

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Optimization of the sensor system;

The optimum conditions of the system for the detection of acetone and ethanol consisted of flow rate of carrier gas, V_H , V_C , R_L and temperature of the injector port has been performed by injecting $1\mu\text{L}$ of the standard solution mixture at the injection port are as follows:

3.1.1 Effect of flow rate of carrier gas

The flow rate of the eluent is optimized by mixing equal volume of ethanol and acetone standard solution (1000 mg/L). When $1\mu\text{L}$ of these solution is injected into the heated injection port, the vapors of acetone and ethanol reach the column together with the carrier gas. Ethanol and acetone are swept further through the column by the carrier gas. Thus the separation process begins because the component of ethanol and acetone move in the direction of gas flow with different velocities depends on their partition between the carrier gas and the stationary phase.

The flow rate of the carrier gas through the column and chamber are measured with a soap-bubble flow meter at room temperature. The flow rate of the carrier gas is adjusted as 15, 26, 42, 80 and 112 mL/min . The comparison of these flow rates are shown in Table 3.1 and Figure 3.1. The optimum flow rate is found to be 15 mL/min as giving good resolution and response in terms of peak area of ethanol and acetone as shown in Figure 3.1a.

Table 3.1 Optimization of the flow rate.

| Flow rate (mL/min) | acetone | | ethanol | |
|-----------------------|-------------|-----------|-------------|-----------|
| | t_R (min) | peak area | t_R (min) | peak area |
| 15 | 0.57 | 0.146 | 1.95 | 0.224 |
| 26 | 0.40 | 0.118 | 1.50 | 0.182 |
| 42 | 0.29 | 0.067 | 1.10 | 0.099 |
| 80 | 0.17 | 0.038 | 0.65 | 0.055 |
| 112 | 0.13 | 0.031 | 0.52 | 0.044 |

If the flow rate of the carrier gas is high the response of ethanol and acetone give small peak areas because vapor of ethanol and acetone spend short reaction time at sensor head. Therefore, if the flow rate of the carrier gas is low the vapors of ethanol and acetone spend longer reaction time at the sensor head and give larger peak area.

Figure 3.1 shows the chromatograms of the mixed standard solution with different flow rates of the carrier gas.

In this study the flow rate of the carrier gas of 15 mL/min is chosen which gives the largest peak area.

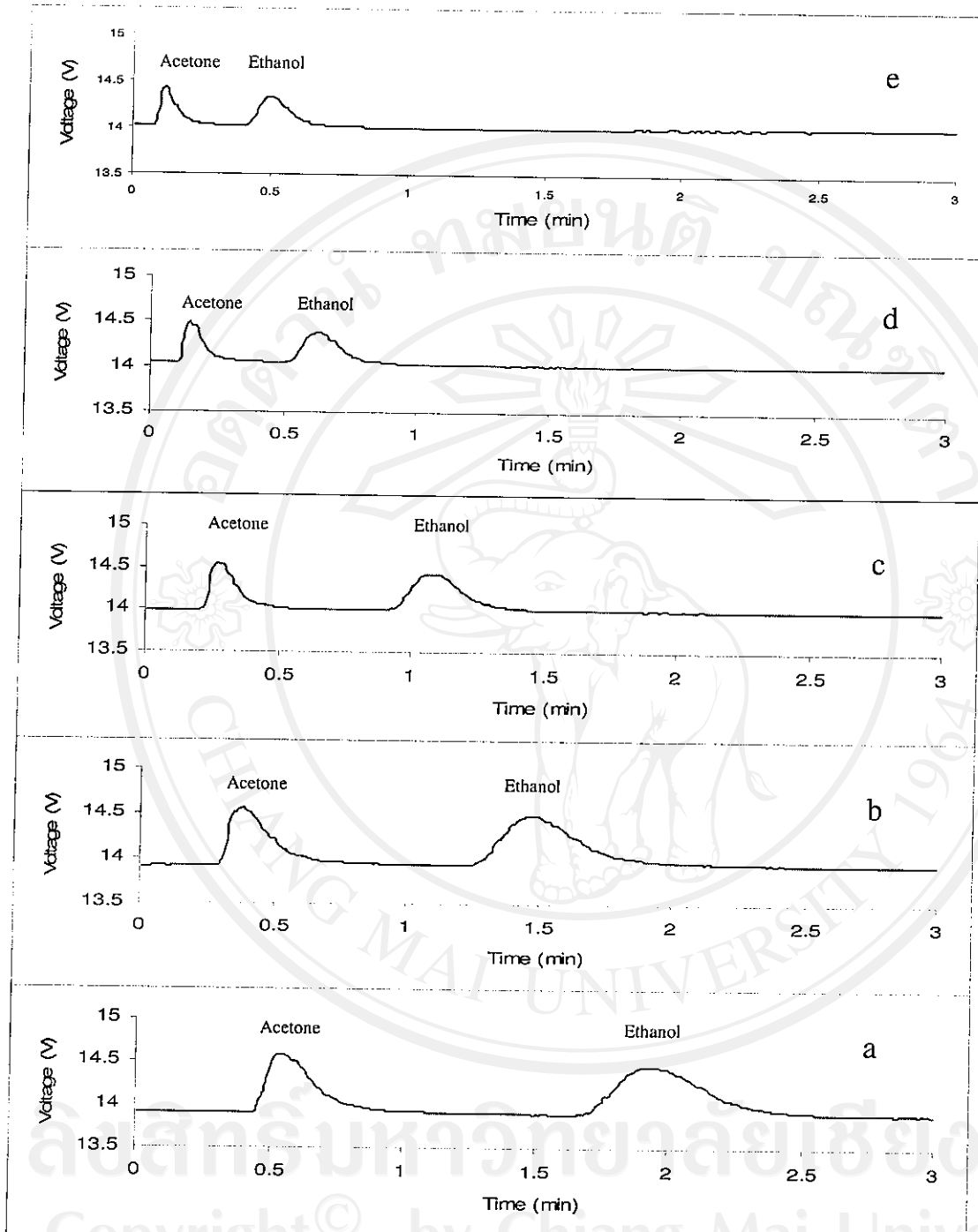


Figure 3.1 Chromatograms of mixed standard solution show the effect of the flow rate;

a) 15 mL/min

b) 26 mL/min

c) 42 mL/min

d) 80 mL/min

e) 112 mL/min

3.1.2 Optimization of V_H of the heating coil

When 1 μL of ethanol solution is injected into the sensor system the peak areas are measured by varying the voltage between 3.5-7.0 V of the dc source. The plot between the peak area vs voltage is shown in Figure 3.2. The optimum voltage of heating coil, V_H is found to be 5.5 V which gives the largest peak area. If the voltage of more than 5.5 V is applied the respond of TGS 822 sensor head has smaller peak area because the sensitivity of SnO_2 thick film depends on the change of chemisorbed oxygen ion on the SnO_2 surface as show in Figure 3.3.



Figure 3.2 Relationship between peak area and voltage at heating coil.

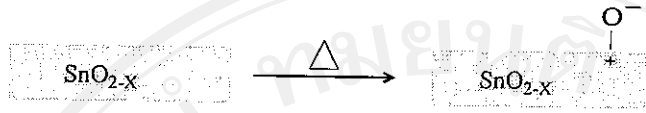
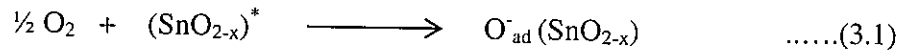


Figure 3.3 Initial state of the heated tin oxide layer at ambient air.⁴⁶

Jiao *et al.*⁴⁶ reported that the atmospheric chemisorbed oxygen ion on the surface of the oxide semiconductor such as O_2^- , O^- and O^{2-} , are present on oxide surface by the following reactions :



According to Ho *et al.*⁴⁷ 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 charge, the density of the adsorbed oxygen ions are then determined. When the vapor of ethanol passes through the SnO_2 surface (Figure 3.4) the density of species O^- is lower at sensor head and the changing of the response at the sensor head is recorded by the PC system. If V_H is more than 5.5 V, the temperature at the heating coil is higher so the oxygen ions are deadsorbed on the SnO_2 surface. Therefore the response of ethanol gives smaller peak area.

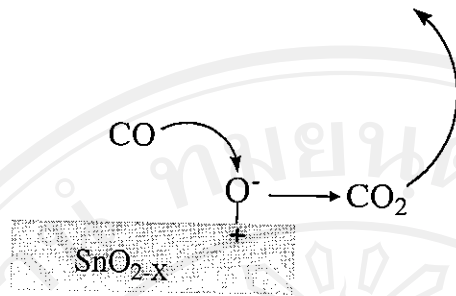


Figure 3.4 Reaction of a reducing gas like CO with surface adsorbed oxygen species.⁴⁶

3.1.3 Optimization of V_C of the circuit sensor

In this part the V_H at the heating coil is fixed at 5.5 V, when 1000 mg/L of ethanol solution with volume of 1 μL is injected into the sensor system, V_C across R_S and R_L are varied by the dc power suppliers between 1-24 V. The results of the response peak areas are shown in Table 3.2. The ethanol peak areas plotted versus voltage of the circuit sensor is shown in Figure 3.5. It is found that the optimum voltage V_C is 24 V.

However, in this work $V_C = 20$ V is selected because the standard condition of TGS 822 sensor head has the maximum V_C of 24 V. If $V_C \geq 24$ V is selected the TGS 822 may have a shorter life time for the detection of ethanol and acetone.

Table 3.2 Optimization of V_C of the circuit sensor.

| V_C (Voltage, V) | Peak area | | | Average | RSD |
|-----------------------|-----------|-------|-------|---------|-----|
| | 1 | 2 | 3 | | |
| 1 | 0.294 | 0.291 | 0.279 | 0.288 | 3 |
| 3 | 0.531 | 0.532 | 0.544 | 0.536 | 1 |
| 5 | 0.698 | 0.710 | 0.770 | 0.726 | 5 |
| 8 | 0.979 | 1.112 | 0.947 | 1.013 | 9 |
| 10 | 1.175 | 1.169 | 1.131 | 1.158 | 2 |
| 13 | 1.364 | 1.259 | 1.470 | 1.364 | 8 |
| 16 | 1.559 | 1.563 | 1.691 | 1.604 | 5 |
| 18 | 1.617 | 1.857 | 1.895 | 1.790 | 8 |
| 20 | 2.214 | 2.224 | 2.430 | 2.289 | 5 |
| 24 | 2.679 | 2.591 | 2.787 | 2.686 | 4 |

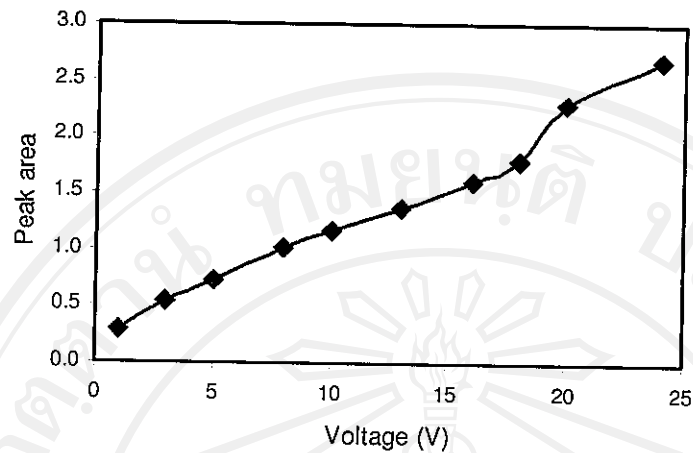


Figure 3.5 Relationship between peak area and voltage at circuit of V_C (the circuit of V_C).

3.1.4 Optimization of R_L of the circuit sensor

When $1 \mu\text{L}$ ethanol solution (1000 mg/L) is injected into the sensor system by fixing $V_H = 5.5 \text{ V}$ of the heating coil and $V_C = 20 \text{ V}$ of the circuit sensor, the peak areas are measured by varying R_L between $6 - 240 \text{ k}\Omega$. The results of the optimization R_L of the circuit sensor are shown in Table 3.3. The relationship between peak area and resistor of R_L is shown in Figure 3.6. It is found that the optimum R_L is $68 \text{ k}\Omega$.

Table 3.3 Optimization of R_L of the circuit sensor.

| R_L ($k\Omega$) | Peak area | | | Average | RSD |
|------------------------|-----------|------|------|---------|-----|
| | 1 | 2 | 3 | | |
| 6 | 1.07 | 1.01 | 1.07 | 1.05 | 3 |
| 10 | 1.11 | 1.11 | 1.14 | 1.12 | 1 |
| 24 | 1.65 | 1.75 | 1.82 | 1.74 | 5 |
| 28 | 2.12 | 2.22 | 2.12 | 2.15 | 9 |
| 38 | 2.42 | 2.29 | 2.54 | 2.42 | 2 |
| 50 | 2.82 | 2.68 | 2.72 | 2.74 | 8 |
| 68 | 2.81 | 2.66 | 2.80 | 2.76 | 5 |
| 100 | 2.61 | 2.49 | 2.53 | 2.54 | 8 |
| 120 | 2.44 | 2.51 | 2.63 | 2.53 | 5 |
| 150 | 2.37 | 2.37 | 2.46 | 2.40 | 4 |
| 180 | 2.32 | 2.29 | 2.29 | 2.30 | 1 |
| 200 | 1.74 | 1.79 | 1.77 | 1.77 | 1 |
| 240 | 1.77 | 1.68 | 1.67 | 1.71 | 3 |

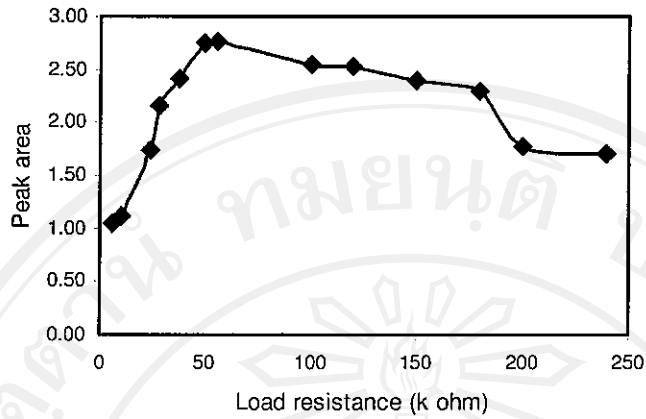


Figure 3.6 Relationship between peak area and load resistance of circuit sensor (the circuit of R_L).

Usually, R_L is the resistance of a loading resistance, which uses to calculate R_S of the TGS 822 sensor head by Ohm Law, the R_S can be calculated by the following equation:

$$R_S = \left[\frac{V_C - V_{RL}}{V_{RL}} \right] \times R_L \quad \dots\dots(3.6)$$

Where

R_S is the resistance of sensor

V_C is the circuit voltage

R_L is the load resistance

V_{RL} is the output voltage in the resistance

When vapor of ethanol passes through the sensor head the R_S of the sensor decreases while the output voltage increases which is measured by the multimeter. However in this work, if the R_S decreases, the response of the ethanol vapor shows larger peak area.

3.1.5 Optimization of the injection port temperature

When the mixture with equal volume of ethanol and acetone is injected into the sensor system by fixing $V_H = 5.5$ V of the heating coil, $V_C = 20$ V of the circuit sensor, $R_L = 68$ k Ω , the injection port temperature is varied between 70 - 190 °C. The injection port temperature should be operated at temperature high enough to cause rapid volatilization in order to avoid condensation of acetone and ethanol. The results of the optimization of the injection port temperature is shown in Table 3.4.

Table 3.4 Optimization of the injection port temperature.

| Temperature (°C) | Acetone (peak area) | Ethanol (peak area) |
|------------------|---------------------|---------------------|
| 70 | 0.138 | 0.212 |
| 100 | 0.137 | 0.227 |
| 120 | 0.140 | 0.222 |
| 150 | 0.150 | 0.230 |
| 190 | 0.136 | 0.225 |

The relationship between peak area and of the injection port temperature is shown in Figure 3.7. In this work the temperature is selected at 150 °C for testing ethanol and acetone with TGS 822 sensor head.

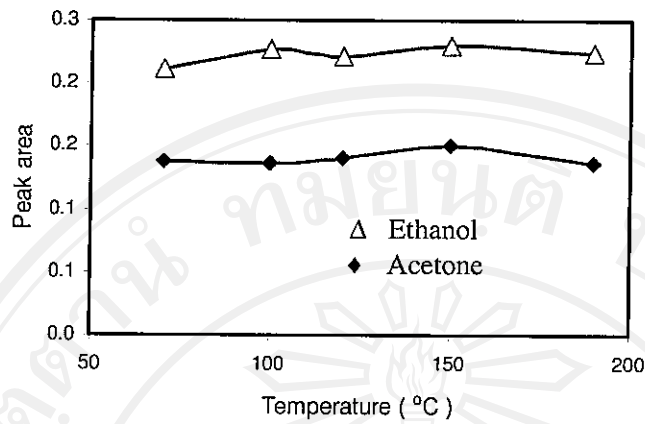


Figure 3.7 Relationship between peak area of ethanol and acetone and the injection port temperature.

3.2 Characteristics of the procedure

3.2.1 Linearity range

Standard mixtures of equal volume of ethanol and acetone are in the range from 10-160 mg/L. When 1 μ L of each concentration is injected into the sensor system under the optimum condition as $V_H = 5.5$ V of the heating coil, $V_C = 20$ V of the circuit sensor, $R_L = 68$ k Ω , the injection port temperature = 150 °C, the peak areas of ethanol and acetone are plotted versus the concentrations as shown in Figure 3.8.

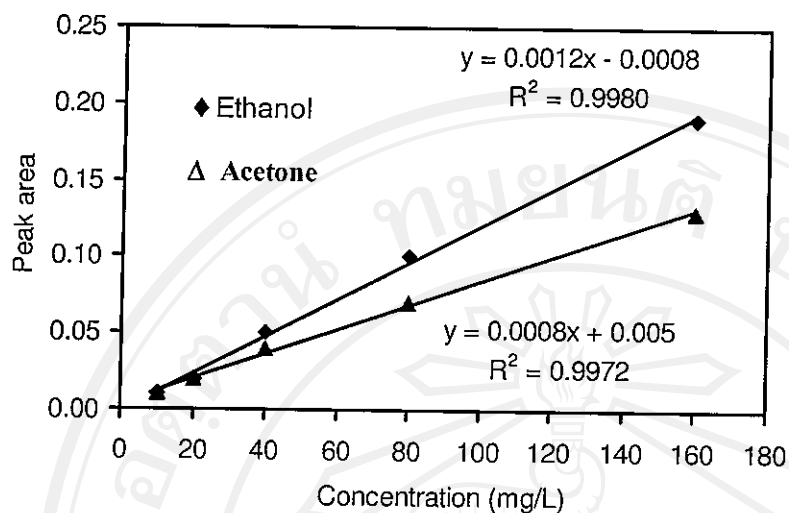


Figure 3.8 Calibration graphs of ethanol and acetone with injection volume of 1.0 μL .

3.2.2 Limit of detection (LOD)

The standard solution of ethanol and acetone are prepared in the range from 10-60 ppm and 5-40 ppm respectively. 1 μL of each concentration is injected into the sensor system under the optimum condition. In this work the TGS 822 response values in term of peak areas are plotted against concentration of standard solution for construction of the calibration graphs as shown in Figure 3.9 and 3.10 for ethanol and acetone respectively. The limit of detections are 4.41 mg/L and 9.27 mg/L for acetone and ethanol respectively as shown in Table 3.5. (see Appendix B)

Table 3.5 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 |

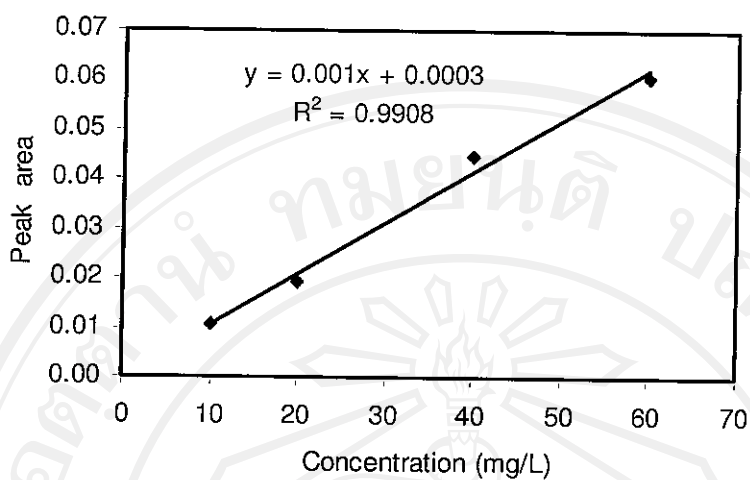


Figure 3.9 Calibration graph of ethanol in the concentration range of 10-60 mg/L.

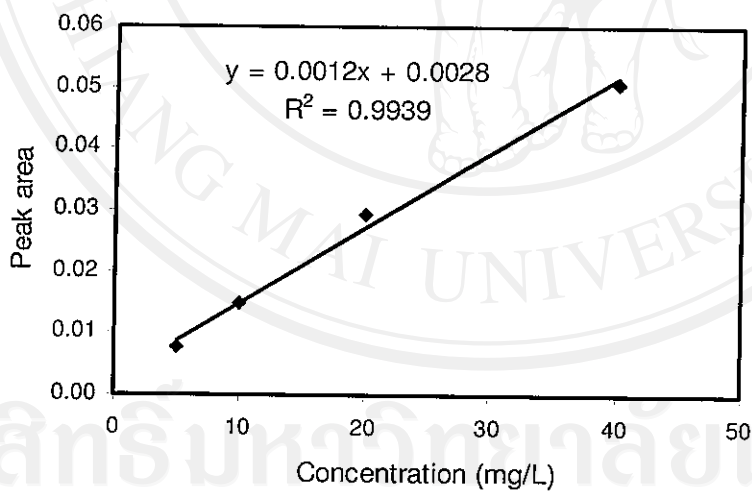


Figure 3.10 Calibration graph of acetone in the concentration range of 5-40 mg/L.