

Full Research Paper

Home-made Detection Device for a Mixture of Ethanol and Acetone

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Abstract: A device for the detection and determination of ethanol and acetone was constructed, consisting of a packed column, a chamber with a sensor head, 2 dc power supplies, a multimeter and a computer. A commercially available TGS 822 detector head (Figaro Company Limited) was used as the sensor head. The TGS 822 detector consists of a SnO₂ thick film deposited on the surface of an alumina ceramic tube which contains a heating element inside. An analytical column was coupled with the setup to enhance the separation of ethanol and acetone before they reached the sensor head. Optimum system conditions for detection of ethanol and acetone were achieved by varying the flow rate of the carrier gas, voltage of the heating coil (V_H), voltage of the circuit sensor (V_C), load resistance of the circuit sensor (R_L) and the injector port temperature. The flow of the carrier gas was 15 mL/min; the circuit conditions were $V_H = 5.5$ V, $V_C = 20$ V, $R_L = 68$ k Ω ; and the injection port temperature was 150°C. Under these conditions the retention times (t_R) for ethanol and acetone were 1.95 and 0.57 minutes, respectively. Calibration graphs were obtained for ethanol and acetone over the concentration range of 10 to 160 mg/L. The limits of detection (LOD) for ethanol and acetone were 9.25 mg/L and 4.41 mg/L respectively.

Keywords: Home-made detection device, ethanol, acetone

1. Introduction

Semiconductors are used as gas sensors based on the principle of the variability of electrical conductivity of metal oxides when exposed to these gases [1]. These properties can be utilized to detect NO_x , H_2 , volatile organic compounds (VOCs), SO_x , CO_2 and O_2 , etc [2-11]. Metal oxide semiconductor (MOS) sensor technology is based on the change in resistance of a sensitive metal oxide layer which is induced by the interaction between a surface and ambient gases. Metal oxide semiconductors demonstrate good detection sensitivity, robustness and the ability to withstand high temperatures and the technique is commonly used to monitor a variety of toxic and inflammable gases in a variety of air pollution monitoring systems, the food industry, medical diagnosis equipment and gas leak alarms. A diversity of metal oxides such as SnO_2 [2-5, 16-18], TiO_2 [5, 12], WO_3 [9-11] and ZnO [12-15] can be used as sensor heads. Gong *et al.* [16] have tested the sensitivity of a thin-film tin oxide gas sensor to several organic vapors (methanol, ethanol, isopropanol, acetone and acetic acid) in a designed air flow system. Lee *et al.* [18] have studied the fabrication and characteristics of a SnO_2 gas sensor array for many volatile organic compounds (VOCs). A voltage detecting method was used to calculate the sensitivity of the sensor, which was defined as:

$$(R_{\text{air}} - R_{\text{gas}}) / R_{\text{air}} \times 100 (\%)$$

where R_{air} and R_{gas} were the electrical resistances in VOCs and clear air, respectively.

Sensor arrays for testing alcohol vapors can be modified by integrating them with a gas chromatograph [19]. When the alcohol vapors came into contact with the sensor arrays, a decrease in conductivity of the sensor was observed. The conductivity increased when the alcohol was flushed out of the chamber by the carrier gas. Although many metal oxides are sensitive to volatile organic compounds (VOCs), in the present work the commercially available TGS 822 sensor from Figaro Company Limited was used for the detection of ethanol and acetone because of its low cost, durability and wide dynamic ranges. The TGS 822 sensor is a SnO_2 thick film deposited on the surface of an alumina ceramic tube which contains a heating element inside. The TGS 822 cannot be used for the detection of the mixture of ethanol and acetone [20], so in the present work an analytical column was added into the detection system to separate ethanol and acetone before the gas reached the sensor head; the principle is the same as in gas chromatography. The present work represents an attempt to construct a home-made detection device for a mixture of organic volatile compounds. Ethanol and acetone were chosen to test the availability of the commercially available TGS 822 detector. Later on the detector using metal oxides nanopowders synthesized by chemical processes such as sol-gel, hydrothermal, oxalate and especially flame spray pyrolysis which gives primary particles with size ranging from 5-10 nm in a single step. This simple home-made detection device was capable of separation of organic volatiles compounds with the aid of a used analytical column from a gas chromatograph. The response data could be collected by a written software program which converted the resistance signal into a chromatogram like those shown by expensive equipment, so the use of a simple detection device to detect the mixture of organic volatile compounds such as ethanol and acetone represents an achievement. We expect to test other organic volatile compounds in the future using this device.

2. Preparation of the stock standard solution

2.1 Ethanol stock solution (1000 mg/L)

Pipette 1.277 mL of AR grade ethanol (99.7%, Carlo Erba, France) into a 1-litre volumetric flask and make up to volume with reverse osmosis (RO) water. Mix well.

2.2 Stock standard solution of acetone (1000 mg/L)

Pipette 1.267 mL of AR grade acetone (99.8%, Carlo Erba, France) into a 1-litre volumetric flask and make up to volume with RO water. Mix well.

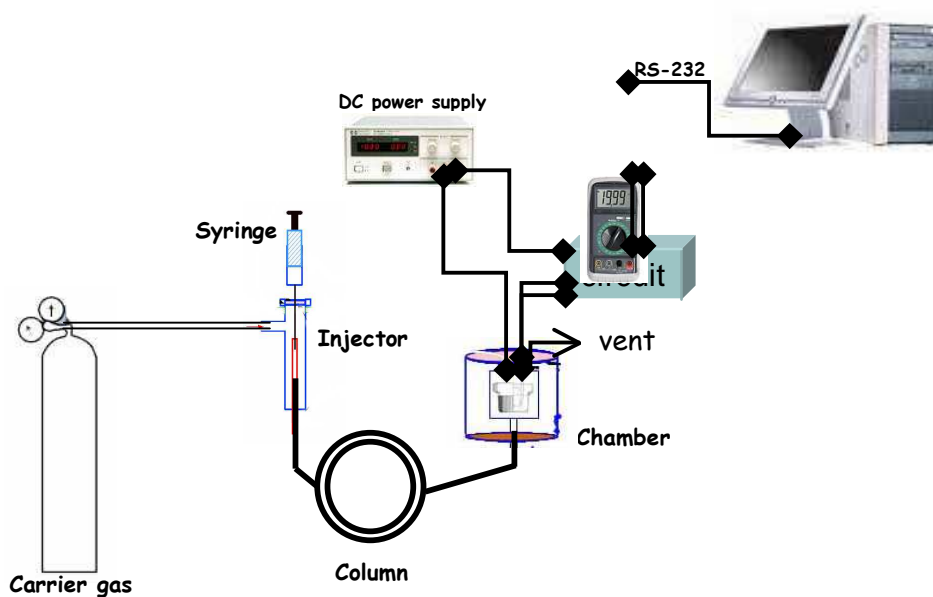
2.3 Preparation of the standard ethanol and acetone concentration of 10.00, 20.00, 40.00, 80.00 and 160.00 mg/L

Standard ethanol and acetone solutions with concentrations of 10.00, 20.00, 40.00, 80.00 and 160.00 mg/L were prepared by pipetting equal volumes of ethanol and acetone (50, 100, 200, 400 and 800 μ L of 1000 mg/L ethanol and acetone stock solution) into a 5 mL volumetric flask, then adjusting the volume to 5 mL with RO water.

3. Construction of the detection device

The schematic diagram for the device for detection of ethanol and acetone sensitivity measurements is shown in Figure 1. The system consists of a carrier gas, an injector port, an analytical column, a chamber with a sensor head, 2 dc power supplies, a circuit sensor, a multimeter and a computer. The optimum conditions of the system for the detection of acetone and ethanol were determined by varying the flow rate of the carrier gas, voltage of the heating coil (V_H), voltage of the circuit sensor (V_C), load resistance of the circuit sensor (R_L), and the injector port temperature.

Figure 1. Schematic diagram for the detection device of ethanol and acetone



In order to establish the optimum conditions, 1:1 solutions of ethanol and acetone with concentrations of 10 mg/L, 20 mg/L, 40 mg/L, 80 mg/L and 160 mg/L were mixed together. When the base line voltage (V_{air}) was stabilized, the mixture (1 μL) was injected into the injection port and the responses were measured. The chromatograms were displayed on the monitor and the peak areas were recorded. The optimum conditions for the detection of ethanol and acetone were as follows:

- (i) The carrier gas flow rate was 15 mL/ min.
- (ii) Circuit conditions were $V_{\text{H}} = 5.5 \text{ V}$, $V_{\text{C}} = 20 \text{ V}$ and $R_{\text{L}} = 68 \text{ k}\Omega$.
- (iii) The temperature of the injection port was 150 °C.

3.1 Characteristics of the procedure

3.1.1 Linearity range

In order to determine the linearity range, standard mixtures of ethanol and acetone prepared by mixing proportions of equal volume in the range from 10-160 mg/L were prepared. Then these solutions (1 μL) were injected into the sensor system using the optimum conditions.

3.1.2 Limit of detection (LOD)

LOD was calculated from the linear regression line of the calibration curve by means of the blank signal plus three standard deviations of the blank [21]. Standard solutions of ethanol and acetone in the 10-60 mg/L and 5-40 mg/L range were prepared. One μL of each concentration was injected into the sensor system under the optimum conditions. The TGS 822 response values in term of peak area were plotted against concentration of the standard solution. The limits of detection of ethanol and acetone were evaluated from these plots.

4. Results and discussion

4.1 Optimization of the sensor system.

The optimum conditions of the ethanol and acetone system in terms of 1) flow rate of carrier gas, 2) V_{H} 3. V_{C} 4. R_{L} and 3) temperature of the injector port were determined as follows:

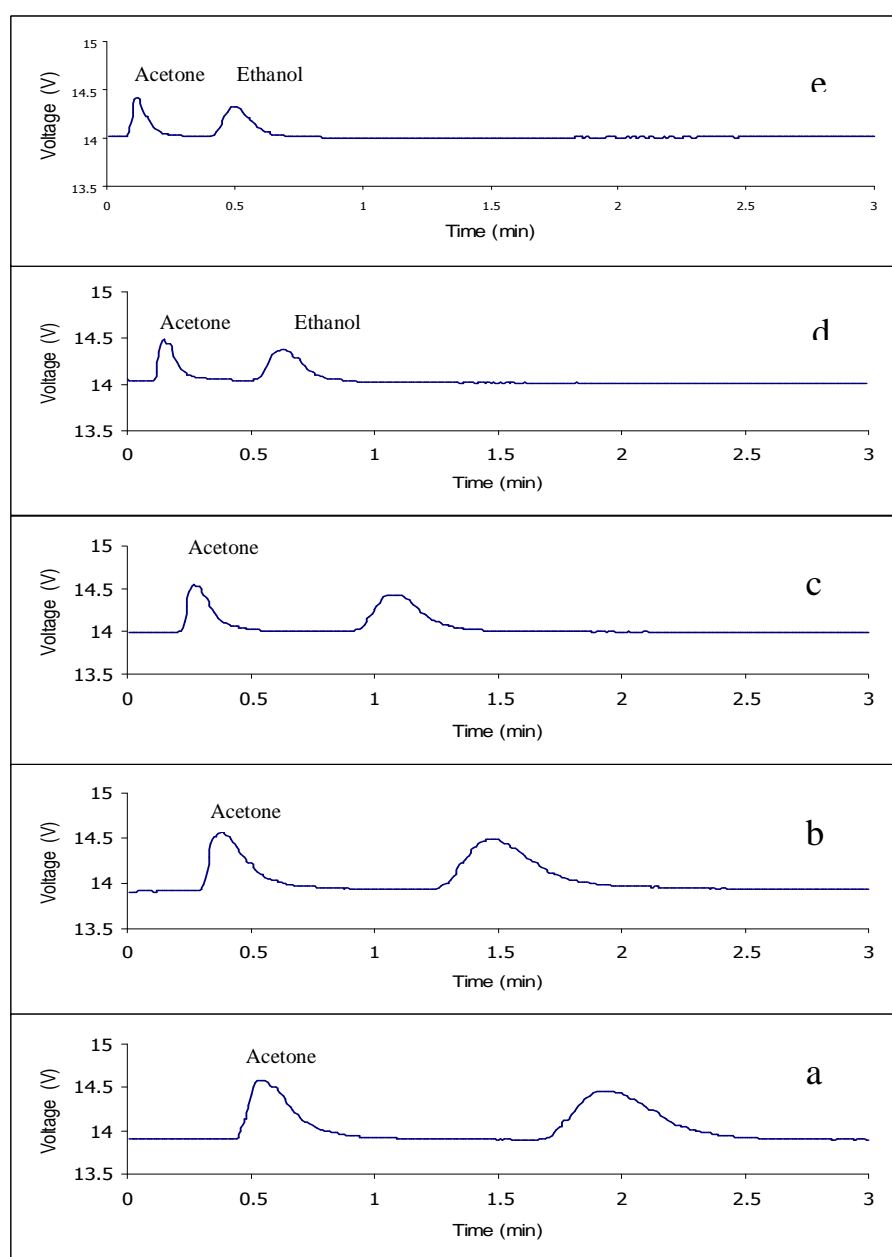
4.1.1 Effect of flow rate of carrier gas

The flow rate of the eluent was optimized by mixing equal volumes of ethanol and acetone standard solution (1000 mg/L). When 1 μL of these solutions was injected into the heated injection port, the vapors of acetone and ethanol reach the column together with the carrier gas. Ethanol and acetone were swept further through the column by the carrier gas. The flow rate of the carrier gas passing through the column and chamber were calibrated at room temperature with a soap-bubble flowmeter. The separation process began as the ethanol and acetone components moved along in the same direction of

the gas flow with different velocities depending on their respective partition coefficients between the carrier gas and the stationary phase.

The flow rate of the carrier gas was adjusted to 15, 26, 42, 80 and 112 mL/min. Figure 2 shows the chromatograms of the mixed standard solution with different carrier gas flow rates. A carrier gas flow rate of 15 mL/min was found to be the optimum one, since as shown in Figure 2a, it shows a larger peak area of ethanol and acetone. If the carrier gas has a high flow rate the responses of ethanol and acetone will give smaller peak areas because the ethanol and acetone vapors have a shorter reaction time at the sensor head. Viceversa, if the flow rate of the carrier gas is low the ethanol and acetone vapors have a longer reaction time at the sensor head and give larger peak areas.

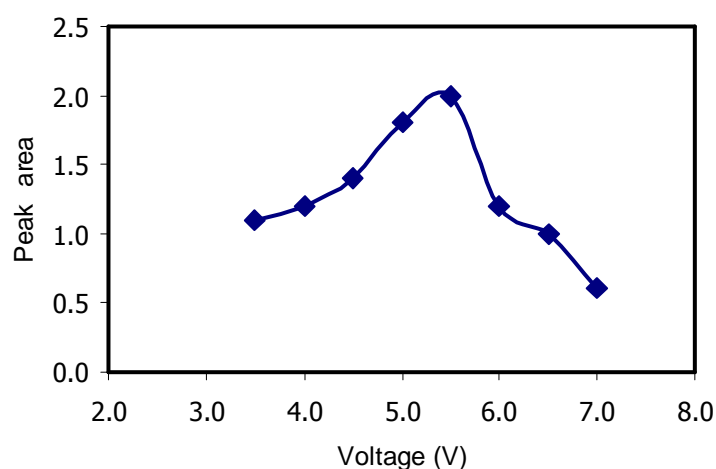
Figure 2. Chromatograms of mixed standard solution show the effect of the flow rate; a) 15 mL/min, b) 26 mL/min, c) 42 mL/min, d) 80 mL/min, and e) 112 mL/min



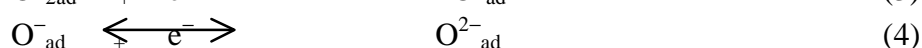
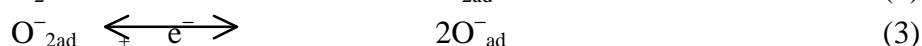
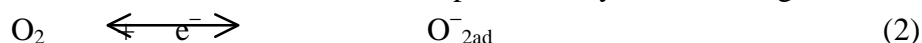
4.1.2 Optimization of the heating coil V_H

The best operating temperature of the TGS 822 sensor was determined by applying a voltage from a dc source to the heating coil by varying the voltage between 3.5–7.0 V. When 1 μL of ethanol solution was injected into the sensor system, the peak areas were measured. The plot of the peak area vs voltage is shown in Figure 3. The optimum heating coil voltage, V_H , which gave the largest peak area, was found to be 5.5 V. When a voltage greater than 5.5 V was applied, the response from the TGS 822 sensor head showed a smaller peak area because the sensitivity of the SnO_2 thick film depended on the change of chemisorbed oxygen ion on the SnO_2 surface [22].

Figure 3. Relationship between peak area and voltage of the heating coil



Jiao *et al.* [22] have reported that the atmospheric chemisorbed oxygen ion species such as O_2^- , O^- and O^{2-} presented on the surface of the oxide semiconductor are represented by the following reactions:



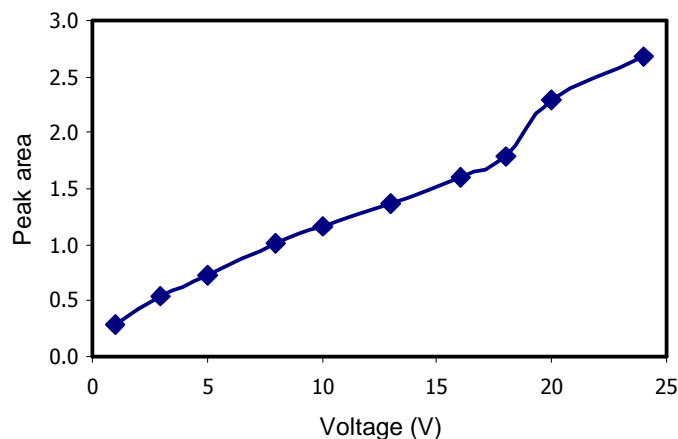
According to Ho *et al.* [23] the type of chemisorbed oxygen ion on the SnO_2 surface is O^- . When the resistance is measured in air, the oxygen ions adsorbed on the SnO_2 surface are negatively charged; the density of the adsorbed oxygen ions are then determined. When the ethanol vapour passes through the SnO_2 surface, the O^- species density is lower at sensor head and the change in the response at the sensor head is recorded by the PC system. If V_H is more than 5.5 V, the heating coil temperature is higher, and the oxygen ions are then desorbed from the SnO_2 surface. Thus the response of ethanol gives a smaller peak area.

4.1.3 Optimization of V_C of the circuit sensor

V_C is the circuit voltage that was applied across R_S and R_L by a dc power supply operating between 1–24 V. The V_H at the heating coil was fixed at 5.5 V. When 1 μL of 1000 mg/L of ethanol solution was injected into the sensor system, the ethanol responses in terms of peak areas were measured. The peak areas were then plotted against the voltage of the circuit sensor, as shown in Figure 4. It was found that the optimum voltage V_C was 24 V. Nevertheless, $V_C = 20$ V was selected because the standard

specifications of TGS 822 sensor head specify a maximum V_C of 24 V. If a $V_C \geq 24$ V were selected the TGS 822 might have a shorter half-life.

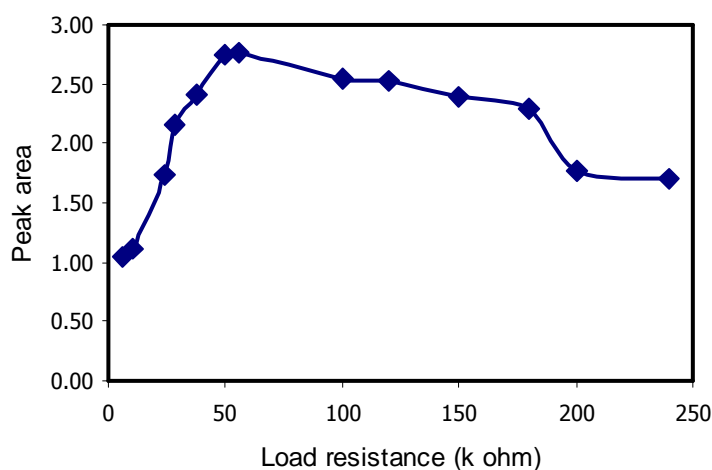
Figure 4. Relationship between peak area and voltage at circuit of V_C (the circuit of V_C)



4.1.4 Optimization of R_L of the circuit sensor

After fixing $V_H = 5.5$ V on the heating coil and $V_C = 20$ V on the circuit sensor, the peak areas when 1 μ L ethanol solution (1000 mg/L) was injected into the sensor system were measured by varying R_L between 6– 240 $k\Omega$. The relationship between peak area and resistance of R_L is shown in Figure 5. It was found that the optimum R_L was 68 $k\Omega$.

Figure 5. Relationship between peak area and load resistance of circuit sensor (the circuit of R_L).



Normally, R_L is the load resistance of the circuit sensor which is used to calculate R_S of the TGS 822 sensor head by Ohm's Law as in the following equation:

$$R_S = \left[\frac{V_C - V_{RL}}{V_{RL}} \right] \times R_L$$

where R_S is the resistance of sensor

V_C is the voltage of the circuit sensor

R_L is the load resistance of the circuit sensor

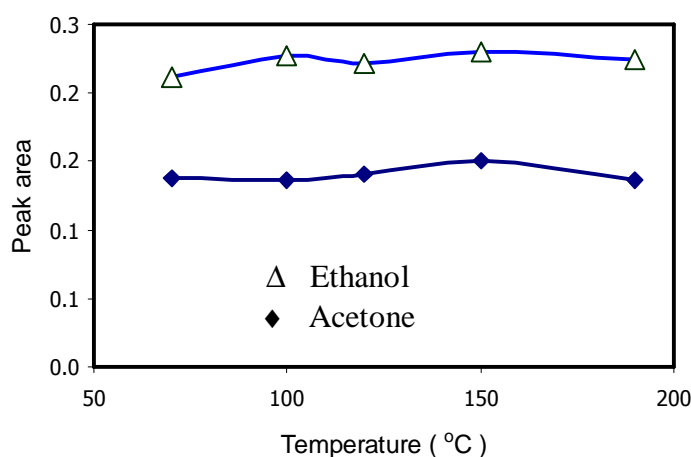
V_{RL} is the output voltage in the resistance

In pure air R_S is high. In the presence of a detectable gas, R_S changes proportionally with the gas concentration. The load resistance on the resistor (R_L) is measured by a multimeter. The output voltage (V_{RL}) increases as R_S decreases, therefore the change in the R_S depends on the concentration of ethanol and acetone.

4.1.5 Optimization of the injection port temperature

A mixture with equal volumes of ethanol and acetone was injected into the sensor system after fixing the following parameters, $V_H = 5.5$ V of the heating coil, $V_C = 20$ V of the circuit sensor, $R_L = 68$ k Ω . The injection port temperature was varied between 70 and 190 °C. The injection port temperature was operated at a temperature high enough to ensure rapid volatilization of the liquid mixtures in order to avoid the condensation of acetone and ethanol. The relationship between peak area and of the injection port temperature is shown in Figure 6. A temperature of 150 °C was selected for the entire testing of ethanol and acetone with the TGS 822 sensor head.

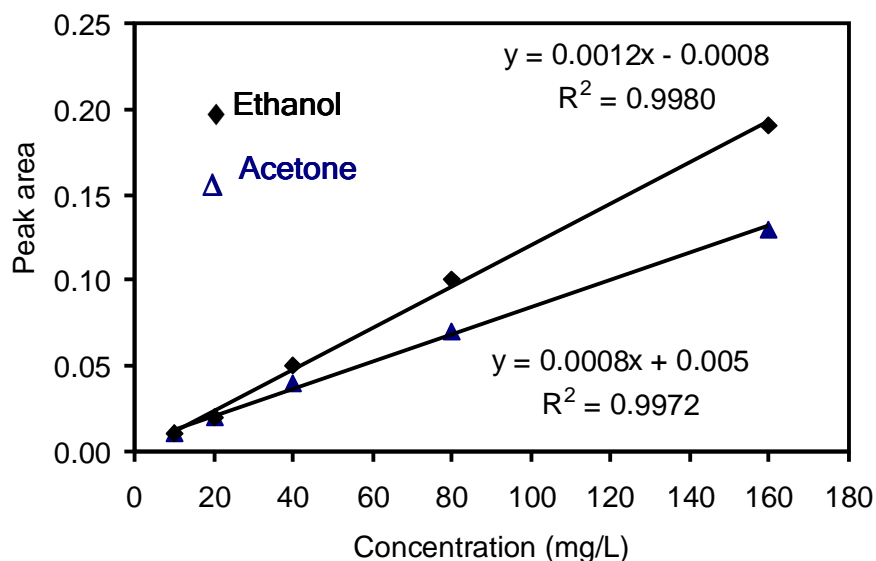
Figure 6. Relationship between peak areas of ethanol and acetone and the injection port temperature.



4.2 Characteristics of the procedure

4.2.1 Linearity range

Standard mixtures of equal volumes of ethanol and acetone used were in the range from 10-160 mg/L. When 1 μ L of each concentration was injected into the sensor system under the optimum conditions of $V_H = 5.5$ V on the heating coil, $V_C = 20$ V on the circuit sensor, $R_L = 68$ k Ω , injection port temperature = 150 °C, the peak areas of ethanol and acetone were plotted versus the concentrations as shown in Figure 7.

Figure 7. Calibration graphs of ethanol and acetone with injection volume of 1.0 μL 

4.2.2 Limit of detection (LOD)

Standard solutions of ethanol and acetone the range from 10-60 ppm and 5-40 ppm, respectively, were prepared. 1 μL of each concentration was injected into the sensor system under the optimum conditions. The TGS 822 response values in terms of peak areas were plotted against concentration of standard solution for construction of the calibration graphs as shown in Figures 8 and 9 for ethanol and acetone, respectively. The limits of detection were 9.27 mg/L and 4.41 mg/L for ethanol and acetone, respectively, as shown in Table 1.

Table 1. Detection limit and correlation coefficient of acetone and ethanol (n=3)

Standard	Detection limit (mg/L)	Correlation coefficient (r^2)
Acetone	4.41	0.9938
Ethanol	9.27	0.9908

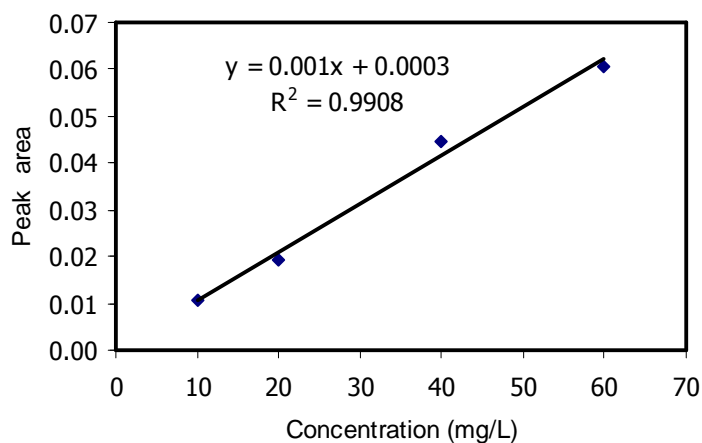
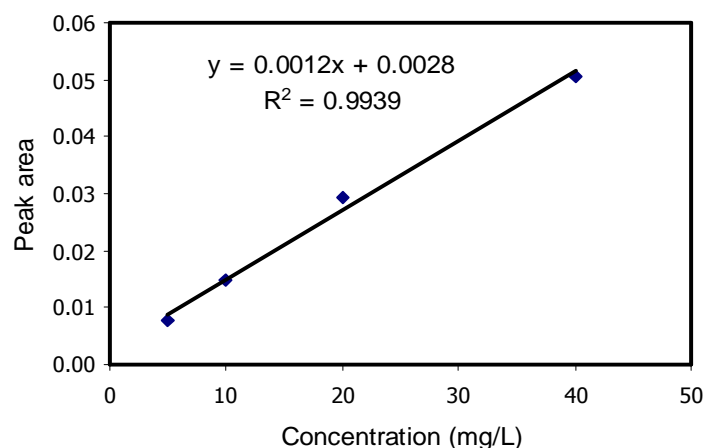
Figure 8. Ethanol calibration curve in the 10-60 mg/L concentration range

Figure 9. Acetone calibration curve in the 5-40 mg/L concentration range

5. Conclusions

Although many metal oxides are sensitive towards ethanol and acetone, the commercially available TGS 822 sensor head from Figaro Company Limited was selected for the detection of these substances. TGS 822 by itself cannot be used for the detection of the mixture of acetone and ethanol, therefore an analytical column was added into the detection system to separate ethanol and acetone before they reached the sensor head. The response data can be collected by a software program on the PC system.

The optimum conditions of the system for the detection of acetone and ethanol were achieved by varying the flow rate of the carrier gas, V_H , V_C , R_L and the injection port temperature. It was found that the best flow rate of the carrier gas was 15 mL/min, with circuit settings of $V_H = 5.5$ V, $V_C = 20$ V, $R_L = 68$ k Ω and an injection port temperature of 150 °C.

The oxide semiconductor sensor detection principle is based on the chemical adsorption and desorption of gas on the sensor surface. Under normal atmospheric condition, the types of chemisorbed oxygen ion on the surface of the oxide semiconductor are O_2^- , O^- , and O^{2-} . The type of chemisorbed oxygen ion on the SnO_2 surface is found to be O^- . Therefore, the change in density of the oxygen negative ion on the SnO_2 surface is used to determine the amount of ethanol and acetone quantitatively while the retention times (t_R) of ethanol and acetone were 1.95 and 0.57 min respectively. The limits of detection were 9.27 mg/L for ethanol and 4.41 mg/L for acetone.

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