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Selective Detection of Hazardous Indoor VOCs Using Metal Oxide Gas Sensors

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Abstract

A strategy for detecting and identifying trace levels of hazardous volatile organic compounds (VOCs) in indoor air is presented. A metal oxide semiconductor gas sensor in temperature cycled operation is used to detect formaldehyde, benzene and naphthalene in ppb and sub-ppb concentrations with a varying background of ethanol with concentrations of up to 2 ppm.
Measurement results from a laboratory device have been compared with an integrated sensor system designed for use in field tests. We found that gas emissions from the system itself are an important issue. The emissions have been identified and quantified using analytical methods in order to derive design rules for a proper field test system. However, the results show that selective detection of VOCs in the ppb range is possible even with an intensive background of various VOCs, although sensitivity is reduced compared to the ideal laboratory case.

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Keywords: Volatile Organic Compounds; Indoor Air Quality, Metal Oxide Gas Sensor, Temperature Cycled Operation

1. Introduction

Many hazardous components in indoor air are Volatile Organic Compounds (VOCs) [1]. A number of these substances pose health risks even at very low concentrations (of a few ppb or even less) if people are exposed to them for a long time, for example at work places or at home. Smart building ventilation can help reducing exposure to hazardous VOCs by ventilating rooms with cleaner air from outside. In order to control the ventilation for best

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health effects but also for energy efficiency, the indoor air must be checked specifically for harmful compounds like formaldehyde, benzene and naphthalene. On the other hand, for optimized energy efficiency, benign substances like ethanol at low concentrations (up to approximately 1 ppm) should not lead to increased ventilation. Thus, sensor systems for selective detection of hazardous VOCs are necessary. Here, a sensor system based on metal oxide semiconductor (MOS) gas sensors is presented. Laboratory measurement results of a single SnO_2-based gas sensor (Type GGS1330, UST Umweltsensortechnik GmbH, Germany) and a field test sensor system using the same type of sensor are shown. Successful detection and discrimination of three different target VOCs, even with a high interferent background, is demonstrated.

2. Temperature Cycled Operation of MOS gas sensors

One method of improving selectivity, sensitivity and stability of metal oxide semiconductor (MOS) gas sensors is temperature cycled operation [2, 3]. In this operating mode, the integrated heater structure of the sensor is periodically set to several temperature steps or slopes (Fig. 1). The sensing MOS material is going through various states and transitions of these states, which leads to changing characteristics of the sensing material within such a temperature cycle. Using pattern recognition techniques, gas specific sensor responses throughout a temperature cycle can be assigned to the corresponding gas.

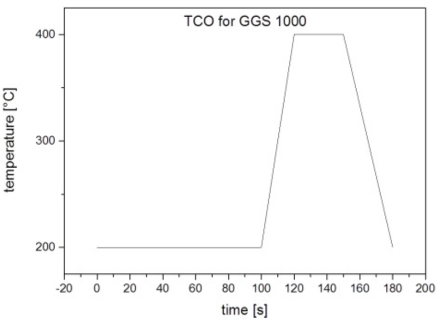

Fig. 1: 3-minute temperature cycle for MOS sensors of type UST GGS1000

3. Field test sensor systems

The MOS gas sensors were integrated into field test electronics systems by 3S GmbH, Germany. Each system can operate two gas sensors independently, with different temperature cycles. Calibration data and interpretation parameters are stored for each sensor in an EEPROM on the sensor PCB. Temperature cycles and general measurement configuration is read from a memory card on which raw measurement data can be stored at up to 10 ksps along with a real-time clock based time stamp. Air humidity and temperature are measured with an on-board sensor to monitor ambient conditions; the system can also be equipped with a dual beam NDIR CO_2 sensor. A multi-purpose extension connector allows for online preview of the measurement via a selection of communication interfaces.

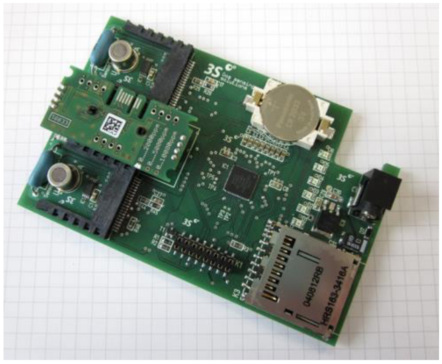

Fig. 2: Sensor system electronics for independent operation of two MOS gas sensors

4. Measurements of sensors and systems

The sensors and the sensor systems were characterized in laboratory tests using a gas mixing system specifically designed for very low test gas concentrations [4]. The target test gases were applied in two concentrations each, the relative humidity and the concentration of the ethanol interferent background were also varied, see Table 1. The low concentration of each VOC represents a value below the recommended threshold value, where no increased ventilation would be required, while the high values represent concentrations above the threshold where additional ventilation would be recommended.

Table 1: Target gas concentrations, relative humidity and ethanol interferent background values for lab tests

Gas	Concentration [ppb]	Relative humidity. [%]	Ethanol [ppm]
Pure air		40; 60	0; 0,4; 2
Formaldehyde	10; 100	40; 60	0; 0,4; 2
Benzene	0,5; 4,7	40; 60	0; 0,4; 2
Naphthalene	2; 20	40; 60	0; 0,4; 2

For data processing, secondary features describing the shape of the sensor response, i.e. mean value and slope, were extracted from several sections of the sensor signals for each temperature cycle of the measurement and used as input data for an LDA (linear discriminant analysis). This pattern recognition method evaluates these features and groups datasets of the same target gas at different concentrations while separating datasets of different target gases.

The result of the LDA evaluation of a single MOS sensor for laboratory test data is shown in Fig. 3. In this case, datasets of all the different gas configurations were input for the analysis. The two concentrations of each target gas (with and without interferent) are grouped together; thus, the supervised LDA algorithm only tries to separate the gases, not the two concentrations of the target gases. Therefore, each group contains all the cycles where a target VOC was applied with all background ethanol concentrations and both humidities.

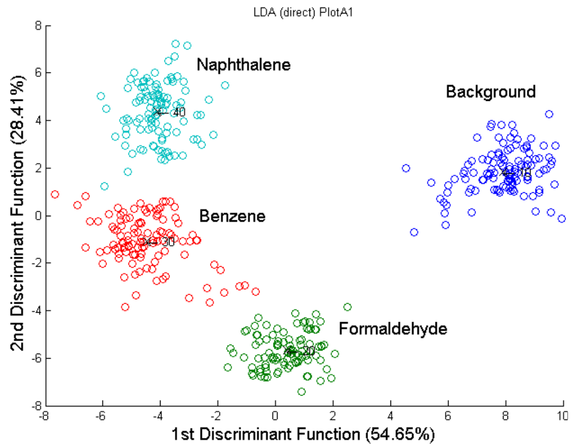

Fig. 3: LDA result of test measurement with single MOS sensor

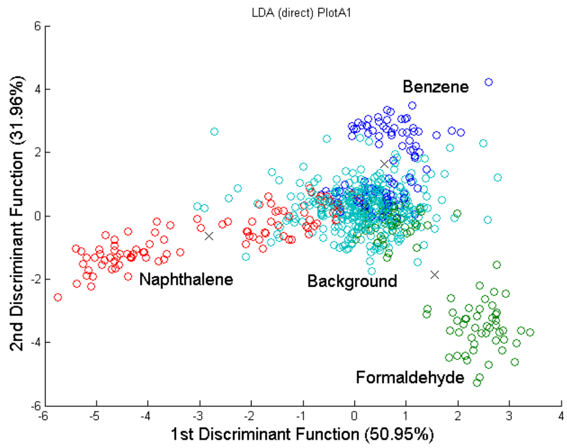

Fig. 4: LDA result of test measurement with sensor system; one of the two sensors was evaluated

Although all ethanol interferent concentrations and both humidities are included in the input data, discrimination of the gases is quite successful. The groups are not separated completely, but there is little overlap of the gases, and the three target gases are well separated from the group without the target VOCs (background). Thus, selective detection of the three target gases at ppb level is possible. A reduction of the input data set, e.g. by taking data from one relative humidity level only, improves the discrimination significantly [5]. Therefore the discrimination can be improved for the whole dataset using a hierarchical classification approach [6].

The integrated sensor system was tested with the same test gas profile as the single sensors; the air exchange rate during these measurements was 13.7 air changes per hour (ach). The result is shown in Fig. 4. Separation of the groups is not as distinct as for the measurement with the sensor alone. The target gas groups are split in two, representing the high and the low concentration of each VOC compound, respectively. While the high concentrations are still discriminated from background and from each other, the low concentrations are not separated from the background. Especially for benzene the sensitivity seems to be reduced.

As a reason for this, gas emissions from the sensor systems themselves were identified. GC/MS analysis of air flowing through a stainless steel chamber with and without the systems (at 2 ach) showed a significant increase of various substances emanating from both the PCB and the housing when two systems were placed in the test chamber, especially if they were switched on and therefore heated up. Table 2 shows an excerpt of the GC/MS analysis results listing only the most significant components. The analytical measurements were performed according to the ISO 16000 standard.

The total VOC (TVOC) values already show that the increase in gas emissions is considerable if the systems are operating. The most noticeable increase of a single compound is 1,2-dimethoxy-ethane, the precise origin of this component could not be determined.

Table 2: Excerpts of the GC/MS measurements of gas emissions from the sensor systems, air change rate of 2 ach; all values in µg/m³

Compound	Pure air	Test chamber, no systems	Systems OFF	Systems ON	Systems ON after heat treatment
Acetone	4.51	63.5	76.5	70.8	
1,3-Dioxolane	1.81	2.87	12.6	165	85.5
Ethane, 1,2-dimethoxy-	0.94	12.5	68.6	1125	561
Benzene	0.76	2.06	0.00	76.0	38.2
Toluene	0.76	30.6	26.8	48.8	6.41
m/p-xylene	0.51	2.11	0.76	67.7	21.0
TVOC	11.6	93.9	148	1800	1097

One of the target gases in this investigation, benzene, is also emitted from the systems in a concentration of 76 µg/m³ or 24 ppb. This leads to a high benzene background in the sensor signal (approx. 3.5 ppb during the gas measurement due to higher air change rate) and explains the reduced sensitivity to this gas compared to the individual sensor characterization in pure air.

The high concentrations of formaldehyde (100 ppb) and naphthalene (20 ppb) are still clearly discriminated from the background and each other; identification of these gases in these concentrations is possible with the systems.

The last column of table 2 shows data from an additional measurement of the emitted gases after heat treatment of the systems (13 h at 70 °C). It is obvious that emissions can be reduced significantly with this method, and this should be a first step in optimizing the systems for low concentration measurements.

5. Conclusions

The results show that MOS gas sensors with temperature cycled operation and signal analysis based on pattern recognition can achieve sufficient sensitivity and selectivity for ppb-level VOC detection. Three highly relevant hazardous target gases in the ppb and sub-ppb range have been detected and identified even in varying interferent concentrations of up to 2 ppm. Use of this strategy for controlling ventilation systems seems promising to achieve energy efficient and healthy buildings.

The characterized measurement systems can operate the sensors to achieve similar performance. However, detection of very low VOC concentrations is limited due to gas emissions of the PCB and housing if the devices heat up when running. Two ways to reduce this influence are heat treatment of the systems and use of low power gas sensors, which would considerably reduce self-heating of the devices. Nevertheless, 100 ppb of formaldehyde and 20 ppb of naphthalene can be identified with the systems.

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