite this, the results of laboratory tests and on-the-spot measurements in a room where temperature, humidity and the ratio of chemicals were constant, the sensors were able to measure TVOC with considerable accuracy. The reliability of the sensors as a simplified tool for measuring interior TVOC levels will be improved in future through a process of optimization that will include combining two or more sensors with different characteristics and introducing concurrent temperature and humidity measurements.

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