CHAPTER 1

INTRODUCTION

1.1 Background

Acetone and ethanol are colorless liquid widely used as solvent in a variety of organic reactions and miscible with water in all proportions. Industrially, acetone (see Figure 1.1) is used as a solvent in cellulose acetate process (for fiber), cellulose nitrate (an explosive) and other chemicals.[1] While, ethanol is used in automotive fuel by mixing with gasoline. In the United States, ethanol is commonly blended with gasoline as a blend of up to 10% ethanol (E10) which nicknamed as gasohol. In 2010 it is estimated of that, Thailand will have 10% ethanol in 95 Research Octane Number (RON) and 91 RON gasoline as a standard.[2]

1.2 Health effects of acetone and ethanol

Small amount of acetone is metabolically produced in the body. Acetone can be elevated in diabetes patients. Frequent exposure to exogenous acetone can be chronic due to contamination of acetone in water supply, food (e.g. milk), or breathing air (acetone is volatile). Acetone is not a very toxic compound. However, it can irritate and damage skin. Accidental intake of large amount of acetone may lead to unconsciousness and death. While ethanol beverage is swallowed, it passes through the stomach and goes to the small intestine where the ethanol is rapidly absorbed and distributed through out the body. Ethanol enters body tissues in proportion to its water content. Therefore, ethanol is found to be in the blood and the brain more than in muscle or fat tissues. Over 90% of ethanol is processed by the liver. In the liver, it converts ethanol into acetaldehyde, which is a toxic substance.[3]

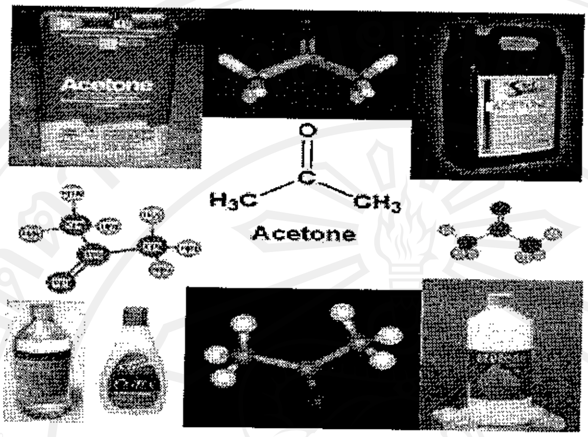


Figure 1.1 Acetone solution and structure of acetone.[1]

In the analysis of volatile organic compounds, usually, gas chromatography is the method used for the determination of ethanol and acetone. Chromatography is a separation process that is achieved by distributing the substances to be separated between a moving phase and a stationary phase. Those substances distributed preferentially in the moving phase pass through the chromatographic system faster than those that are less distributed preferentially in the stationary phase. Thus the substances are eluted from the column in the inverse order of the magnitude of their distribution coefficients with respect to the stationary phase.

1.3 Type of gas sensors [4-6]

Sensors are devices that detect a measurable change in output to a known input stimulus. This stimulus can be a physical stimulus like temperature and pressure or a concentration of a specific chemical or biochemical materials as shown in Figure 1.2. The output signal is typically proportional to the input variable, which is also called the measurand. For example, temperature sensors respond with a voltage, resistance, color, or other change when the temperature is changed.

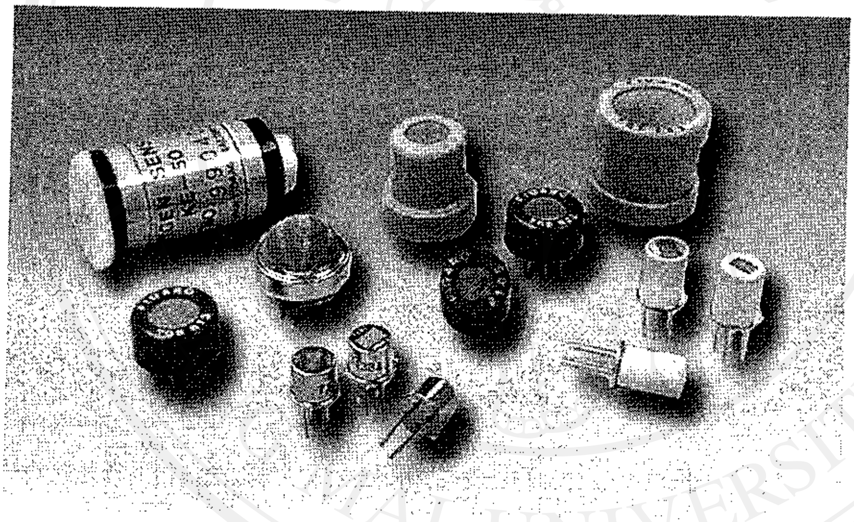


Figure 1.2 Type of commercial sensors head.[4]

The necessities of modern living reflected in industry, automotive, health and safety, and care for the environment have created the need for a wide variety of gas sensors that are required to operate in ever widening and critical operating conditions. These needs can be simply classified as shown in Figure 1.3. Some of the most commonly used gas sensors as follows.

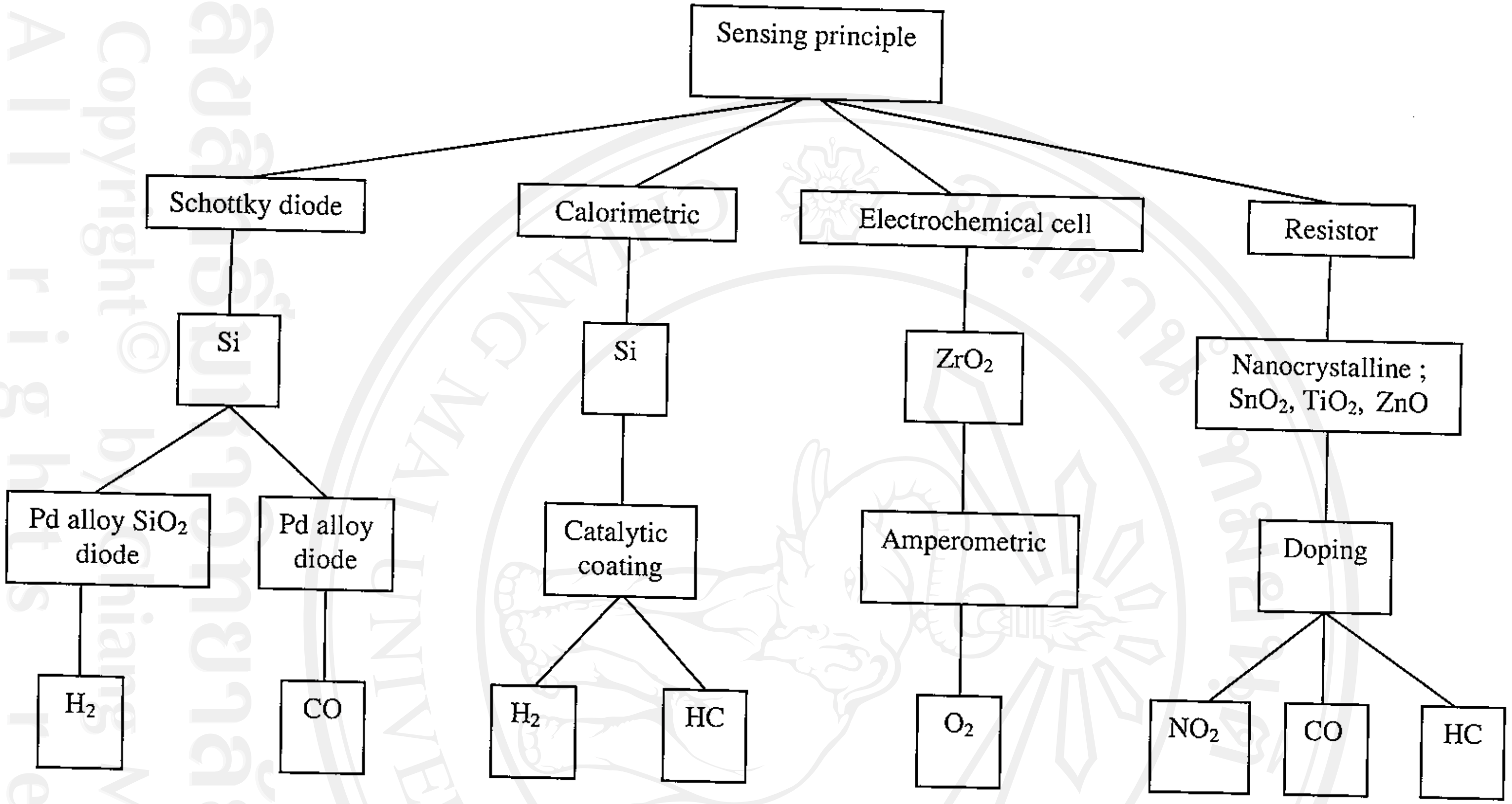


Figure 1.3 Type of gas sensors.[4]

1.3.1 Schottky diode-based sensors [4-6]

A Schottky diode is composed of a metal in contact with a very thin barrier layer of a semiconductor. The semiconducting properties of the semiconductor such as silicon enable sensor operation. The metal layer serves as a gate for the diode. When a gas component adsorbs selectively on the surface of the gate layer, the Schottky energy barrier changes and this change is measured and correlated with the gas concentration. A Schottky diode-based hydrogen gas sensor has been developed, which employs a palladium-alloy gate and the sensor is fabricated with silicon-based processing techniques. Figure 1.4 shows the sensor structure. Hydrogen can be selectively adsorbed in a palladium-alloy gate lowering the Schottky energy barrier. The change in diode characteristics can be used to quantify the hydrogen gas present. A platinum thin-film resistance temperature detector (RTD) and heater are integrated into the sensor structure. This permits the sensor to be operated at a controlled elevated temperature enhancing response time of the sensor.

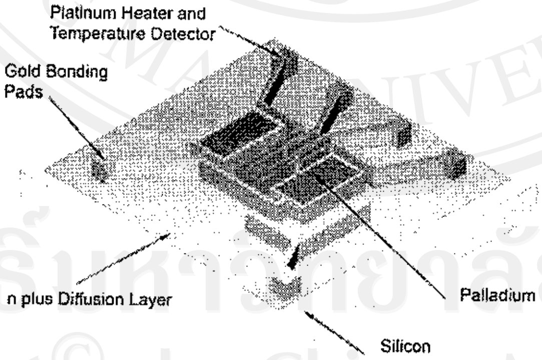


Figure 1.4 Schottky diode-based microsensor (hydrogen sensor).[4]

The Schottky diode platform can be modified to detect a wide range of gases by altering the gate material or changing the semiconductor, such as, silicon carbide. Changing the gate alloy can change the viable concentration range of hydrogen detected. Hydrocarbons, which dissociate at higher temperatures, can be detected by replacing the silicon substrate with a high temperature semiconductor like silicon carbide.

1.3.2 Calorimetric sensors [4]

Calorimetric sensors detect the amount of heat released by a combustible gas oxidizing in the presence of oxygen. This heat may help quantify the combustible gas present. The calorimetric sensor that employs two temperature detectors, one detector is coated with catalyst for the combustible gas. When the temperature detectors are heated, normally to around 400°C, the combustible gas is then oxidized on the catalyst coated detector resulting in a temperature increase on this detector. The difference in the temperature measured by these two detectors is then used to quantify the combustible gas present. The design of such a calorimetric sensor is shown in Figure 1.5. The heating and temperature detection functions are provided by different elements enhancing the control of heating and the sensitivity of the detection. The sensor is relatively small and requires low heating energy. The fabrication of these sensors can be cost effective by using batch processing techniques. However, catalytic combustion sensors are typically not selective with a response proportional to the amount of combustible gas in a given oxygen concentration.

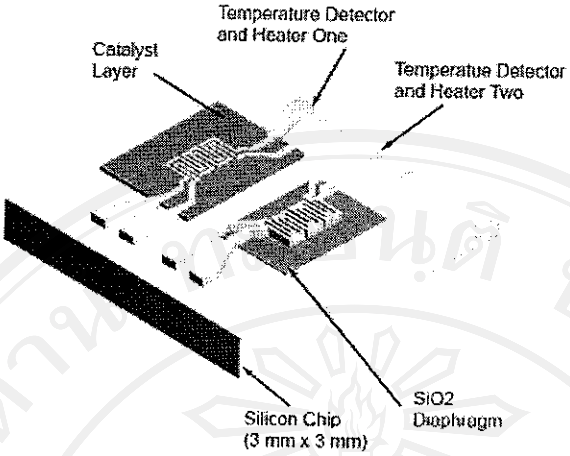


Figure 1.5 Calorimetric sensor (hydrogen and hydrocarbons).[4]

1.3.3 Electrochemical Sensors [7-8]

Electrochemical sensors are used primarily to detect oxygen, toxic gases, hydrogen sulphide, carbon monoxide, sulphur dioxide, chlorine, ammonia, ethylene oxide, nitrogen dioxide, ozone and other toxic gases. Each sensor is designed to be specific to the gas it is intended to detect. Electrochemical sensors are essentially fuel cells composed of noble metal electrodes in an electrolyte.

An electrochemical sensor composes of a sensing-electrode (sometimes called the working-electrode, measuring-electrode, or anode), a counter-electrode (sometimes called the cathode) and an electrolyte. The electrolyte is normally an aqueous solution of strong inorganic acids. When gas is presented the cell generates a small current which proportional to the concentration of the gas. When carbon monoxide, a reducing gas, diffuses through the sensing electrode, it is oxidized causing the potential of the sensing electrode to shift in a negative (cathodic) direction. The cell's chemical processes are as follows :

Sensing-electrode

$$CO + H_2O \longrightarrow CO_2 + 2H^+ + 2e- \qquad ......(1.1)$$

Counter-electrode

$$O_2 + 2H^+ + 2e \longrightarrow H_2O \qquad ......(1.2)$$

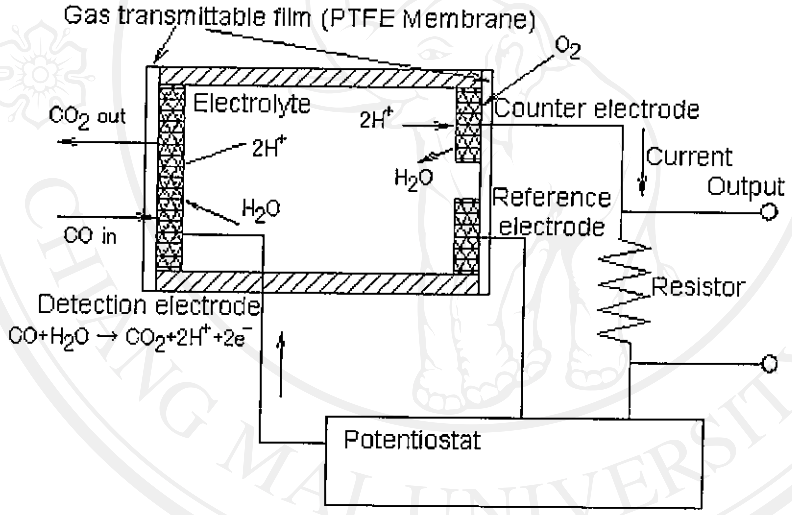


Figure 1.6 Detection principle of electrochemical sensor.[7]

As shown in Figure 1.6, in this diagram carbon monoxide is oxidized on the surface of the detection electrode, and hydrogen ions are generated. On the counter electrode, hydrogen ions (equal to the hydrogen ions on the detection electrode) react with oxygen from the environmental air and generate water as a result. The electricity generated by this reaction chain is proportional to the carbon dioxide gas concentration, thus the gas concentration can be determined by monitoring the generated electricity.

1.3.4 Metal oxide semiconductors [9]

Metal oxide semiconductor (MOS) sensor technology is based on the changing in resistance of a sensitive metal oxide layer which induced by the surface interaction with ambient gases. The MOS is commonly used to monitor a variety of toxic and inflammable gases in various air pollution monitoring systems, food industry, medical diagnosis equipment, and gas leaking alarms. The MOS sensor with targeted selectivity for specific gases are shown in Table 1.1, and a typical list only materials used for air quality monitoring sensors.

The sensor usually can be made simply by coating a metal oxide layer on a substrate with two type of electrodes pre-embedded on it. Two typical designs with tubular and planar structures are shown in Figure 1.7a and 1.7b.

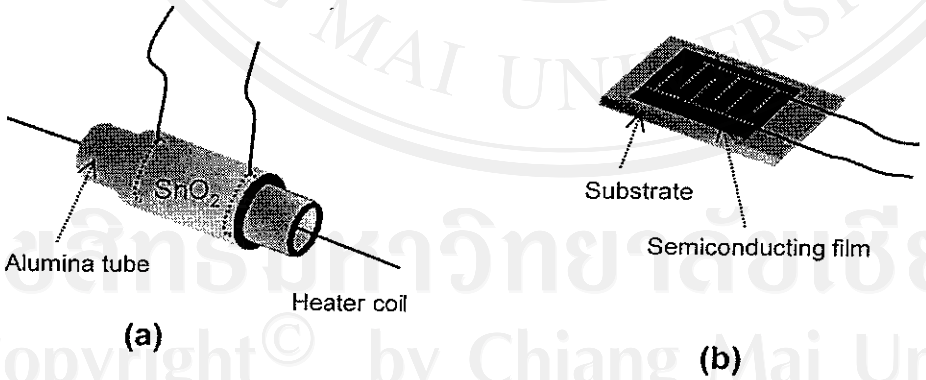


Figure 1.7 Typical of sensors: (a) tubular type SnO_2 gas sensor

(b) planar semiconductor sensor.[9]

Table 1.1 The metal oxide semiconductors with targeted selectivity for specific gases for environmental and air quality monitoring.

Oxide Type	Detectable Gas	References
SnO_2	C_2H_5OH, H_2,CO,NO_2,H_2S, CH_4	10-13
TiO_2	H_2, C_2H_5OH, O_2, CO, CO_2	14-16
ZnO	NO_2 , CH_3COCH_3, C_2H_5OH	17-19
Fe_2O_3	CO, NO_2, C_2H_5OH	20-22
$LaFeO_3$	C_2H_5OH ,NO_2, CH_4	23-25
In_2O_3	O_3, CO, H_2	26-28
WO_3	H_2S, O_3,	29-31

1.4 Analytical applications

Gong *et al.*[32] used thin-film tin oxide gas sensor to test the sensitivity of the organic vapors in an air flow system for the sensitivity to each organic vapor (methanol, ethanol, isopropanol, acetone and acetic acid) in the designed system. The designed flow system is shown in Figure 1.8. The resistance of the sensor was monitored by a digital multimeter and the temperature was indicated by a digital thermometer. The sensitivity was defined as $(R_a - R_g) / R_a$, where R_a and R_g were the electrical resistance of the sensor before and after exposure to each organic vapor, respectively.

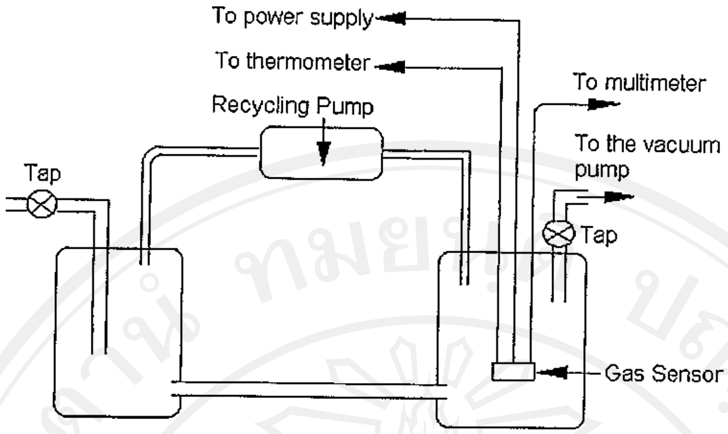
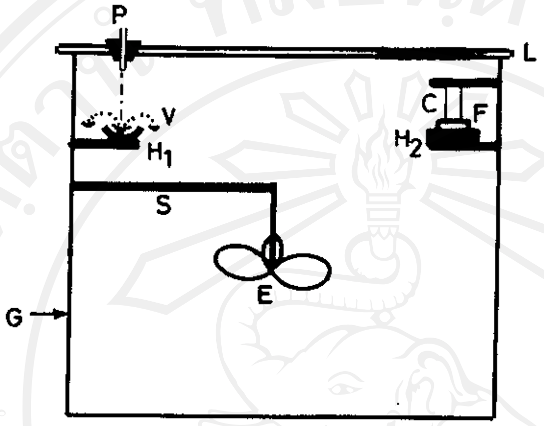


Figure 1.8 The flow system for testing the sensing properties of SnO_2 to organic vapors.[32]

Varghese *et al.*[33] used SnO_2 thin films detecting ethanol. The schematic diagram of the sensitivity measurement for this sensor is shown in Figure1.9. It consisted of a chamber fitted with a micro fan and two heaters. Liquid ethanol was introduced into the chamber with micro pipette, reached the heater H_1 kept at 353 K and vaporized instantly. The fan E fitted at the center of the chamber helped in the fast equilibration of the vapor. The second heater H_2, which could go to high temperature, was used for heating the sample to the designated temperature. The circuit diagram for sensitivity measurements is shown in Figure 1.10. The sample unit was connected to a 9 V dc source through a small variable resistor r whose resistance ' r ' was adjusted in such a way that $r << R_s$, the sample resistance. Voltage across r was connected to a *x-t* recorder and measured using a micro voltmeter. The sensitivity of the SnO_2 films to ethanol was then calculated from the measurement of $V_{r(gas)}$ and

$V_{r(air)}$,where $V_{r(gas)}$ and $V_{r(air)}$ were the voltages across r before and after introducing ethanol vapor into the chamber respectively.



P- Micro pipette

V- Ethanol vapor

F- Sample

H_2- Sample heater

G- Glass chamber

L- Lid

C- Pressure contacts

H_1- Heater (353K)

E- Fan

S- Fan support

Figure 1.9 Schematic diagram of the sensitivity measurement set up of SnO_2 thin films.[33]

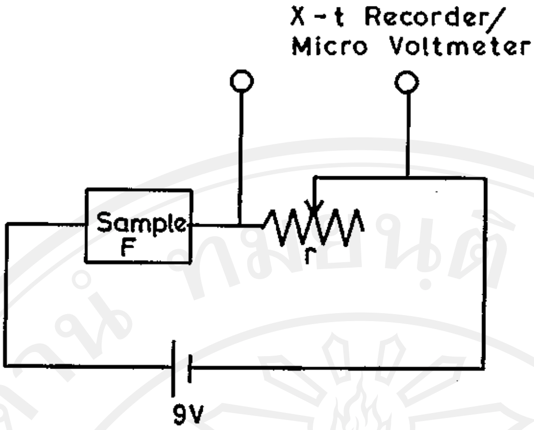


Figure 1.10 Circuit used for sensitivity studies of SnO_2.[33]

Lee *et al.*[34] studied the fabrication and characteristics of SnO_2 gas sensor array for many volatile organic compounds (VOCs). The designed system is shown in Figure 1.11. Three mass flow controllers were used along with dry air as the carrier gas. The characteristics of the sensor array were then tested in a testing chamber after flow injection of the VOCs vapor. A voltage detecting method was used to calculate the sensitivity of the sensor. The sensitivity was defined as $(R_{air} - R_{gas}) / R_{air} \times 100$ (%) where, R_{air} and R_{gas} were the electrical resistances in VOCs and clear air, respectively.

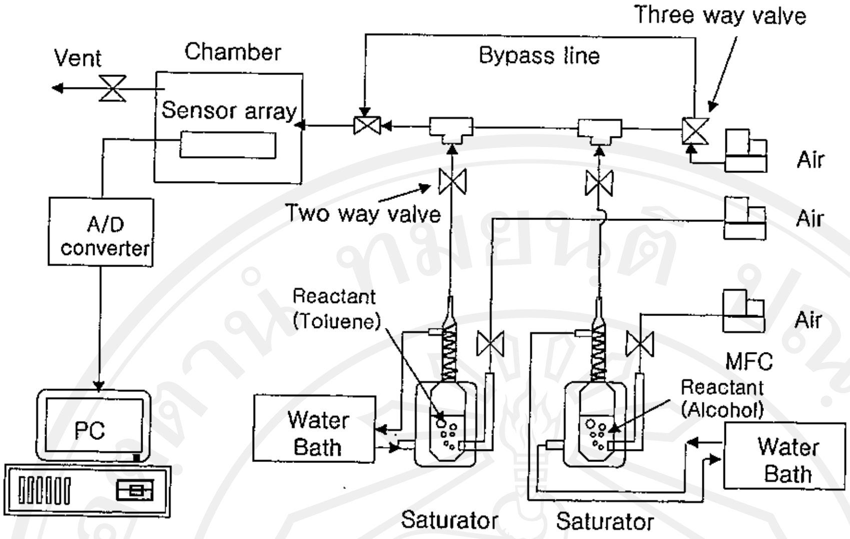


Figure 1.11 Schematic diagram of measuring apparatus for VOCs.[34]

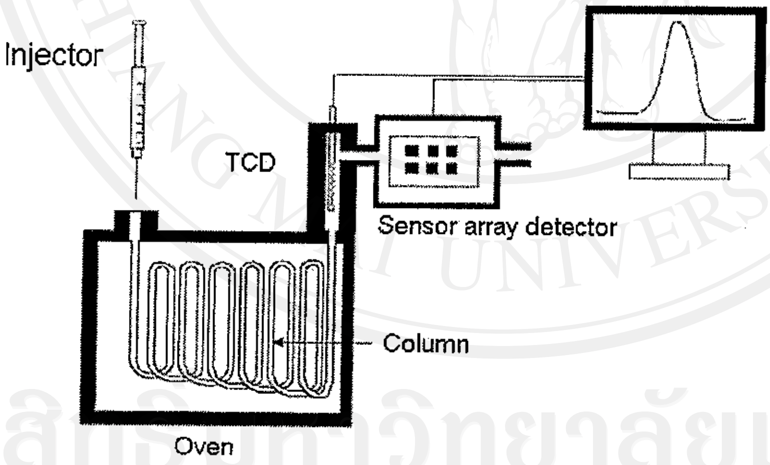


Figure 1.12 Schematic representation of the GC-TCD sensor arrays system.[35]

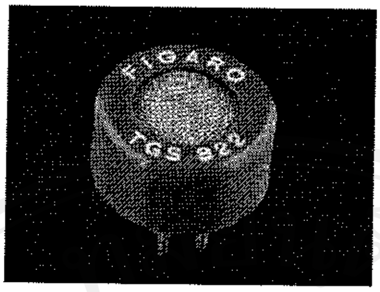


Figure 1.13 A commercial TGS 822.[36]

The sensor arrays for testing alcohol vapors can be modified by integrating with a chromatograph as shown in Figure 1.12.[35] When the alcohol vapors came into contact with the sensor arrays, there was a decrease in conductivity of the sensor. The conductivity increased when the alcohol were flushed out of the chamber by the carrier gas. Although, many metal oxides are sensitive to volatile organic compounds (VOCs), in this work, commercial available TGS 822 from Figaro Company Limited (see Figure 1.13) is used for the detection of ethanol and acetone, because it has low cost, long-life and wide dynamic range. The TGS 822 is a SnO_2 thick film on the surface of an alumina ceramic tube which contains an internal heater. TGS 822 cannot be used for the detection of the mixture of ethanol and acetone.[36] Therefore in the present work an analytical column is added into the detection system to separate acetone and ethanol before reaching the sensor head and using the same principle as in gas chromatography.

1.5 Gas Chromatography

1.5.1 The principles of a chromatographic separation [37-38]

All chromatographic separations are carried out using a mobile phase and a stationary phase. As a result of this prerequisite, the primary classification of chromatography is based on the physical nature of the mobile phase. All separation processes that utilize a gas as the mobile phase are classified as gas chromatography (GC). Conversely, all separation processes that utilize a liquid as the mobile phase are classified as liquid chromatography (LC). In a similar manner the subclasses of chromatography are defined on a basis of the physical nature of the stationary phase. Consequently, if the mobile phase is a gas and the stationary is a liquid, then the technique is called gas-liquid chromatography (GLC) and if the mobile phase is a gas and the stationary phase is a solid, then the technique is called gas-solid chromatography (GSC). If the mobile phase is liquid, then there will be two complementary sub-classes of liquid chromatography, that is, liquid-liquid chromatography (LLC) and liquid-solid chromatography (LSC). The classification of chromatography is shown in Table 1.2.

Table 1.2 Classification of chromatographic techniques.[37]

Mobile phase gas GAS CHROMATOGRAPHY		Mobile phase liquid LIQUID CHROMATOGRAPHY	
Stationary phase Liquid	Stationary phase Solid	Stationary phase Liquid	Stationary phase Solid
Gas-Liquid Chromatography GLC	Gas-Solid Chromatography GSC	Liquid-Liquid Chromatography LLC	Liquid-Solid Chromatography LSC

i. Retention time

The retention time (t_R) is a measurement of the amount of time a solute spends in a column as shown in Figure 1.14. It is the sum of the time spent in the stationary phase and the mobile phase. It can also be used for qualitative analysis.

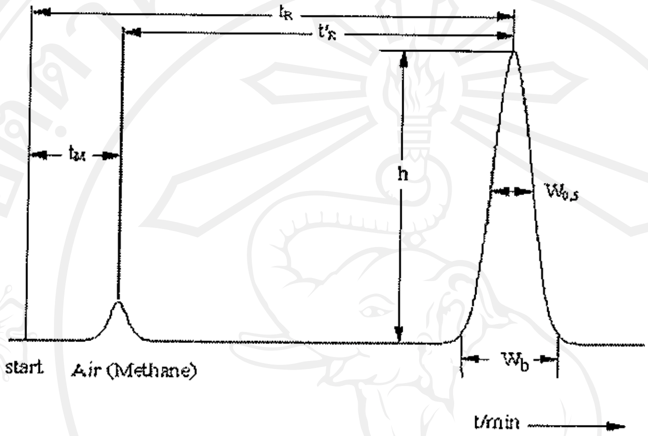


Figure 1.14 Scheme of a chromatogram.[37]

ii. Column Efficiency

The theoretical number of plates (N) can be measured from the width and retention time is defined as :

$$N = 5.54\,(t_R/W_{0.5})^2 = 16\,(t_R/W_b)^2 \qquad \text{......(1.3)}$$

Where $W_{0.5}$ = peak width at half height

W_b = peak width at baseline

The value of N for a column varies with many factors such as column length, particle size and mobile phase flow rate. The long columns packed with small particles give the highest plate numbers, thus a good column will have a large N, the calculation and symbols are shown in Figure 1.15.

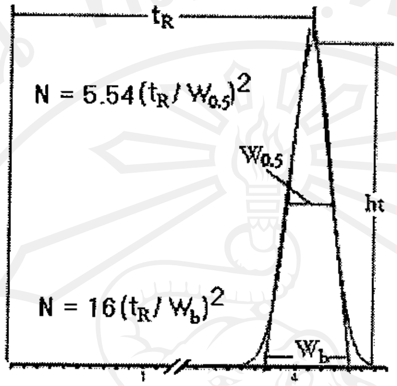


Figure 1.15 Plate number (N) calculated from retention time (t_R) and peak width.[38]

iii. Resolution factor (R_s)

The resolution factor of a column provides a quantitative measure of its ability to separate two analytes. The significance of this term is illustrated in Figure 1.16 , which consists of chromatograms for species A and B on three columns with different resolving power. R_s is difference between the retention times for the two peaks divided by their average widths (base widths).

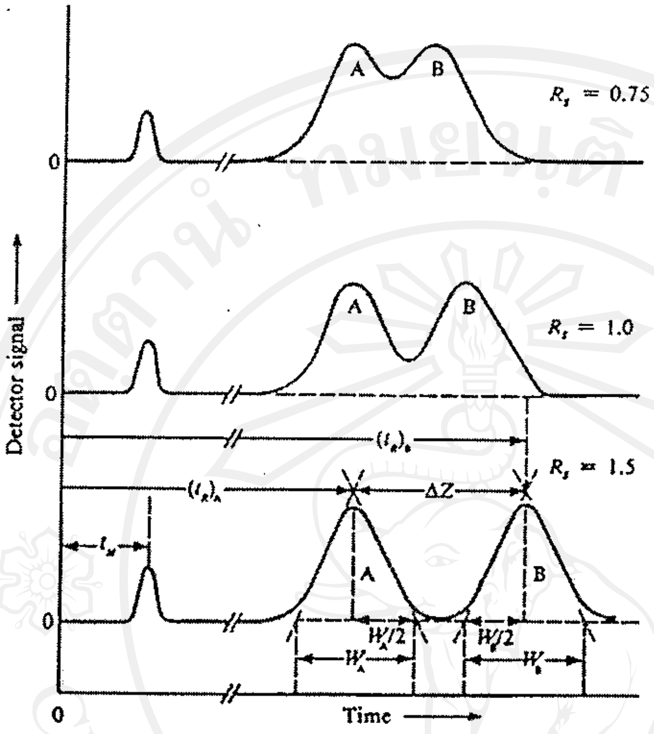


Figure 1.16 Separation at three resolution factor where $R_S = 1.5$ complete separation between two peaks, $R_S = 1.0$ almost complete separation between two peaks and $R_S = 0.75$ incomplete separation between two peaks.[37]

1.5.2 Components of a gas chromatograph [39-43]

The gas chromatograph is composed of several components. These components include the injector, the column and the detector. The mobile phase that transports the analytes through the column is a gas and referred to as the carrier gas. The carrier gas flow, which is precisely controlled, allows precision in the retention time. The column containing the stationary phase is situated in a variable temperature oven. At the end of column, the mobile phase passes through a detector before it exits to the atmosphere.

i Sample introduction

The sample solution in the order of 1μL is introduced into the system with a microsyringe (Figure 1.17). Several types of syringe exist because of the diversity of injectors and column.

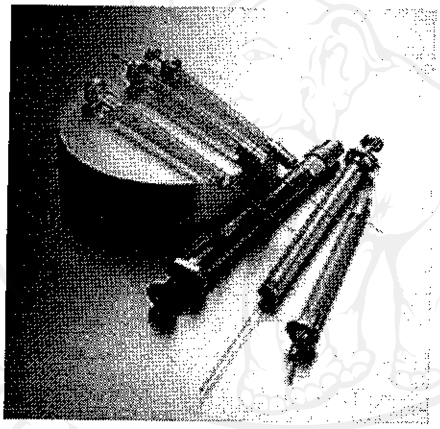


Figure 1.17 Typical of syringe for gas chromatography.[41]

ii Injector

The injector is an inlet for the sample, when the sample is vaporized and mix the sample with the carrier gas before the sample enters the head of the column. The injection is of paramount value to quality of the separation (see Figure 1.18). The injector temperature should be operated high enough to cause rapid volatilization in order to avoid condensation of the sample in the injector which may produce broadened peaks in the resulting chromatogram.

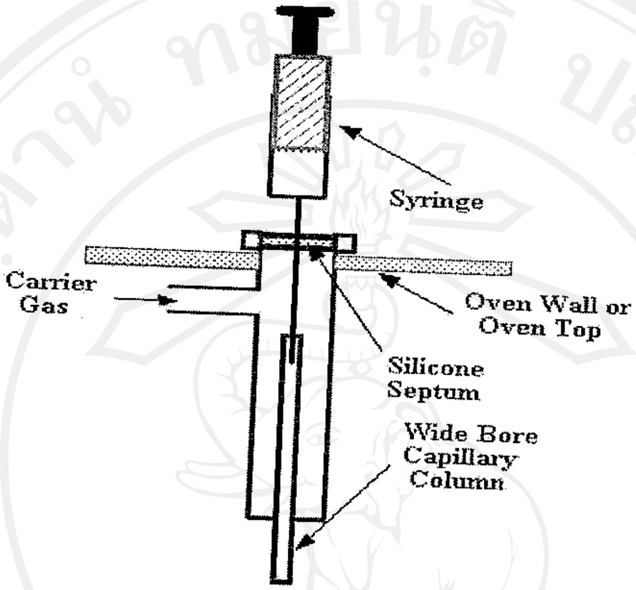


Figure 1.18 Scheme of an injection port.[41]

iii Column

The column is the heart of the separation system in chromatographic technique since the separation process takes place in the column. The column system consists of (a) material of construction or tubing, (b) a packing material which is either an adsorbent or a solid support coated with a liquid phase, and (c) packing retainer such as glass wool inserted into the tube ends. There are two types of column employed for GLC, namely packed column (see Figure 1.19) and capillary or open tubular columns (see Figure 1.20a). For packed columns are usually constructed from stainless steel or Pyrex® glass. Before packing, stainless steel columns washed with dilute hydrochloric acid, then extensively with water followed by methanol, acetone, methylene dichloride and n-hexane. The washing procedure remove any corrosion products and traces of lubricating agents used in the tube drawing process. The columns are then ready for packing. In packed column, the nonvolatile liquid phase is supported on a powder solid support which is contained by the tube while in capillary columns with internal diameter varies from 0.1 to 0.35 mm and the length from 15 to 100 m. Capillary columns are usually coated on the outside with polyimide(see Figure 1.20b). The internal surface of the silica is usually treated, depending on the technique used to bond the stationary phase.

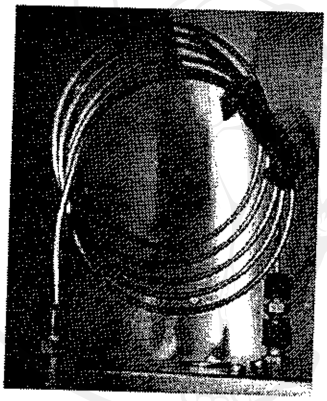
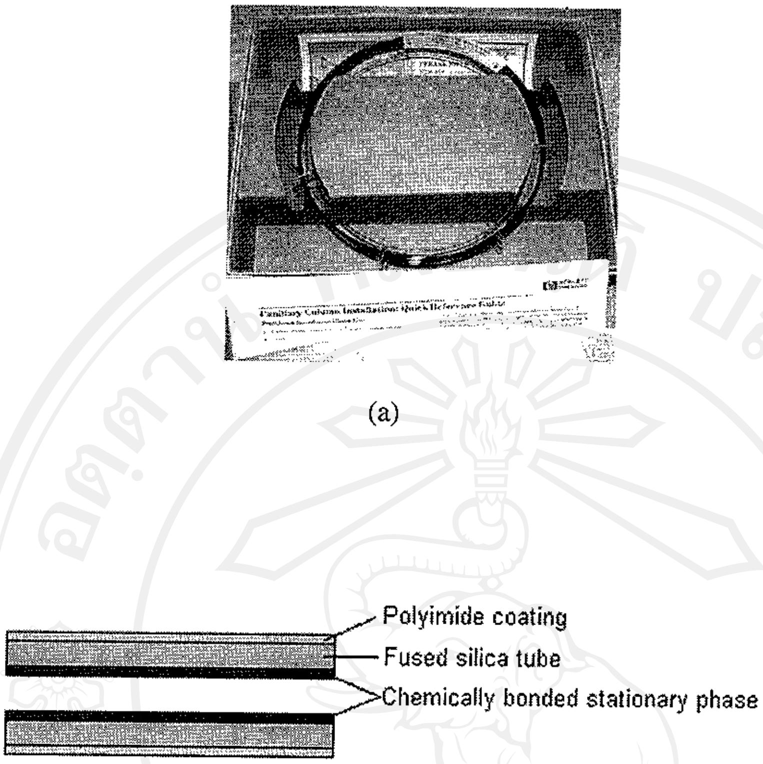


Figure 1.19 Packed column of gas chromatography.[42]



(a)

(b)

Figure 1.20 Capillary Column (a) capillary column length from 15 to 100 m (b) cross section of a fused silica open tubular column.[43]

iv Detector

The detector is located at the end of the column. This device measures the presence of the eluted solutes quantitatively and/ or qualitatively in the carrier gas as it leaves the column. The type of detectors that is chosen depends on the compounds of interest and the detection limits required for the analysis. Some detectors are universal, this is because they are sensitive to almost every compounds that elute from the column. However, most detectors are sensitive to a particular type of compound.

These are called selective detectors. A selective detector is one that can detect only certain compounds. The ideal determination of an analysis is to have a detector that can detect only certain type of analyte. In this work, TGS 822 is used as sensor head for detecting of ethanol and acetone.

1.6 The objective of this work

The device for the detection of acetone and ethanol is constructed, which consists of a pack column, a chamber with a sensor head, 2 dc power supplies, a multimeter and a computer. A commercially available TGS 822 from Figaro Company Limited is used as a sensor head. An analytical column is coupled with the set up to enhance the capability for the separation of ethanol and acetone.