



CHAPTER III EXPERIMENTAL

3.1 Materials

Analytical grade aniline monomer (Merck) was used as a monomer. Analytical grade ammonium peroxydisulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Merck) was used as an oxidant. Twenty five percent of analytical grade ammonia solution, $(\text{NH}_3 \cdot \text{H}_2\text{O})$ (Merck) was used as a base reagent. Analytical grade calcium hydride, (CaH_2) (Fluka) was used in drying the aniline monomer. Thirty eight percent of analytical grade hydrochloric acid (Merck), purum 99% camphor-10-sulfonic acid (Fluka), seventy percent of analytical grade nitric acid (LAB-SCAN) and ninety five percent of ethane sulfonic acid (Aldich) were used as the protonic acid in doping process. Analytical grade 1-methyl-2-pyrrolidone (NMP) (Merck) was used as a solvent for polyaniline film preparation. Nitrogen gas (N_2), of UHP grade with 99% purity, (TIG) was used as a carrier gas. The 1000-ppm of sulfur dioxide (SO_2) balanced with nitrogen (TIG) was used as a target gas.

3.2 Methodology

3.2.1 Purification of aniline monomer

Aniline monomer was distilled by the method of Perrin (1985). 100 ml of aniline monomer was dried with 0.25 grams of calcium hydride (CAH_2) for 30 minutes. The dried aniline was twice distilled

under reduced pressure at 50-60°C. The colorless of aniline monomer was obtained and stored in nitrogen atmosphere at 0°C prior to use. Figure 3.1 show the apparatus for distillation method.

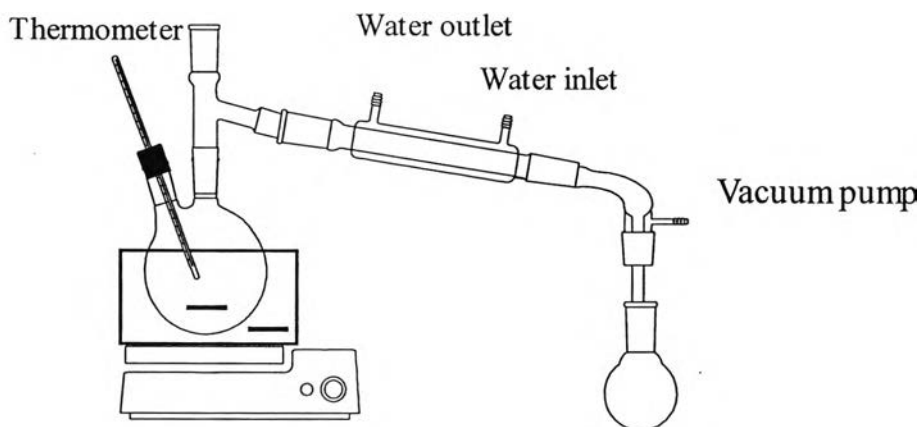
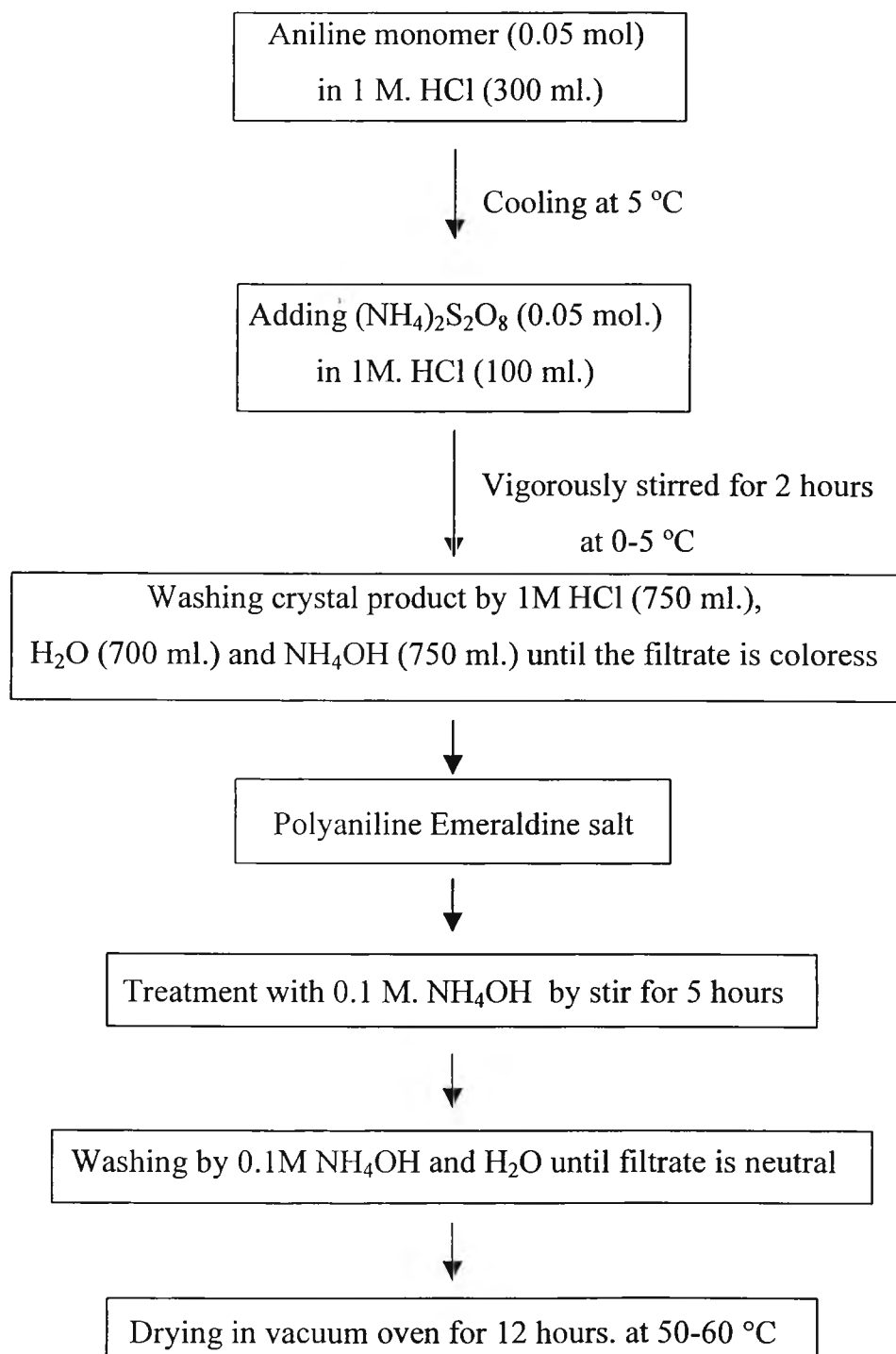


Figure 3.1 A scheme of the apparatus for distillation method.

3.2.2 Synthesis of Polyaniline Emeraldine Base

Polyaniline emeraldine base was synthesized by the method of Wei (1992). 300 ml of HCl (1 mol/l) containing 5 ml (0.05 mole) of aniline monomer was cooled at 0-5°C. A solution mixture of 11.4 grams (0.05 mole) of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 100 ml of HCl (1 mol/l) was slowly added into the mixture of aniline solution within 30 minutes. The solution mixture was stirred vigorously at 550 rpm for 2 hours. The dark green precipitate of polyaniline emeraldine salt was recovered from the polymerization flask, filtered and then washed with 750 ml of HCl (1 mol/l), 700 ml of water and 750 ml Of NH_4OH (0.1 mol/l). Polyaniline emeraldine salt was converted to the emeraldine base form by stirring the emeraldine salt form in 500 mL of NH_4OH (0.1 mol/l) for 5 hours. The dark blue powder of polyaniline emeraldine base was filtered and washed by using 750 ml of NH_4OH (0.1 mol/l) and water until the filtrate was neutral. The dark blue powder of polyaniline emeraldine base was dried in a

vacuum oven at 50-60°C for 12 hours. A diagram for the synthesis of polyaniline emeraldine base is shown in Figure 3.2.



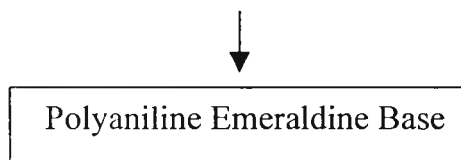


Figure 3.2 A diagram of synthesis polyaniline emeraldine base.

3.2.3 Preparation of Undoped and Doped Polyaniline Film

3.2.3.1 Undoped Polyaniline Films

Undoped polyaniline solution was prepared by mixing 4 grams of polyaniline emeraldine base with 1000 ml of 1-methyl-2-pyrrolidone (NMP). The solution was then stirred for 3 hours at room temperature. A 0.45 ml of undoped polyaniline solution was cast on a glass substrate with a size of $2.5 \times 2.5 \text{ cm}^2$. The wet films were dried at $50\text{-}60^\circ\text{C}$ for 96-120 hours in a vacuum oven.

3.2.3.2 Doped Polyaniline Films

- Hydrochloric Acid Doped Polyaniline (HCl-doped polyaniline)

Polyaniline solution was prepared by mixing 4 grams of polyaniline emeraldine base with 1000 ml of 1-methyl-2-pyrrolidone (NMP). The solution was then stirred for 3 hours at room temperature. The solution was divided into 5 ml/sample. A 8.67 ml (4 mole) of 37% HCl in 1000 ml of water was added into each polyaniline solution sample at particular volumes of 0.14, 0.65, 6.86, 13.71, 68.57 ml. The mixture doped solution was then stirred or shaking to reach equilibrium for 15-20 hours. A 0.45 ml of HCl doped polyaniline solution was cast on a glass substrate with a size of $2.5 \times 2.5 \text{ cm}^2$. The wet films were dried at $50\text{-}60^\circ\text{C}$ for 96-120 hours in a vacuum oven. The ratios of C_a/C_p on the ratios of HCl concentration in g/l divided by

polymer concentration in g/l in mixture solution of HCl doped polyaniline were 1, 5, 10, 50, 100 and 500.

- Camphor Sulfonic Acid Doped Polyaniline (CSA doped polyaniline)

4 mol/l of CSA at particular volumes of 0.1, 0.4, 0.9, 4.3, 8.6, 13 and 17 ml was added into 4 g/l of polyaniline solution prepared as the same procedure as HCl doped polyaniline. The mixture was then stirred or shaken to reach an equilibrium for 15-20 hours. The ratios of C_a/C_p of CSA doped polyaniline were 1, 5, 10, 50, 100, 150 and 500. 0.45 ml of CSA doped polyaniline solution was cast on a glass substrate with a size $2.5 \times 2.5 \text{ cm}^2$. The wet films were dried at $50-60^\circ\text{C}$ for 96-120 hours in a vacuum oven.

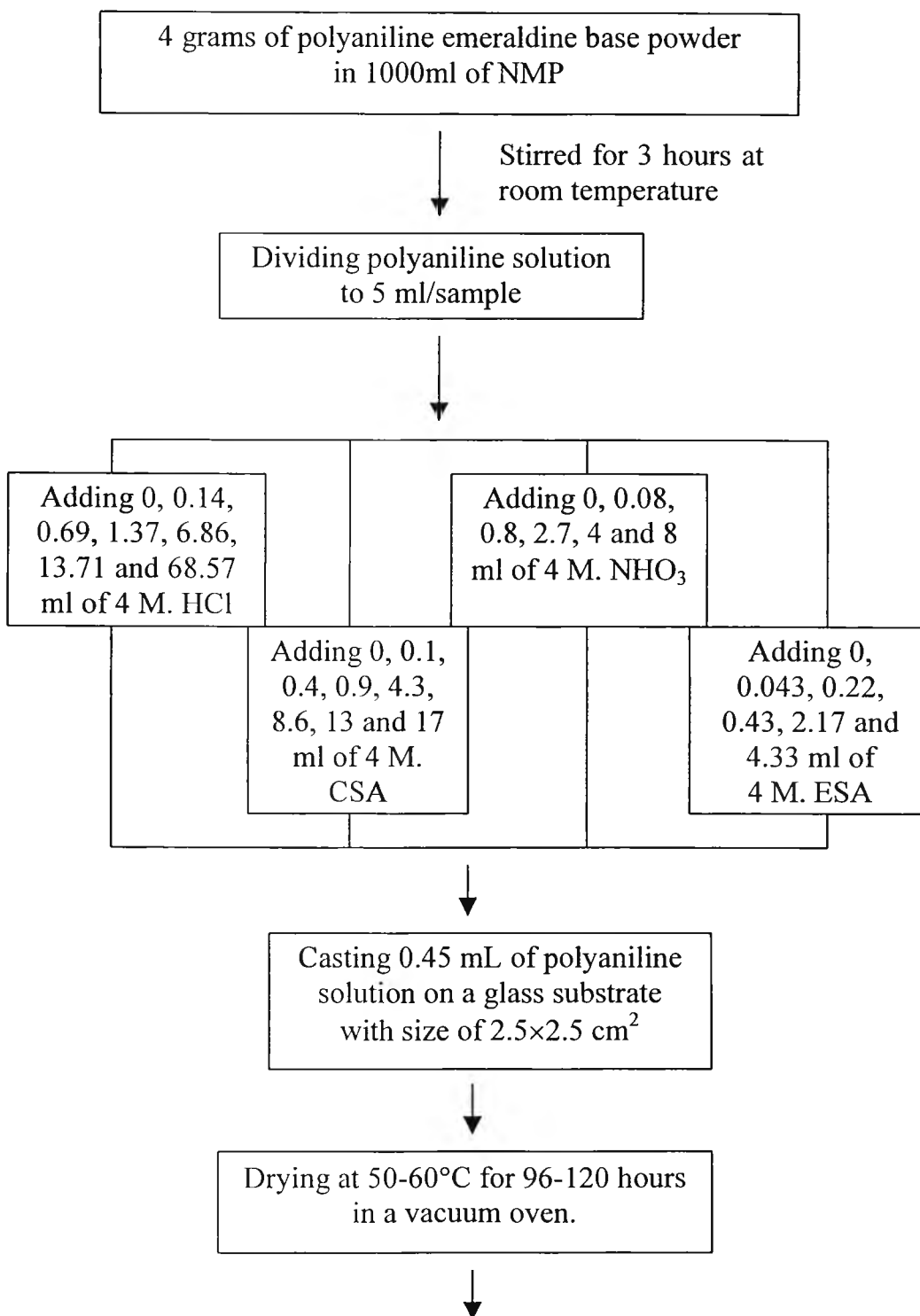
- Nitric Acid Doped Polyaniline (NHO_3 doped polyaniline)

4 mol/l of NHO_3 at particular volumes of 0.08, 0.8, 2.71, 4 and 8 ml was added into 4 g/l of polyaniline solution. The mixture solution was then stirred or shaken to reach an equilibrium for 15-20 hours. The ratios of C_a/C_p of NHO_3 doped polyaniline were 1, 10, 30, 50 and 100, respectively. 0.45 ml of NHO_3 doped polyaniline solution was cast on a glass substrate with a size $2.5 \times 2.5 \text{ cm}^2$. The wet films were dried at room temperature for 96-120 hours.

- Ethane Sulfonic Acid Doped Polyaniline (ESA doped polyaniline)

4 mol/l of ESA at particular volumes of 0.043, 0.22, 0.43, 2.17 and 4.33 ml was added into 4 g/l of polyaniline solution. The ESA doped polyaniline films were prepared as the same procedure as HCl doped polyaniline. The ratios of C_a/C_p of ESA doped polyaniline were 1, 5, 10, 50 and 100.

A diagram of preparation of undoped and doped polyaniline film is shown in Figure 3.3.



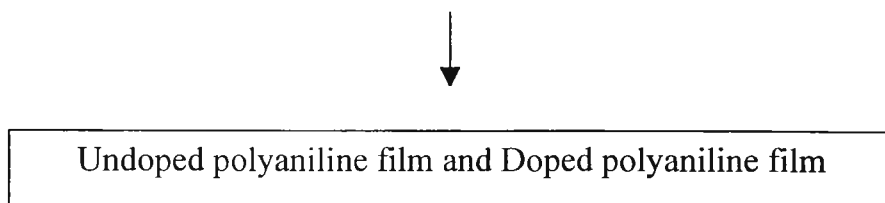


Figure 3.3 A diagram for the preparation of undoped and doped polyaniline film.

3.2.4 Characterization

3.2.4.1 Fourier-Transform Infrared Spectrometer (FTIR)

Infrared spectra were recorded using FT-IR spectrometer (Bruker, FRA 106/S) in the wavenumber range of $400\text{-}40000\text{ cm}^{-1}$ using the absorbance mode with 64 scans. The resolution of this instrument was $\pm 4\text{ cm}^{-1}$. The KBr technique was used to prepare the powder samples for recording spectrum.

Specimens for the synthesized polyaniline, undoped polyaniline, doped polyaniline and doped polyaniline after exposing to a gas at each C_a/C_p ratio were prepared by grinding powdered polyaniline with KBr powder. The sample mixture was pressed with special dies under the pressure of 10 tons. The sample spectrum was recorded by using KBr as a background.

FTIR was used to identify the functional group characteristics of the synthesized polyaniline and the differences in the functional groups between undoped and doped polyaniline film as well as between before and after exposing to a gas.

3.2.4.2 UV-visible Spectrophotometer (UV-Vis)

UV-visible spectra were recorded with a UV-Vis spectrometer (Perkin Elmer, Lamda 10). The solution samples were filled in a quartz cell to measure absorbance in the wavelength range of 300-1000 nm.

The undoped and doped polyaniline solution samples were prepared by dissolving in NMP at the concentration of 0.01 g/l. The undoped polyaniline solution and doped polyaniline solution at various C_a/C_p ratios were put in a quart cell and recorded the UV-visible spectra by using NMP as a background.

UV-visible spectrophotometer was used to investigate the electronic structure of polyaniline between undoped and doped polyaniline solution. The absorption spectra of the excitation of benzinoid segments, quinoid segments, and polaron state were identified.

3.2.4.3 Elemental Analysis (EA)

Elemental analysis (Perkin-Elmer, 2400 Series II CHNS/O Analyzer) was used to determine the amount of the elements in polyaniline samples. The amount of carbon (C), hydrogen (H), nitrogen (N_2) and sulfur (S) atoms in undoped and doped polyaniline were obtained. The doping level of the doped polyaniline film at various acid concentrations was also calculated from those amounts.

The undoped and doped film samples were weighed at 1.5-2.5 mg and sealed in the tin capsules and put in the sample cell. The sample was dropped in the combustion zone at a temperature between 975-1100°C with helium as a carrier gas. The amounts of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) were determined. The doping level of HCl doped polyaniline and CSA doped polyaniline was determined in term of the ratio of H/N and S/N, respectively.

3.2.4.4. Scanning Electron Microscope (SEM)

Scanning electron microscope (JOEL, model JSM-5200) was used to identify the microstructure of the undoped and doped polyaniline thin films. SEM digitized photographs were obtained with a magnification range between 35-20,000 times.

The undoped and doped polyaniline films were cut in to small pieces and adhered on a brass-stub by using an adhesive tape. The samples on stub were coated with thin layer of gold by using JFC-1100E ion sputtering device before operating in scanning electron microscope. The morphology of polyaniline films was obtained by using an acceleration voltage of 25 kV with a magnification of 5000 time

3.2.4.5. Thermogravimetric Analyzer (TGA)

A thermal gravimetric analyzer (DuPont, model TGA 2950) was used to study thermal stability, moisture contents and degradation process of the undoped and doped polyaniline film. Thermogravimetric Analyzer was operated from 50 to 780°C at the heating rate of 20°C/min.

The undoped and doped polyaniline films were weighed at 2-5 mg and put in a titanium pan. The samples were then heated from 50 to 780°C.

3.2.4.6. X-ray Diffraction Analyzer (XRD)

An X-ray diffractometer (Rigaku model) was used to investigate orderly arrangements of atoms or molecules and also determine the crystal structures of polymer. X-ray diffraction patterns were recorded on a Phillips PW 1830/00 No. DY 1241 diffractometer. The XRD samples were prepared by putting undoped or doped polyaniline films on aluminum specimen holder and examined between $2\theta = 5-50^\circ$.

3.2.5. Conductivity Measurement

The electrical conductivity of polyaniline thin film was measured by using a four point probe meter. The four point probe meter consists of two outer electrodes connected with a current driver and two inner electrodes connected with a voltmeter as shown in Figure 3.4.

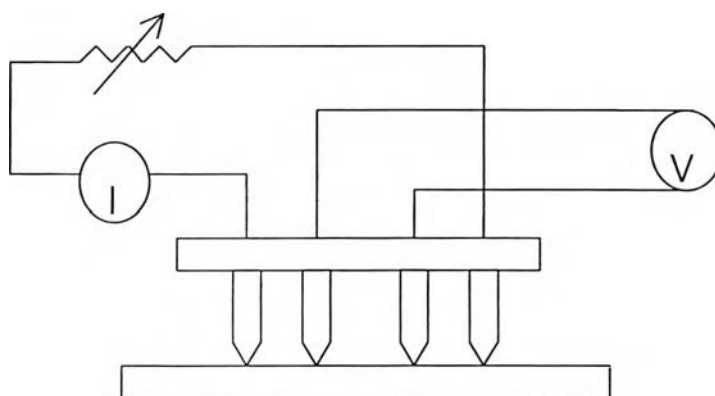


Figure 3.4 A schematic of the Four Point Probe Meter.

A constant current (I) was applied to the two outer electrodes and the sample voltage (V) was measured between the two inner electrodes. The specific conductivity of doped polyaniline film was calculated from Equation 2.1.

$$\sigma = \frac{1}{\rho} = \frac{1}{R \times t} = \frac{I}{K \times V \times t} \quad (3.1)$$

where

σ	=	specific conductivity (S/cm)
ρ	=	specific resistivity (Ω .cm)
R	=	resistance (Ω)
I	=	current (A)
V	=	voltage drop (V)
T	=	thickness (cm)

K = geometric factor

The constant K value depending on the probe geometry can be calculated by using Equation 3.2.

$$K \equiv \frac{w}{l} \quad (3.2)$$

where

w = probe width (cm)

l = probe length (cm)

In this measurement, the constant K value was determined by using a standard sheet with known resistivity: silicon wafer chip (SiO). It was calculated by using Equation 3.3.

$$K = \frac{\rho_{ref}}{R \times t} = \frac{l \times \rho_{ref}}{V \times t} \quad (3.3)$$

where

ρ_{ref} = known resistivity from the chemical handbook
($\Omega \cdot \text{cm}$)

t = standard sheet thickness

Measurements of conductivity responses of polyaniline films to SO_2 were recorded by using a specially constructed gas-sensitivity cell. It consisted of two chambers connected in series. The chambers were made from stainless steel No.316 m with thickness of 3 mm with a high corrosion resistivity. A schematic of the apparatus is shown in Figure 3.5. The first chamber was connected to two Perkin-Elmer Flow meters No. 62-01 with stain steel floats for controlling various SO_2 concentrations. The second chamber contained the four point probe meter for conductivity measurement.

The temperature controller (Shinoh, Digital DCN 720) connected to both chambers with a thermocouple was used to monitor and control temperature within the chamber.

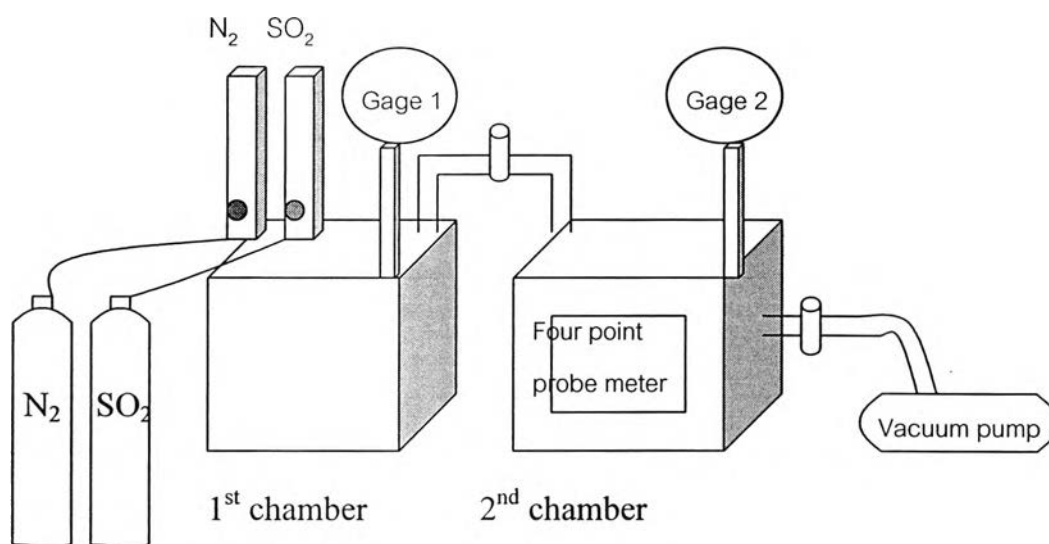


Figure 3.5 A schematic of Conductivity Detector With Gas Chamber.

3.2.5.1 Operating Procedure

The doped polyaniline film was located on the sample holder and pressed by four probes of the conductivity detector in the second chamber. Both chambers were evacuated by using a vacuum pump to remove other gases. The SO_2 and N_2 gases were fed into the first chamber at specific concentration and temperature. The feeding step was finished when the pressure in the first chamber became 1 atm as observed from pressure gage. The current was applied to polyaniline film to measure conductivity before exposing to a gas. After the conductivity of polyaniline film reached equilibrium, the gas mixture was fed into the second chamber. The voltage drop was detected until the response became saturated. The voltage drop was calculated to be specific conductivity by using Equation 3.1.