



Identification and quantification of different vapours using a single polymer chemoresistor and the novel dual transient temperature modulation technique

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ABSTRACT

This paper presents a novel signal processing technique for a square wave temperature modulated carbon black/polymer composite sensor. The technique consists of only two mathematical operations: summing the off- and on-transients of the conductance signals, and subtracting the steady-state conductance signal. The technique has been verified through its application to a carbon black/polyvinylpyrrolidone composite chemoresistor. Identification of water, methanol and ethanol vapours was successfully demonstrated using the peak time of the resultant curves. Furthermore, quantification of those vapours was found to be possible using the height of the peak heights, which was linearly proportional to concentration. The technique does not require zero-gas calibration and thus is superior to previously reported techniques.

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1. Introduction

Although there is a considerable demand for portable, handheld gas or vapour monitors, they have not yet enjoyed great commercial success. The diversity of gases related to air pollution makes it difficult to identify the species and to measure their concentration using a small, low cost instrument. For example, indoor air pollution can be caused by different types of volatile organic compounds (VOCs), such as formaldehyde, benzene, toluene and xylene, emitted from sources inside buildings [1]. Outdoor air pollution can also be caused by various gases such as carbon monoxide, nitrogen oxides, hydrocarbons and again VOCs emitted by automobiles [2].

Currently the most reliable way to identify and quantify hazardous gases is by using expensive, bulky analytical instruments (e.g. gas chromatographs, mass spectrometers and optical spectrometers). There has been significant effort put into reducing the size and the cost of such instruments through miniaturization (e.g. [3]). However, the degree of miniaturization is still limited, due to the nature of the parts required to be replicated, e.g. high voltages, vacuum systems, pumps.

There are two other possible approaches towards developing handheld gas monitors: to either use an array of gas sensors with different sensing materials [4] or temperature modulation of a single gas sensor [5,6]. The feasibility of the former approach has

been already demonstrated [4]. However, the development cost in manufacturing 10–20 different types of chemical sensors with guaranteed reliability is high and thus is not suitable for ubiquitous sensing. Concerning the second approach, previous research has been carried out on the temperature modulation of metal oxide chemoresistors [5,6]. Although the identification and quantification were successfully demonstrated, a major issue has to be resolved before commercialization; that is a pre-calibration of the sensors is required for both single gases and importantly their mixtures. This is because the response of high power metal oxide gas sensors is non-linear with gas concentration and thus a simple superposition of the responses for different gases is not always possible [7]. Provided that the identification and quantification of five different types of gases are required, which is a reasonable assumption for environmental gas monitor, pre-calibration has to be carried out for all the possible concentration combinations of those five gases, which makes commercialization difficult.

We recently reported on a novel low power temperature modulation technique using a carbon black/polymer composite chemoresistor sensor capable of identifying and quantifying single vapours by using either the off or on temperature transient of the sensor signal [8,9]. However, the technique was found to have some significant drawbacks as given below:

1. It was not easy to identify the components when mixed, as the curves used are always monotonously increasing (or decreasing). This restricts its application to identifying individual vapours in air and not mixtures.

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2. The technique requires the measurement of the transient conductance of air (zero-gas). This means that it is necessary to measure the zero-gas transients on a regular basis and ideally before each measurement of a vapour—adding complexity and cost to an instrument. Secondly, the sensor cannot be used easily in environments where there is no zero-gas (unless a bottled dry air is included within the unit). This limits the practical application of this method.

In this paper, an improved technique is proposed that overcomes these two limitations and thus significantly enhances the applicability of thermally modulated polymer composite based sensors.

2. Improved signal processing technique

A carbon black/polymer composite is an insulating polymer in which carbon black nanoparticles disperse to form electrical pathways. When the material is exposed to a vapour, the vapour molecules diffuse into the film causing it to swell. This swelling increases the average separation of the conducting nanoparticles and thus decreasing the electrical conductance. In the previous paper, a carbon black/polymer composite film was deposited onto a micro-hotplate and a square wave voltage was applied to a resistive microheater to modulate the temperature [9]. Identification and quantification of water, methanol and ethanol vapours with different concentrations were shown to be possible using either the off- or on-transient of the electrical conductance of the carbon black/polymer composite with two drawbacks described above.

The novel technique proposed in this paper uses both the off- and on-transient responses, unlike the previous technique described in [9]. First, the new technique is explained conceptually, then it is expressed in an analytical form and finally simulations and measurements are given.

The concept of the proposed technique is illustrated in Fig. 1. Here, a square wave temperature modulation of a gas sensor is induced between two temperatures T_1 and T_2 ($T_1 < T_2$) in the presence of a vapour. Fig. 1 (a) and (b) show the conductances of the sensor during the off- and on-transients, respectively. They are aligned so that their temperature changes occur at the same time. Here, $G_{1,\infty}$ and $G_{2,\infty}$ are the steady-state conductance at temperatures T_1 and T_2 of the vapour, respectively. One can note that the thermal response time of the micro-hotplate is smaller than the thermal time constant of the diffusion effect as shown in [9]. The thermal time constant of the diffusion effect for the off-transient is smaller than that for the on-transient because the temperature is lower. Thus, the off- and on-transient curves are not line-symmetric (i.e. The on-transient curve saturates faster than the off-transient one). Next, by simply adding the curves in Fig. 1 (a) and (b), we obtain the curve shown in Fig. 1 (c). A peak is formed as a consequence of the difference in the shapes of the off- and on-transient curves. Although the steady-state conductances $G_{1,\infty}$ and $G_{2,\infty}$ are the final values in the vapour, they will be affected by the baseline drift [9]. However, it is possible to find these values by waiting long enough for the diffusion process to reach equilibrium. Then, by subtracting the curve in Fig. 1 (c) by $(G_{1,\infty} + G_{2,\infty})$, we obtain the curve shown in Fig. 1(d). Thus, one can make the following predictions about the characteristics of the resultant curve:

- The time of the peak depends only on the diffusion coefficient at T_1 and T_2 (independent of the vapour concentration) and thus is specific to a vapour type.
- The height of the peak is linearly proportional to the vapour concentration since the amplitudes of both the off- and on-transients are proportional to the vapour concentration.

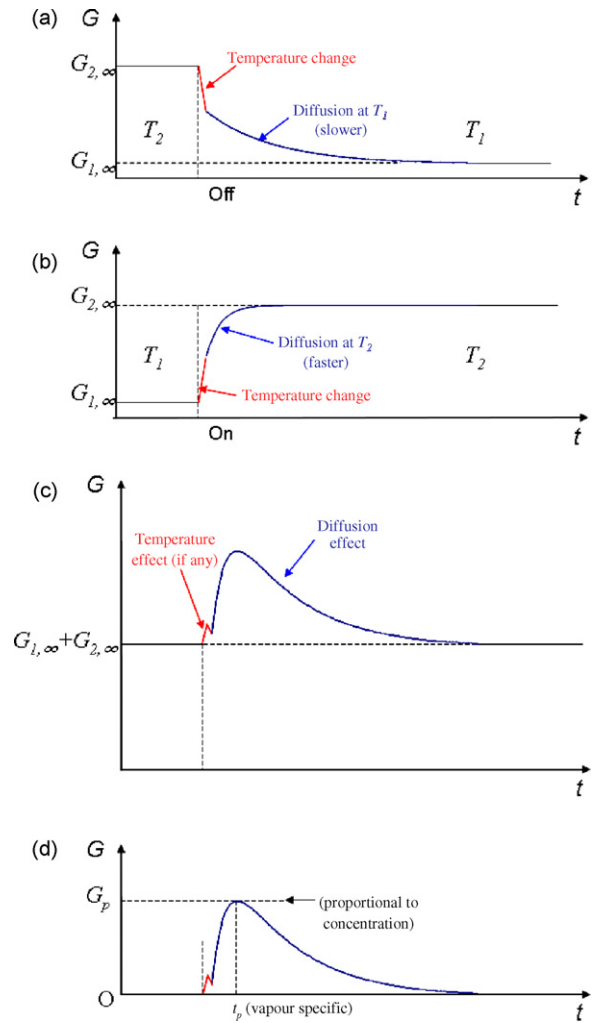


Fig. 1. (a) Sensor conductance of off-transient, (b) sensor conductance of on-transient, (c) sum of off- and on-transients, (d) final peaked curve for identification and quantification (G : conductance, t : time).

c. The curve for a mixture will simply be made of the linear superposition of the individual curves for each vapour, assuming that the species are independent of each other. (Small interactions could be modelled by extension to perturbation or non-linear theory).

To verify the above predictions (a and b), a rigorous mathematical discussion is now given. (Note: Prediction c will not be proven mathematically. This is because the assumption for prediction c is needed for Fick's equation, which our theory starts from. The prediction will however be proven experimentally later).

To calculate the transient conductance for a step temperature decrease from T_2 to T_1 as illustrated in Fig. 2, we first assume that the diffusion of vapour in the polymer simply follows Fick's law [10]

$$\frac{\partial c(x, t)}{\partial t} = D_{T_1} \frac{\partial^2 c(x, t)}{\partial x^2} \quad (0 < x < h) \quad (1)$$

where c is the concentration of the vapour in the polymer, D_{T_1} is the diffusion coefficient of the vapour molecule at T_1 , h is the thickness of the film. The initial concentration profile is uniform at T_2 as follows:

$$c(x, 0) = c_{\text{polymer}}(T_2) \quad (0 < x < h) \quad (2)$$

where c_{polymer} is the steady-state vapour concentration in the polymer, which is related with the vapour phase concentration c_{vapour}

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