Temperature Profile Investigation of SnO2 Sensors for CO Detection Enhancement.

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Abstract – SnO2 sensors are widely used for the detection of air contaminants such as CO. Nevertheless, their application encounters many problems, first of all the effect of interfering gases. The low selectivity is in fact a well-known problem of these sensors. Moreover, the high operating temperature of metal oxide sensors implies in general high power consumption. In this work we present a study aimed at the selection of an appropriate measurement technique for the detection of CO for indoor applications (lower threshold 100 ppm), also in presence of high concentrations of ethanol (up to 1000 ppm) by using only one sensor. Moreover, the work aims at developing very low size and power consumption devices, that could be battery operated, to be used for the development of portable CO detectors.

Keywords – Tin Oxide Sensors, Carbon monoxide, Ethanol, Temperature modulation.

I. INTRODUCTION

To provide adequate environmental and health protection, an effective CO monitoring system is a necessary instrument. The system must be simple, reliable, sensitive and cost-effective. The current trend for CO alarm development is to increase the sensitivity and to reduce the response time, in particular at low CO concentrations. This requirements are related to the low regulatory limits: in fact, attention levels and alarm levels are specific for each country but are often in the range of hundred ppms for indoor applications. SnO2 sensors are widely used for the detection of air contaminants such as CO ([1-4] and the references therein). Nevertheless, their application encounters different problems, first of all the effect of interfering gases. Indeed, the low selectivity is a well-known problem of these sensors and its improvement is a research field open to different solutions. As an example, Horrillo et Al. studied the influence of the SnO2 grain size, surface morphology and internal porosity on the sensor performance [5]. Selectivity can also be increased through the use of array of sensors with different sensitivity to the gas to be detected and with the use of efficient pattern recognition techniques [12, 13]. A different interesting approach consists in operating the sensors with variable temperature profiles [6-8]. Many different shapes and periods of the sensor temperature have been proposed depending also on the particular structure of the sensors used. In any case, it was proved that the selection of the temperature profile characteristics has a strong influence on the sensitivity and selectivity to CO. Moreover, coupling the variable temperature measurement technique with the use of micromachined sensors allows the use of fast temperature pulses, and offers the further advantage to significantly reduce the power consumption [6]. In fact, the high operating temperature of metal oxide sensors implies in general a high power consumption. This problem has been recently studied in the literature [6, 7, 9, 10]. Reduction of power consumption and sensor size [11] is a key aspect in order to develop portable equipment and sensor networks inside buildings. In this work we present a study aimed at the selection of an appropriate measurement technique for the detection of CO for indoor applications (lower threshold 100 ppm), also in presence of high concentrations of ethanol (up to 1000 ppm). Charcoal filters, suffering from poisoning problems, are not used in this work. The effect of humidity variation on sensors response will be taken into account in future studies. In this paper, measurements are performed under constant humidity. Both the selection of the most appropriate temperature profile and of the most significant sensor response features are addressed in this paper. In particular in this work the fast temperature pulse trains technique [1] is applied to commercial 'fast' SnO2 sensors. For a comparison, slow temperature modulation techniques were applied to conventional sensors.

II. MEASUREMENT SYSTEM

Measurements were performed with a laboratory electronic nose, controlled by a PC. The system, already described in [12], was improved by the addition of a faster and more flexible sensor temperature control system (see Figure 1).

Figure 1. Laboratory electronic nose set-up.
This is a dedicated microcontroller-based board that allows to individually control each sensor temperature (with an absolute error lower than 1°C) by using the sensor heaters also as temperature sensing devices. A different temperature profile can be selected for each sensor, to optimize the sensor performance. Temperature profiles are chosen through a software program, written in the Labview environment, and sent through a RS232 serial interface to the microcontroller (Hitachi H8S2345). The microcontroller controls the sensors’ temperature with a fast sampling rate (minimum sampling period 100 µs) allowing driving also micromachined sensors with fast temperature responses. The gas-sampling unit is a digitally controlled system providing the possibility to inject the desired gas or gas mixture into the measurement chamber and to control the gas flow (up to 500 ml/min) by means of three mass flow controllers. The sensors are arranged in a cylindrical symmetry configuration with respect to the gas flow direction, so that each of them receives in parallel the same amount of gas. In this way, problems with the decay of volatile organic compounds or with the appearance of combustion products observed for serial sensor arrangements can be excluded. The measurement chamber is placed inside an incubator for precise temperature control. In this work the following commercial sensors (Figaro USA Inc.) were used: TGS2600, TGS2610, TGS2611, TGS2620, TGS2442. The TGS2442 are ‘fast’ SnO2 sensors, as far as the thermal dynamic is concerned (time constant in the ms range). They are designed for pulsed temperature operations. These sensors are optimized for CO detection and have a charcoal filter, which reduces the ethanol interference. In this work these filters were removed before the measurements.

### III. RESULTS AND DISCUSSION

Different mixtures of CO and ethanol have been chosen to select the most appropriate temperature profile and to test the sensor performance (see Table 1). The goal was to obtain the recognition of 100 ppm of CO in 1000 ppm of ethanol that will allow the reliable use of such devices for CO recognition in presence of one of the most common interfering gases for indoor application. Sinusoidal temperature profiles of different period as well temperature pulses have been used to heat the sensors. Both thermally slow sensors TGS26XX and thermally fast, miniaturized sensors (TGS 2442) were used for measurements. Figure 2 shows ‘slow’ sensor responses to different gas mixtures when their temperature varies sinusoidally from 100°C to 400 °C in a 40 s period. It can be observed from measurements that some sensors (e.g. TGS2620 –Figure 2a) provide CO recognition, while other sensors (e.g. TGS2600 –Figure 2b) act as a ‘zero’ reference for ethanol cancellation as they are sensitive only to ethanol. The visual analysis was confirmed by the principal component analysis (PCA) showed in Figure 3, where the signatures obtained by PCA analysis for the different mixtures are shown. The features used for the PCA are the magnitude of the first two FFT harmonic components of the sensors’ responses.

<table>
<thead>
<tr>
<th>CO [ppm]</th>
<th>Gas #1</th>
<th>Gas #2</th>
<th>Gas #3</th>
<th>Gas #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>#1</td>
<td>#2</td>
<td>#3</td>
<td>#16</td>
</tr>
<tr>
<td>200</td>
<td>#4</td>
<td>#5</td>
<td>#6</td>
<td>#7</td>
</tr>
<tr>
<td>500</td>
<td>#8</td>
<td>#9</td>
<td>#10</td>
<td>#11</td>
</tr>
<tr>
<td>1000</td>
<td>#12</td>
<td>#13</td>
<td>#14</td>
<td>#15</td>
</tr>
</tbody>
</table>

Table 1. Test gases and gas mixtures. Hereafter each mixture will be addressed with the number reported in the corresponding table cell.

![Figure 2](image)

Figure 2. TGS2620 responses (a) and TGS2600 responses (b) to the mixtures reported in Table 1.
Figure 3. PCA obtained analyzing the mixtures reported in Table 1, using slow conventional sensors and sinusoidal temperature profiles.

The system is able to differentiate among the mixtures containing ethanol alone and those containing also CO. The discrimination among different concentrations of CO is possible only when analyzing the two lowest concentration of ethanol. When 1000 ppm of ethanol are present the CO presence can be detected but its concentration is difficult to derive. The markers in Figure 3 represent measurements obtained in different days in a period of one month. It can be noted that, when analyzing mixtures containing CO (without ethanol), a lower repeatability can be obtained. On the contrary, mixtures with a high concentration of ethanol (low sensor resistance) tend to give more repeatable results. In this case gas mixture identification is performed in a relative short time thanks to a very efficient measurement technique but the requirement of low power consumption is not fulfilled because the sensors require a continuous heating (typical VRMS = 3V).

Lower power consumption can be achieved by using sensors with thermal time constant in the ms range like the TGS2442. This sensor, alike the majority of the metal oxide sensors, is very sensitive to ethanol (without charcoal filter). This yields to the impossibility to discern between the presence of CO rather than ethanol when a pulsed heating cycle with the same amplitude is used and the sensor resistance value is sampled only once during the heating cycle (see Figure 4). This measurement protocol could lead to a false alarm when the sensor is exposed to interfering gases such as ethanol because the measured conductance variation doesn’t allow any discrimination. The recognition of different gases with only one sensor was exploited in this work making use of one TGS2442 heated with various temperature shapes. The temperature modulation reported in Figure 5 was first applied during the tests with the same gas mixtures of the previously described experiment (Table 1). The first pulse at 440°C has the aim to generate adsorbed O⁻ species that are more reactive than O²⁻ and O₂⁻ in order to improve the CO recognition [14]. The pulses at 150°C were chosen after tests that showed the maximum CO sensitivity at this temperature. The sensor conductance was normalized with respect to the cycle mean value (Figure 6) and the values at 0.9s, 2.9s, 4.9s (‘hot points’, before cooling the sensor) were considered. To reduce the electrical noise, the measurement value was taken as the average of samples in a 50ms range around the considered time. The parameters extracted for classification were the three coefficient \(a, b, c\) of the 2\textsuperscript{nd} order polynomial fitting of the considered points (see Eq. 1).

\[G = a + b + c + t^2\]  

In figure 7 an example of the PCA results are reported. The results obtained with this technique are in general less satisfactory than those reported previously for ‘slow’ sensors. Even if 200ppm of ethanol can be distinguished from the same amount of CO, the presence of CO in ethanol can be hardly recognized and not at all when greater ethanol concentrations are injected (data not reported in figure). It is very interesting to highlight that the sensor response was stable only after roughly 100s that the first heating cycle was applied, thus showing that chemical reactions need this time to get into regime when using this temperature profile. This means that measurements taken before 100s should be neglected in order to obtain reproducible results with the proposed technique. However, the detection of 100ppm or 200ppm of CO can be accomplished within a time in accord to the UL2034 standard (e.g. for 200ppm CO: after 5min–before 35min) [15].

Sensor performance can be improved by using the same heating cycle but with wider pulses (e.g. 10s) thus preserving the same heating signal RMS value (figure 8) of the previous one. Nevertheless, the drawback of using long heating pulses is the possible migration of heater material into the sensing element causing a long-term drift of the sensor resistance (see TGS2442 datasheet [16]).

The sensor responses to some gas mixtures of Table 1, normalized with respect to the cycle mean value, are shown in figure 9 and, as mentioned before, the slow phenomena can now take place. In particular we can notice how the presence of CO causes a raising in the conductance at low temperature showing that CO reacts with oxygen ions also at 50°C though very slowly whilst ethanol does not.
Figure 5. 1s pulses temperature profile.

Figure 6. Normalized TGS2442 sensor conductance upon temperature modulation depicted in figure 5, when exposed to the gases reported in the label.

Figure 7. PCA obtained analyzing three of the mixtures reported in Table 1, using only one TGS2442 sensor without charcoal filter and pulsed temperature profiles.

Figure 8. 10s pulses temperature profile.

Figure 9. Normalized TGS2442 sensor conductance upon temperature modulation depicted in figure 8, when exposed to the gases reported in the label.

Figure 10. PCA obtained analyzing the mixtures reported in Table 1, using only one TGS2442 sensor without charcoal filter and pulsed temperature profiles. The arrows indicate the direction on which the CO concentration, [CO], raises. The plot is zoomed in the gas region leaving the air cluster outside on the far left side.
This behavior could be exploited to improve CO recognition by sampling the sensor response in the ‘cold region’ [17] but it cannot help when also ethanol is present. In fact, the sensor response at 50°C to ethanol and ethanol+CO is quite the same (see figure 9, lines • and ).

However, the presence of CO can be recognized also with high ethanol concentration and by using only one sensor if the response in the ‘hot’ regime (150°C) is considered. Here, after an initial conductance decrease we can notice a peculiar rising. This could be possibly due to the reaction products from ethanol oxidation such as acetylene (C_2H_2), ethylene (C_2H_4) and acetaldehyde (C_2H_4O) [18,19], which, in turn can generate further reaction intermediates. Anyway, it is not the aim of the present paper to get into details of these reactions but only to explore this behavior to improve the CO detection. Thus, in this case the three ‘hot points’ taken into account were at 9s, 24s and 49s. Also in this case the measurements were averaged (0.5s range around the considered time). The parameters used for discrimination were again the coefficients of the 2nd order polynomial fitting (see Eq. 1).

Figure 10 shows the PCA of the gas mixture reported in Table 1, and a clear discrimination between gas mixtures can be noticed. In particular the presence of CO can be noticeably detected also in the presence of ethanol.

IV. CONCLUSIONS

This paper described different techniques for CO discrimination even in presence of high ethanol concentrations (up to 1000 ppm). The presence of CO can be detected by using both slow and fast sensors without using charcoal filters. The measurement technique was demonstrated to be the key element for robust gas discrimination and allowed the use of only one fast sensor instead of an array. Power consumption is reduced with the latter technique but long (at least 10s) temperature pulses should be used to allow slow phenomena to take place and thus to obtain better discrimination. The time required to detect CO also in presence of ethanol is in accordance with the requirements of the UL2034 standard.

The time-expensive measurement trials showed that it would be desirable to have a model of the sensor to simulate the sensor response to different temperature profiles. This requirement will be the dealing of the future studies.

REFERENCES