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Thick film organic vapour sensors based on binary mixtures of metal oxides

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Abstract

Previously, composite sensors incorporating differing proportions of tin dioxide and zinc oxide were reported which exhibited high sensitivity to a range of organic vapours under dry conditions (0% relative humidity, RH). Most importantly, the composite sensors exhibited significantly higher sensitivity than sensors constructed solely from tin dioxide or zinc oxide when tested under identical experimental conditions.

Work is reported which was carried out on an extended range of composite materials, and involved testing these composites to a range of vapours that have been identified as being associated with the microbial spoilage of cereal grains in storage.

Both previously and in this investigation, tests at 0% RH showed that the tin dioxide/zinc oxide sensor elucidated the highest sensitivity to alcohol vapours. However, for the purpose of a practical device it would be necessary to operate the sensors under a flow of high humidity in order to nullify the effects of variations in grain moisture levels. The sensitivity of the composite sensors to known concentrations of volatile organic compounds was measured over a range of relative humidities (0–100%) at a constant temperature of 20 °C. A composite sensor comprising 50:50 (w/w) tin dioxide/indium oxide was found to give the highest sensitivity when tested to alcohol vapours at 100% relative humidity.

The work also highlighted a difference in the response of sensors to classes of organic compounds when operated at differing humidities. For example, the response to alcohols was reduced significantly when operated at high humidity, whereas the response to carbonyl containing compounds particularly ketones was relatively unaffected.

Keywords: Tin dioxide/indium oxide; Composite sensors; Relative humidity effects; Wheat quality assessment

1. Introduction

Semiconducting metal oxides have been utilised extensively at elevated temperatures for the detection of simple gases [1]. Sensors such as those based on tin dioxide or zinc oxide exhibit a high sensitivity but poor selectivity to organic vapours [2]. These sensors are also highly sensitive to humidity. Previously, base materials have been doped with catalytic metals or metal oxides to improve sensitivity, selectivity and stability [3]. Work has also been reported on the use of complex oxides [4] that may also improve the sensors' stability, sensitivity, or allow operation of the device under a wider range of environmental conditions.

Recently, composite materials such as those based on tin dioxide and zinc oxide have been utilised [5,6]. These composites were shown to exhibit a higher sensitivity than either tin dioxide or zinc oxide alone when exposed to sub-ppm concentrations of vapour [5]. Reasons for the apparent synergistic effects observed with these composites have been postulated. One suggestion invokes complementary catalytic activity [5], whilst another is based on the formation of hetero-junctions and changes in the micro-structure on sintering [6].

When wheat is colonised by fungi such as *Penicillium* sp. and *Fusarium* sp. volatile compounds are released [7]. A range of compounds, consisting predominantly of alcohols, was identified which increased when wheat was in the early stages of an infection. The concentration and type of these compounds is indicative of the type and severity of any infection on a given substrate. If any sensor system is to be of use in the determination of wheat quality then it must give an

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early warning of this microbial spoilage and therefore be sensitive to sub-ppm levels of organic vapours. However, it must also be able to differentiate between sound wheat and wheat that was previously colonised by fungi, or grain that had been in contact with contaminated grain.

The work reported here investigates a range of composite materials based on binary mixtures of single oxides, and includes a comparison with the single oxides alone. These composites were tested to a range of vapours that had been identified to increase in the headspace above fungally contaminated wheat. A major focus of the work involved testing the composite sensors under flow conditions and at a range of relative humidities (0–100% relative humidity, RH) in order to nullify the effects of moisture. The aim was to find sensors with high sensitivity and long-term stability when operated under high humidity conditions.

2. Experimental

2.1. Sensor preparation

2.1.1. Interdigitated electrode substrates

Uncoated substrates for the production of sensors were obtained from Capteur Sensors and Analysers, Abingdon, Oxon, UK. These consisted of a 3 mm alumina square with interdigitated gold electrodes on one side and a platinum heater on the reverse. The substrates were mounted on eight-pin dual-in-line headers before use.

2.1.2. Thick film sensors

Zinc oxide powder (AnalaR grade (99.5% BDH/Merck), tin dioxide powder (99.999%, Janssen Chimica), niobium(V) oxide powder (99.99%, Aldrich) and indium oxide pieces (99.999%) were used in the production of the sensors.

Composites incorporating 50:50 (w/w) tin dioxide/zinc oxide, 50:50 (w/w) tin dioxide/niobium oxide, 50:50 (w/w) tin dioxide/indium oxide, and 50:50 (w/w) zinc oxide/indium oxide were produced along with sensors incorporating indium oxide, tin dioxide, niobium oxide and zinc oxide alone.

In each case, 1 g of the oxide or oxide mixture was ground with a few drops of distilled water using an agate pestle and mortar for 1 h to produce a thick paste. The paste was then applied to the interdigitated electrodes. The paste was dried for 24 h at 25 °C and the sensors were then placed into the test rig and heated at 350 °C for 24 h in dry blended air (MG Gas Products, Reigate, Surrey, UK) prior to testing.

2.2. Sensor testing

2.2.1. Sensor evaluation equipment

The sensors were tested in an in-house designed injection test rig. The test chamber consists of an aluminium base-plate covered by a detachable dome-shaped glass vessel (300 cm^3). Zero-insertion-force sockets mounted on the base-plate permitted the easy fitting and removal of the sensors, which were mounted in the standard dual-in-line packages, as described in Section 2.1.1. Up to nine sensors could be tested at one time. The base-plate also contained two tubular feed-throughs (one inlet, one outlet), connected through electromagnetically operated on/off valves and a flow-measuring device to provide a continuous regulated flow of humidified air. The temperature inside the dome was measured using a semiconductor temperature sensor mounted on the base-plate.

The sensors were connected through a Keithley 7001 scanner to a Keithley 617 electrometer (Keithley Instruments, Reading, Berkshire, UK). Both Keithley instruments were connected via an IEEE488 interface to an IBM-compatible computer. Software written in-house permitted the automated gathering of sensor temperature, sensor conductance, chamber-temperature and purge flow rate data.

2.2.2. Humidity control and introduction of test vapour

The sensors were tested to the following vapours: ethanol, 1-propanol, 1-butanol, 1-hexanol, 3-methyl-1-butanol, 3-octanone, diacetyl, butanal, 2-butanone, ethyl benzene and decane. The vapours were tested at six different concentrations 5, 2.5, 1, 0.5, 0.25, and 0.1 ppm. The vapour was injected using a gas tight syringe into a pre-chamber that was situated prior to the air inlet to ensure full mixing prior to passage into the main chamber and contact with the sensors.

Initially, the testing was carried out under dry conditions (0% RH) at a flow of 1 l/min where the source was a dry blended air cylinder. A range of humidities were produced in the test rig by passing cylinder air through a number of Dreschel bottles maintained in a thermostatted water bath fitted with a cooling coil (Grant Instruments Ltd., Cambridge, UK).

2.2.3. Operation of the testing rig

The sensors to be tested were mounted in the chamber and heated to the operating temperature of 350 °C. The chamber was purged with dry blended air at a flow rate of 1 l/min. The sensors were allowed to equilibrate for 24 h prior to testing.

After the data-acquisition program had been initiated, the following procedure was used:

1. The humidified air was initiated at a flow rate of 1 l/min (not applicable if testing at 0% RH).
2. The sensors were left until a steady baseline was attained.
3. The test vapour was injected into the pre-chamber and subsequently into the sensor chamber.
4. The response was monitored until the current measured had returned to a steady baseline value.

This procedure was repeated for different concentrations of the same vapour. Before testing to a different vapour, the test chamber was removed, cleaned (using water/detergent then acetone followed by drying at 100 °C) and the same procedure was repeated.

3. Results and discussion

All the sensitivity results quoted were calculated using the following relationship: $100(I_g - I_o)/I_o$, where I_g was the peak current of the sensor after the injection of the test vapour, and I_o was the stable baseline current prior to injection.

Composite sensors incorporating niobium oxide were found to exhibit low sensitivity to organic vapours even when operated under dry conditions, and therefore composites of this type were not studied extensively. The typical responses of a range of thick film and composite sensors when exposed to 5 ppm of ethanol vapour (all concentrations are quoted in ppm (v/v)) when operated under a flow (1 l/min) of dry air are shown in Fig. 1. The response of the same sensors exposed to 5 ppm of ethanol vapour but operated under a flow (1 l/min) of air at 100% RH is shown in Fig. 2. The results show that composites of tin dioxide/zinc oxide and tin dioxide/indium oxide gave enhanced sensitivity at a range of humidities when compared with the single oxide sensors. However, composite sensors comprising mixtures of zinc oxide and indium oxide gave a reduction in sensitivity when compared directly with the equivalent single oxide sensors.

A number of possible mechanisms have been postulated to explain the synergistic effect observed with some composite sensors of this type. In other work by our group [5], more evidence has been gained to suggest that the effect is at least in part a catalytic one. In studying the breakdown products of butan-1-ol and 2-butanone (using ^{1}H NMR and GC-MS) when passed over the composite material and the individual materials at 350 °C we have ascertained that there are important differences in the catalytic pathways operating in each material. For example, tin dioxide appears to catalyse an initial dehydrogenation (butan-1-ol to butanal and 2-butanone to methyl vinyl ketone (MVK)) whereas zinc oxide more efficiently catalyses the further breakdown of the dehydrogenated product (butanal to alkenes/alkanes and MVK to acetone; tin oxide is extremely inefficient at catalysing the further breakdown of MVK at the operating temperature of the sensor). Therefore, the catalytic pathways operating in tin dioxide and zinc oxide are distinct but complimentary when combined in a composite form. This catalytic theory offers some explanation of the synergistic sensitivity effects observed during these and previous experiments with the composite sensors. Other workers who have reported [6,8] the same benefits of bulk composite sensors based on mixtures of tin dioxide and zinc oxide (albeit for sensing different compounds) have cited changes in microstructure (materials made more porous) and the formation of hetero-contacts as reasons for the observed enhancement in sensitivity. More recently, work on composites of tin oxide and zinc oxide has been focused in the area of the photo-catalytic degradation of organic compounds in water and air [9,10]. This work is indirectly related to the use of the composites as gas sensors and it may provide some evidence as to why there is a higher catalytic efficiency when using composite materials for the breakdown of volatile organic compounds.

All the oxide materials exhibit a decrease in sensitivity when operated under high humidity conditions suggesting a

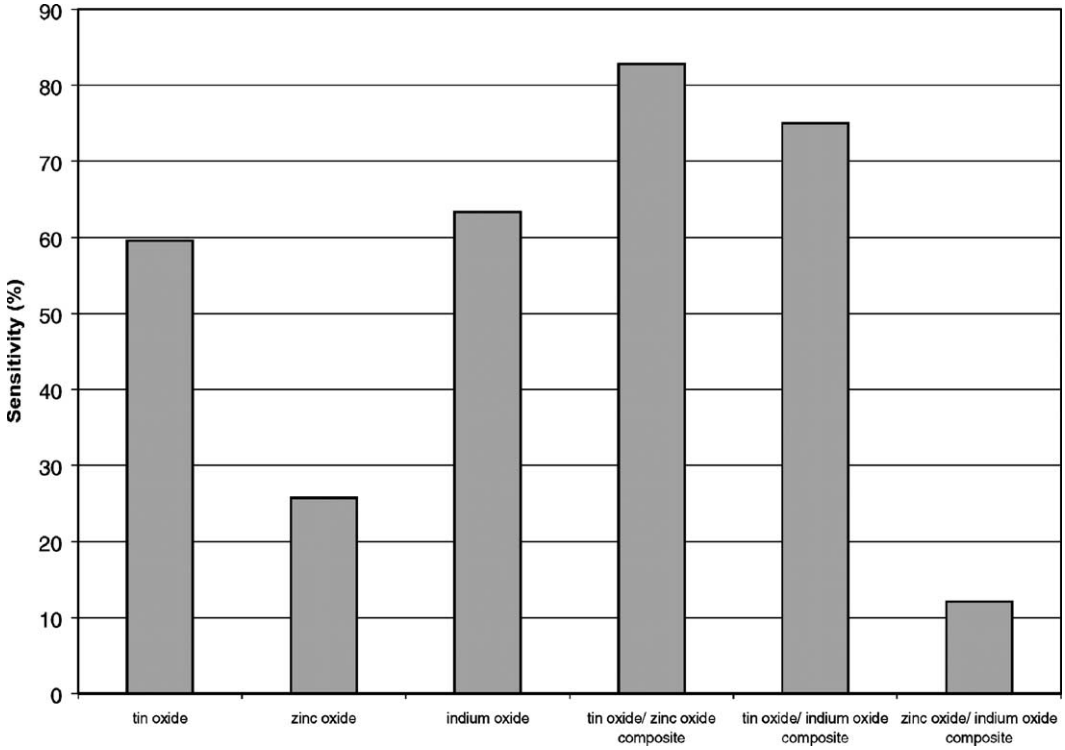

Fig. 1. The response of single oxide and composite sensors to 5 ppm of ethanol vapour at 0% RH.

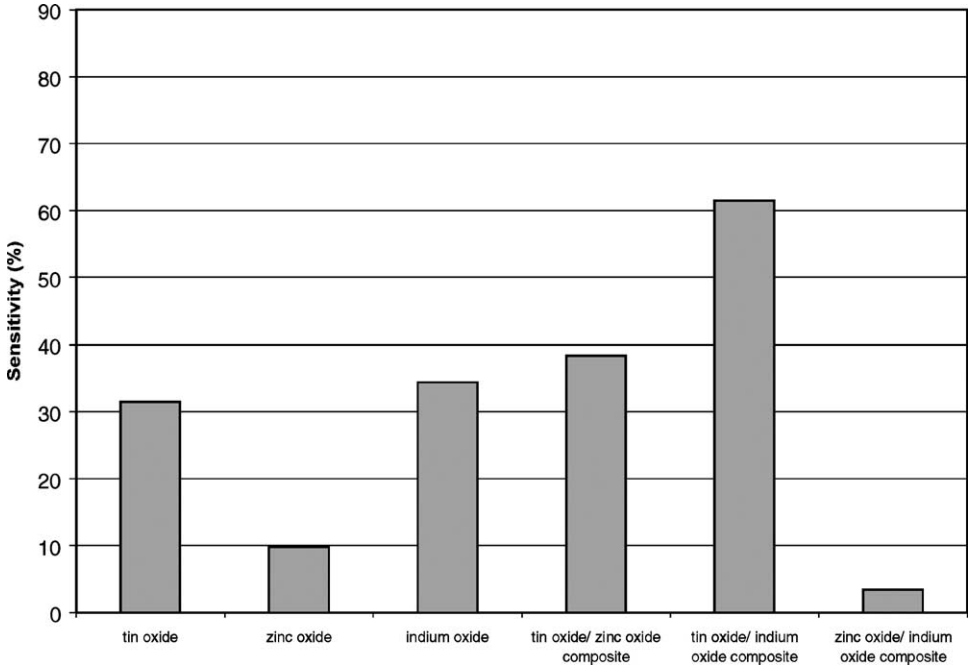

Fig. 2. The response of single oxide and composite sensors to 5 ppm ethanol vapour at 100% RH.

competitive effect with water vapour. In most cases, the sensitivity decrease observed was at least 50%. However, for the case of the tin dioxide/indium oxide composite sensors the decrease was much smaller at circa 15%. For this reason when tested under high humidity conditions, the tin dioxide/indium oxide composite sensor exhibits the highest sensitivity to ethanol vapour of all the sensors tested. Therefore, composites based on tin dioxide and indium oxide offer not only higher sensitivity than either tin dioxide or indium oxide sensors, but also less variation in sensitivity (higher stability) when tested under differing humidity conditions.

The synergistic effects observed with tin dioxide/indium oxide composite sensors when tested at 0% RH were relatively small with a 20% enhancement in sensitivity when compared with either tin dioxide or indium oxide sensors alone. When tested under 100% RH conditions the synergistic effect observed with this composite are greatly increased with a 100% enhancement in sensitivity observed when compared with either tin dioxide or indium oxide sensors alone.

Fig. 3 shows the responses of a range of sensors when exposed to ethanol vapour over the full range of relative humidities (0–100%) at 20 °C. The sensitivity was seen to drop sharply for all sensors tested at 20% relative humidity. However, a subsequent increase in sensitivity was observed when the sensors were tested at 40% RH. This was then followed by another drop in sensitivity at 60 and 80% RH followed by a subsequent rise at 100% RH. Fig. 4 shows the responses of a range of sensors when exposed to 5 ppm 3-octanone over a range of humidities. The pattern is very different from that observed when ethanol was the target analyte. The decrease in sensitivity particularly for the tin dioxide/zinc oxide composite sensor was not as marked. The trends observed for individual sensors were also very different, with the tin dioxide/zinc oxide sensor decreasing gradually in sensitivity when tested between 0 and 40% RH, and then subsequently increasing when tested between 60 and 100% RH. This is in contrast to indium based sensors particularly the indium oxide/tin dioxide composite which exhibited a small increase in sensitivity when tested over the full range of humidities 0–100%. The results suggest that the competitive effects occurring between ethanol and water vapour on the surface of the sensors are more significant than

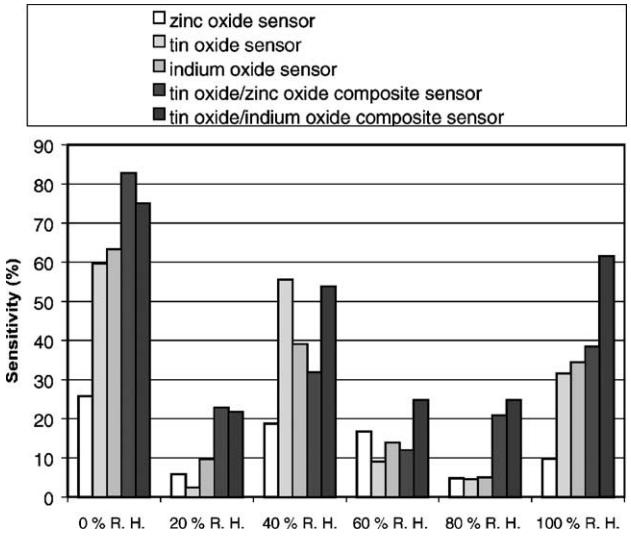

Fig. 3. The response of single oxide and composite sensors when exposed to 5 ppm of ethanol vapour at six different humidities in the range 0–100% RH.

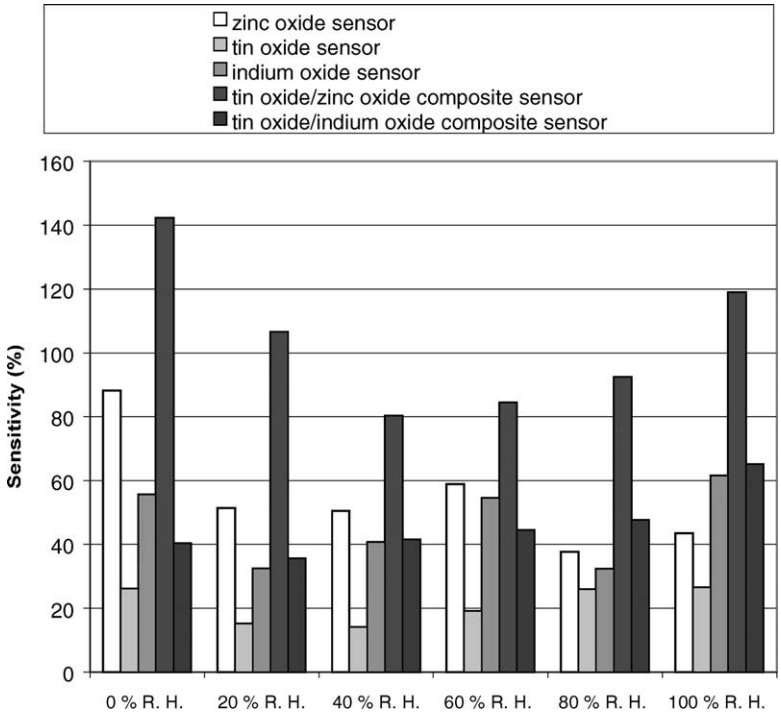

Fig. 4. The response of single oxide and composite sensors when exposed to 5 ppm of 3-octanone vapour at six different humidities in the range 0–100% RH.

for the case of water and 3-octanone vapours. The effects of water on the surface reactions of oxide materials are complex and these results serve to emphasise this further. Some groups have postulated an enhanced sensitivity when water is present: for instance, the response of tin dioxide sensors when exposed to CO [11]. It has been suggested that hydroxyl groups on the surface of tin dioxide increase the oxygen vacancies and therefore the number of surface oxygen ions. However, despite an unexpected pattern in the sensitivity results, the sensors tested in this study suggest an overall competitive effect when water vapour is present, particularly where alcohols are the target vapours. The only exception to this was the composite sensor based on indium oxide and tin oxide which showed enhanced sensitivity to carbonyl containing and non polar vapours when tested under 100% RH.

Figs. 5 and 6 show the two best composite sensors, namely tin dioxide/zinc oxide and tin dioxide/indium oxide, when exposed to a range of 11 vapours at six concentrations between 0.1 and 5 ppm under dry conditions. The results show that sensors of this type are easily capable of detecting sub-ppm levels of a range of organic vapours. The highest sensitivity was observed for polar compounds such as alcohols, ketones and aldehydes. Non-oxygen-containing and non-polar species such as decane and ethyl benzene gave much lower responses. The results suggest that the oxygen functionality of the organic vapour facilitates the adsorption to the tin dioxide surface and is key in the formation of reactive intermediates/surface states. This is in agreement with a mechanistic study [12] using GC-MS that studied the surface reactions of reducing vapours with tin dioxide. Ethanol vapour adsorbing onto the surface of the tin oxide formed an ethoxy-surface group (with an Sn–O bond) prior to the oxidation or dehydration reaction. Adsorbed electrophillic oxygen species will react with the C=O functionalities of the oxidised product (in this case acetaldehyde) to form a carboxylate surface group which breaks down to form the acetate.

When a range of primary alcohols were tested a linear increase in sensitivity was observed with increasing chain length for the tin dioxide/zinc oxide composite sensor. However, this relationship broke down for the case of 1-hexanol (possible steric constraints) and secondary alcohols such as 3-methyl-1-butanol did not follow the same trend as the primary alcohols.

Under dry conditions the tin dioxide/zinc oxide sensor was more sensitive than the indium oxide/tin oxide composite sensor. Figs. 7 and 8 show the same tests repeated at 100% RH. It can be seen that the indium oxide/tin oxide composite sensor exhibits higher sensitivity to a range of compounds at 100% RH than was the case when subsequently tested at 0% RH. Whereas the tin dioxide/zinc oxide composite sensor displayed a marked decrease in sensitivity when tested at 100% RH particularly when tested to alcohol vapours. Furthermore, it can be seen that the indium oxide/tin dioxide sensor now exhibits higher sensitivity to a number of the organic compounds when compared with the tin dioxide/zinc oxide composite sensor. The decrease in sensitivity of the tin dioxide/zinc oxide sensors was most marked when tested to alcohol vapours at 100% humidity whereas the responses to carbonyl-containing compounds, such as butanal and 3-octanone, were relatively unchanged.

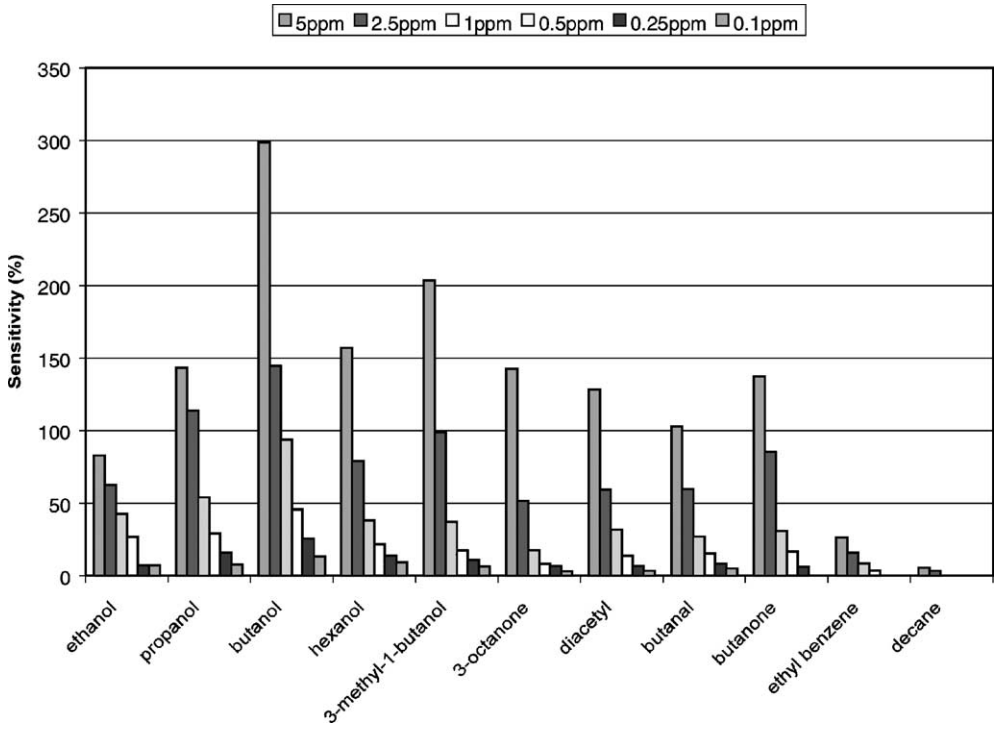

Fig. 5. The response profile of the tin dioxide/zinc oxide composite sensor when exposed to 11 vapours at six different concentrations under a constant flow of dry air at 1 l/min.

The responses to non-polar vapours such as decane and ethyl benzene were also not reduced drastically. For the case of indium oxide/tin dioxide sensors the responses to alcohol vapours were relatively unchanged when tested at 0 and 100% RH with only a small reduction in sensitivity observed. However, the sensitivity to a range of carbonyl-containing compounds was increased when testing at 100% humidity compared to the parallel study in dry conditions.

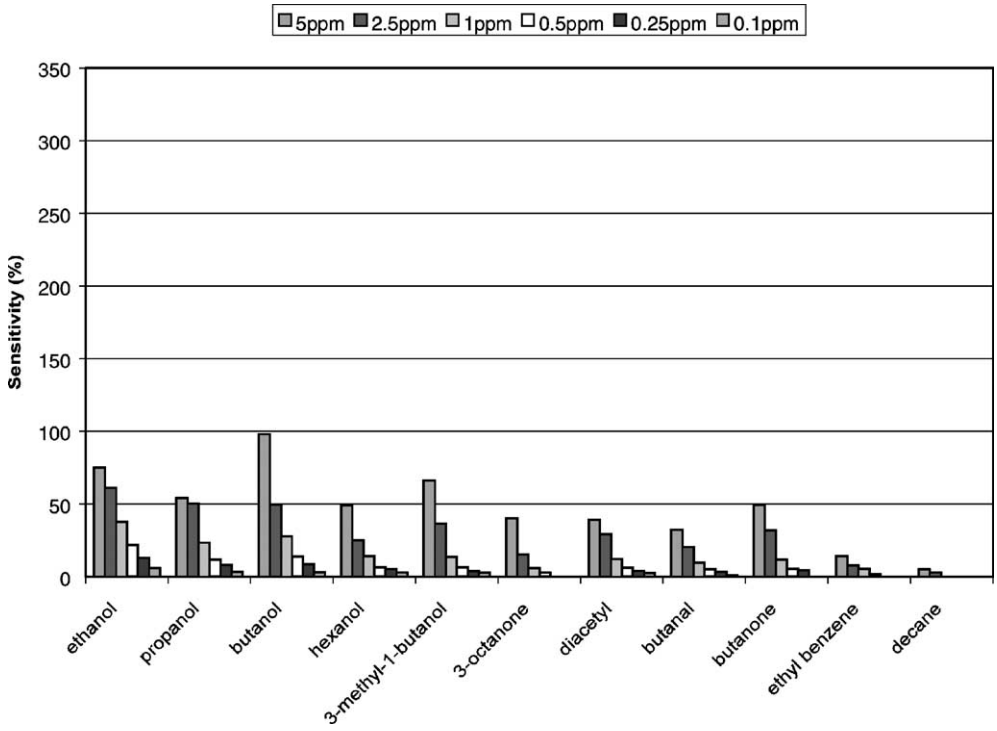

Fig. 6. The response profile of the tin dioxide/indium oxide composite sensor when exposed to 11 vapours at six different concentrations under a constant flow of dry air at 1 l/min.

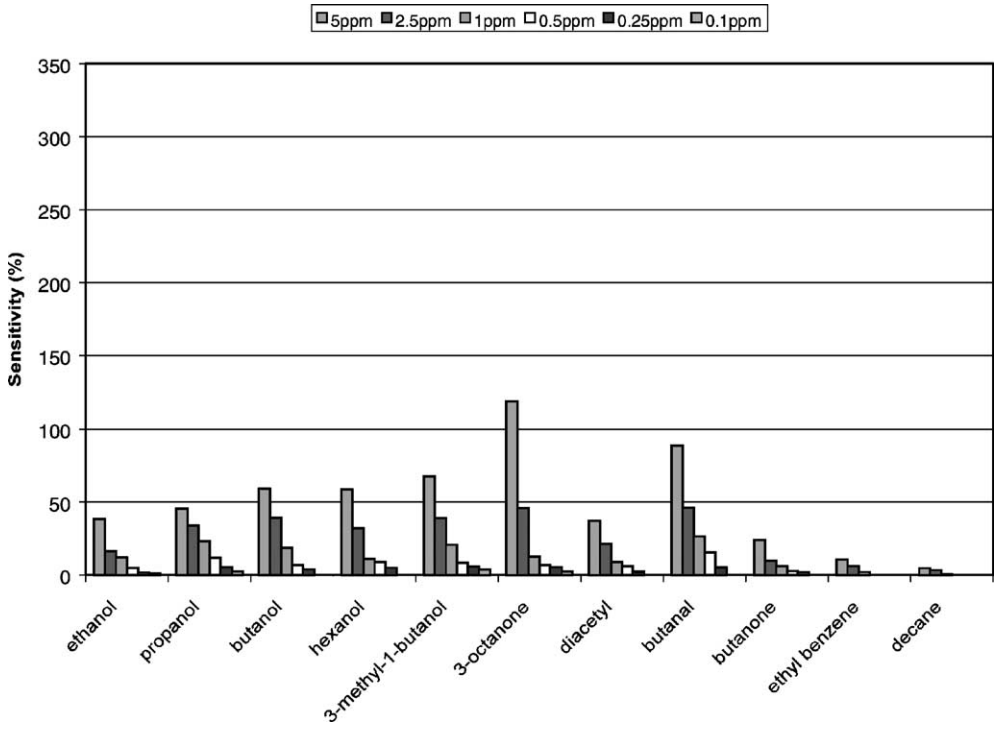

Fig. 7. The response profile of the tin dioxide/zinc oxide composite sensor when exposed to 11 vapours at six different concentrations under a constant flow of humidified air (100% RH) at 1 l/min.

The response to non-polar compounds was also enhanced when operated at 100% relative humidity. This suggests their are some additive effects with water vapour when using the tin dioxide/indium oxide sensor to detect various classes of organic compounds.

It should be noted that the effects described are reversible and that sensors previously operated under high humidity conditions regain their previous sensitivity characteristics when operated subsequently under dry conditions or under lower humidity conditions. It is also worth noting that we

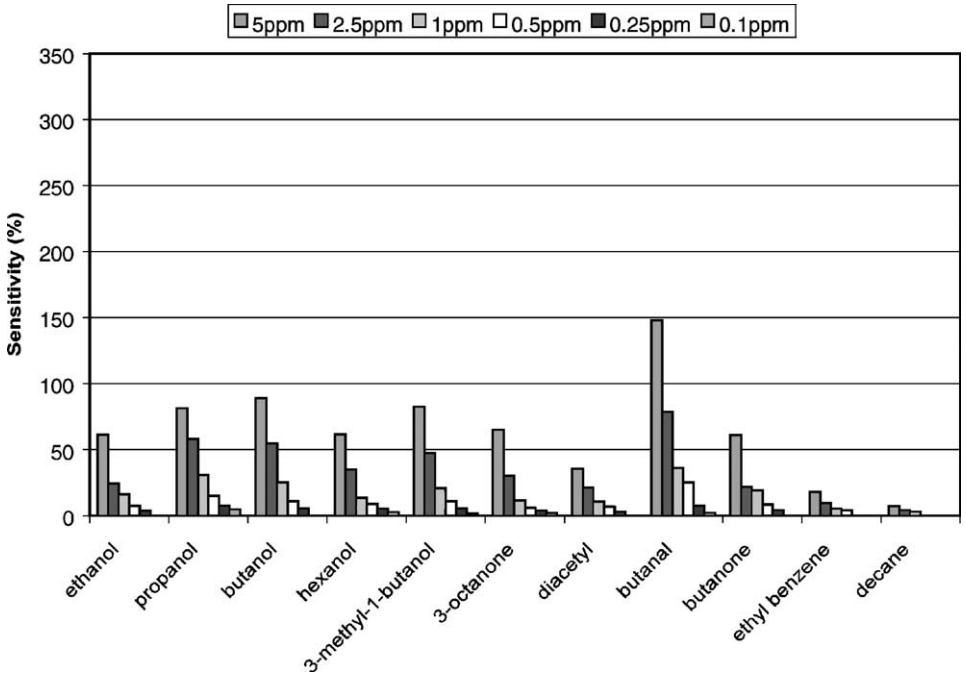

Fig. 8. The response profile of the tin dioxide/indium oxide composite sensor when exposed to 11 vapours at six different concentrations under a constant flow of humidified air (100% RH) at 1 l/min.

have found that cycling the sensors between low and high humidity conditions (when not under test) prolongs the useful lifetime of the sensors when compared to keeping them under high humidity conditions for long periods of time (months) where a marked decrease in sensitivity was observed.

Composite materials of this type produce sensors that exhibit very high sensitivity, relatively high stability and can be made reproducibly. This study has shown that with a limited range of materials and by employing facile production techniques a range of sensors that operate effectively under differing environmental conditions can be produced. This is of use where a range of sensors with differing sensitivities and selectivities are required for array type devices or where a number of materials need to be screened for possible gas sensor applications. Previous work by our group and other groups has shown that changing the proportions of each material in the composite yields a wide range of sensor materials with very different sensing characteristics. This study has highlighted a composite sensor incorporating indium oxide/tin dioxide that gives high sensitivity to a range of vapours under 100% relative humidity conditions. This and other sensors from this study have been incorporated into a practical sensing device that is operated under 100% humidity at high flow rates. The prototype has been in operation with identical sensors for a number of months and has been used to determine wheat quality in laboratory and pilot industrial trials.

4. Conclusions

A range of composite sensors have been identified which exhibit high sensitivity to a range of volatile organic compounds. The study has shown that composite sensors give additional advantages over single oxide sensors as well as the previously described enhancement in sensitivity. A composite sensor incorporating tin dioxide and indium oxide exhibited a high sensitivity to organic vapours, particularly alcohols, when operated under high humidity conditions. However, a composite sensor based on tin dioxide and zinc oxide which exhibited the highest sensitivity to organic vapours when operated under dry conditions suffered a significant loss of sensitivity when operated subsequently at high humidities.

The study gave some insight into the complex surface reactions occurring on metal oxide surfaces when exposed to organic vapours, particularly in the presence of water vapour. When a range of sensors were exposed to alcohol vapours in the presence of high humidity, a significant reduction in sensitivity (typically 50%) was observed compared with the results obtained under dry conditions, suggesting a strongly competitive affect with water. Conversely, when the same sensors were exposed to carbonyl-containing compounds and non-polar alkanes/aromatics in the presence of water vapour only a relatively small reduction in sensitivity was observed. This may provide some evidence to suggest that different classes of organic compounds react at different sites on the metal oxide surface.

These sensors respond to key organic volatiles emitted from fungi colonising wheat grain, some of which are capable of producing mycotoxins, therefore these sensors may provide a method of detecting such fungi.

Acknowledgements

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