CHAPTER III

EXPERIMENT

3.1 Apparatus

3.1.1 pH meter (Radiometer Copenhagen type PHM 28)

3.1.2 Ultraviolet-Visible spectrophotometer (UV-240 Shimadzu) with 1 cm matched quartz cell.

3.1.3 Double Beam spectrophotometer (Jasco-UVIDE 650) with 1 cm matched quartz cell.

3.1.4 Dynacalibrator (VICI Metronics Model 230) (Figure 5) Chamber temperature was 30°C. The dilution flow rates required for the concentration were calculated by the following formula

$$Fd = \frac{PKm}{C} - Fc$$

where Fd = dilution flow rate in cc/min

P = device mass permeation rate in ng/min. at the specified temperature

Km = molar constant of the device gas

C = desired output concentration in parts per million

Fc = carrier flow rate of the Dynacalibrator.

In this experiment

$$Fd = \frac{1010\ (0.382)}{C} - 298$$

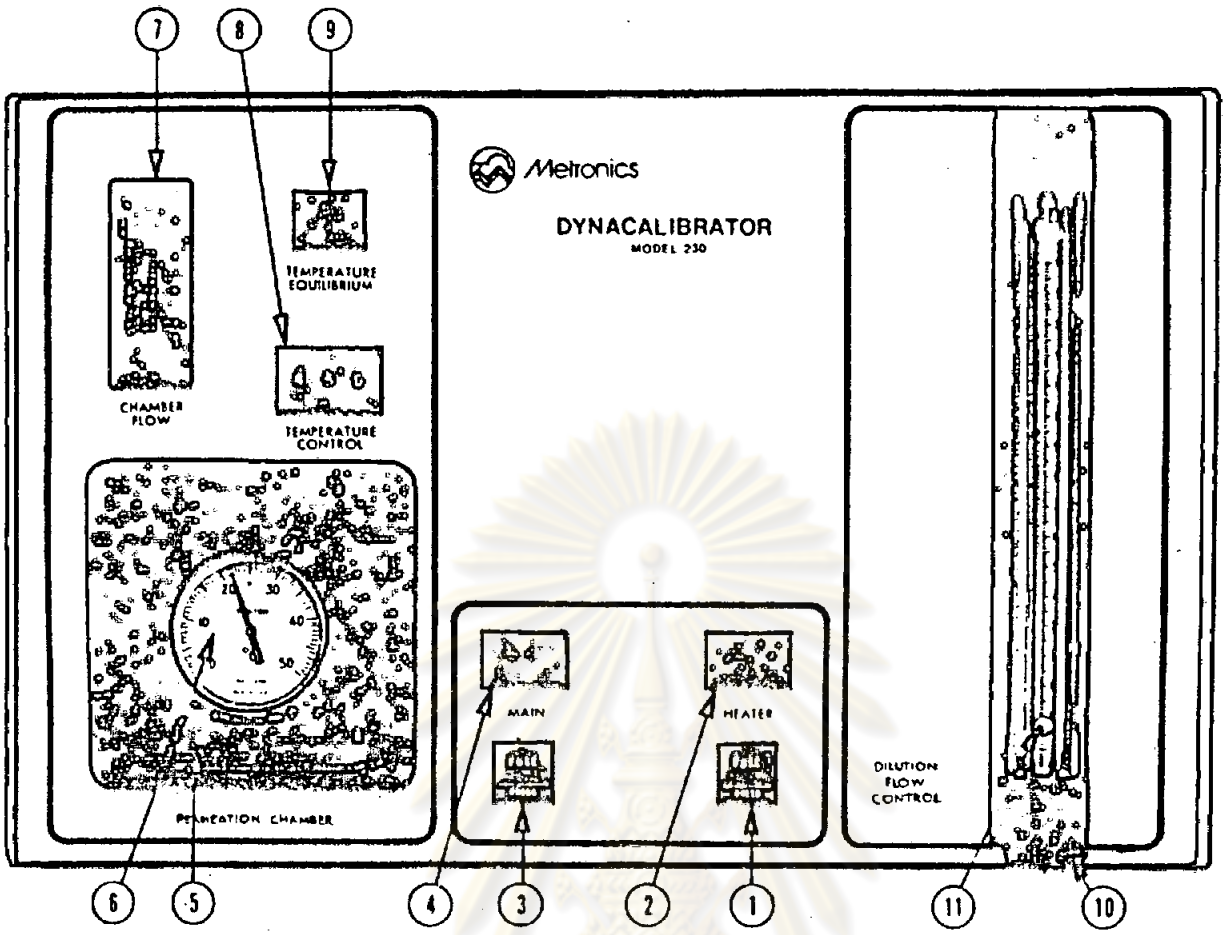

Figure 5. Dynacalibrator (Front Panel Controls and Indicators)

1. Heater Fuse
2. Heater Power Switch and Indicator
3. Main Fuse.
4. Main Power Switch and Indicator
5. Permeation Chamber
6. Dial Thermometer
7. Chamber Flow Meter
8. Temperature Control Potentiometer
9. Temperature Equilibrium Indicator
10. Dilution Flow Control Valve
11. Dilution Flowmeter

Concentrations of sulfur dioxide (C) that used were 0.079, 0.107, 0.234 ppm. Dilution gas was oxygen free nitrogen (TIG : G 1437).

3.1.5 Sampling train for SO_2 in inert gas and ambient air (Figure 6).

3.1.5.1 Absorber

A system that shown in Figure 6 C was recommended. Components for this system were specified as follows:

Absorption tubes : polypropylene tubes, 164 mm x 320 mm.

Disperser : glass impinger, 6 mm. tubing, 6 inches long, one end was drawn to 0.3-0.8 mm. outside diameter. The gas tube should be positioned so as to allow 6 mm from the bottom of the absorption tube.

3.1.5.2 Air pump

A pump was capable of maintaining a pressure differential of at least 0.7 atmosphere across the flow control device.

3.1.5.3 Air flowmeter or Critical Orifice

A calibrated rotameter or critical orifice was capable of measuring air flow within $\pm$ 2 percent (Figure 7). For 30-minute sampling, a 22-gauge hypodermic needle 1 inch long may be used as a critical orifice to give a flow of about 1 liter/minute. For 1-hour sampling, a 23-gauge hypodermic needle five-eights of an inch long may be used as a critical orifice to give a flow of about 0.5 liter/minute. For 24-hour sampling, a 27-gauge hypodermic needle three-eighths of an inch long may be used to give a flow of about 0.2 liter/

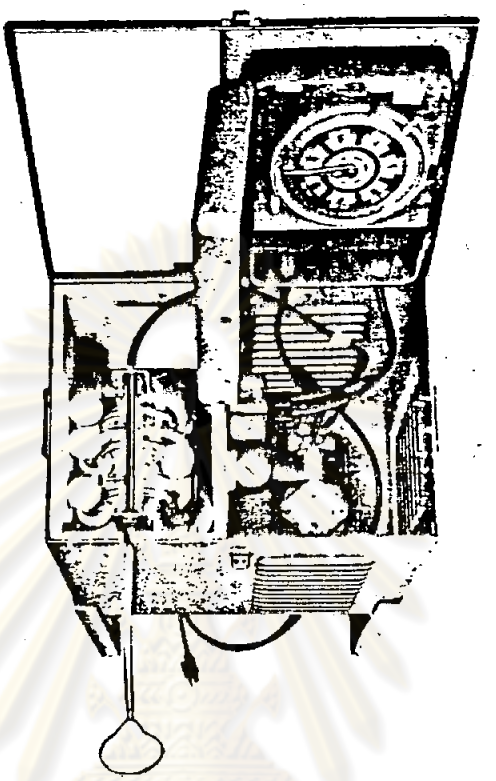

Figure 6 a. Sampling apparatus(61)

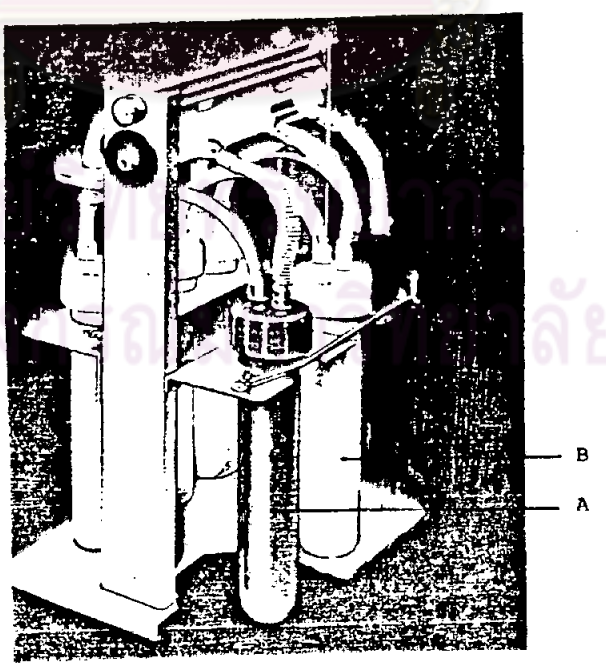

Figure 6 b. Sampling train assembly (61)

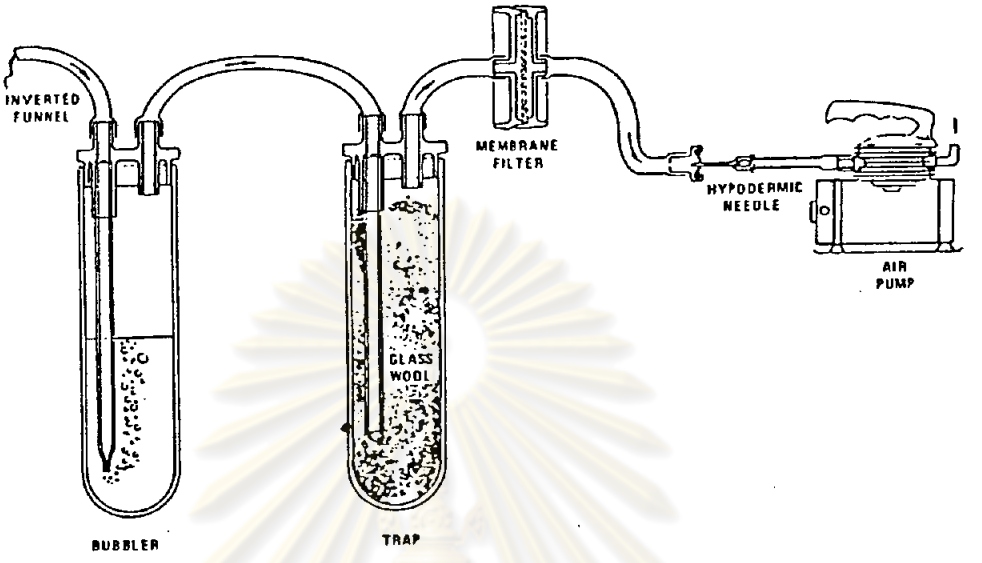

Figure 6 c. Sampling train detail (54)

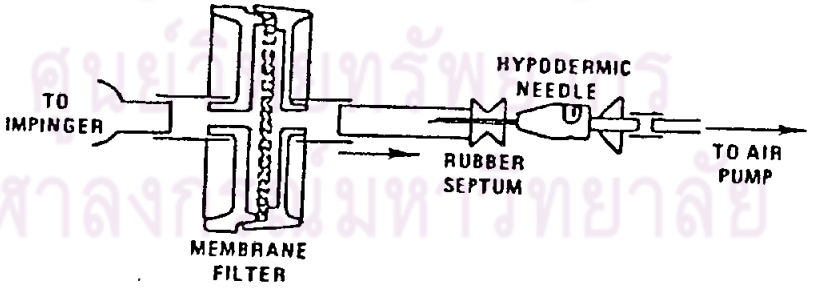

Figure 7. Critical Orifice Flow Control (54)

minute. A membrane filter was used to protect the needle.

3.2 Reagents

All chemicals employed were of analytical reagent grade. Solutions were prepared with the double deionized water.

3.2.1 Absorbing reagents

3.2.1.1 Absorbing reagent A (0.1 N sodium hydroxide solution)

A 4g sodium hydroxide was dissolved in 1000 cm^3 water. This solution was standarized with 0.1 M standard potassium hydrogen phthalate solution.

3.2.1.2 Absorbing reagent B (2 % glycerol in 0.05 N sodium hydroxide solution)

A 2g sodium hydroxide was dissolved with water in a 1000 cm^3 Volumetric flask and 20 cm^3 glycerol was added then the solution was diluted to the volume with water.

3.2.1.3 Absorbing reagent C (Buffered formaldehyde solution: 7 mM HCHO and 1mM KHP)

A 5 cm^3 formaldehyde solution (37 %) was pipetted into a 50 cm^3 volumetric flask, then a 2.04 g potassium hydrogen phthalate was added and the solution diluted to the volume with water. A 5 cm^3 of this solution was pipetted into a 1000 cm^3 volumetric flask and diluted to the volume with water. The diluted solution was used in this study.

3.2.1.4 Absorbing reagent D (Teterachloromercurate solution: TCM)

A 10.86 g mercuric chloride (HgCl), 0.066 g ethylene-diamine tetracetic acid disodium salt and 6.0 g potassium chloride (KCl) were dissolved with water and made up to 1000 cm^3 in a volumetric flask. This solution was 0.04 M TCM solution.

3.2.2 0.1 M Standard potassium hydrogen phthalate solution.

A 2.04 g potassium hydrogen phthalate, dried at 120°C for 2 hours, was accurately weighed and dissolved with water into a 100 cm^3 volumetric flask, then diluted to the volume with water.

3.2.3 Iodine stock solution (0.1 N)

A 12.7 g iodine was placed in a 250 cm^3 beaker, 40 g potassium iodide and 25 cm^3 water were added. The solution was stirred until all were dissolved, then diluted to 1000 cm^3 in a standard flask with water.

3.2.4 0.01 N iodine solution

A 50 cm^3 iodine stock solution was diluted to 500 cm^3 with water.

3.2.5 Starch indicator solution.

A 0.4 g soluble starch and 0.002 g mercuric iodide (preservative) were tritulated with a little water and the paste was added to 20 cm^3 boiling water. The solution was boiled until it was clear. The solution was cooled and transferred to a glass-stoppered bottle.

3.2.6 Sodium thiosulfate stock solution (0.1 N).

Stock solution was prepared by dissolving 25 g sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1000 cm^3 of water that had been freshly boiled and cooled. A 0.1 g sodium carbonate was added to the solution and the solution was let to stand for 1 day before standardization. To standardize, 1.5 g potassium iodate (KIO_3), dried at 180°C for 2 hours, was accurately weighed to the nearest 0.1 mg and dissolved with water in a 500 cm^3 volumetric flask, then diluted to the volume with water. A 50 cm^3 iodine solution was pipetted into a 500 cm^3 flask. A 2g potassium iodate and 10 cm^3 1 N HCl were added. After 5 minutes, this solution was titrated with standard thiosulfate solution to a pale yellow. A 5 cm^3 of starch indicator solution was added and the titration was continued until the blue color disappeared. The normality of the stock solution was calculated by the following equation.

$$N = \frac{W}{V} \times 2.80$$

where N = normality of standard thiosulfate solution

V = volume of thiosulfate required, cm^3

W = weight of potassium iodate, g

2.80= 10^3 (conversion of g to mg) timed 0.1 (fraction iodate used) divided by 35.67 (equivalent weight of potassium iodate)

3.2.7 0.01 N sodium thiosulfate solution

A 100 cm^3 thiosulfate stock solution was diluted to 1000 cm^3 with freshly boiled, cooled water.

3.2.8 Sulfite standard solution

A 0.4 g sodium sulfite (Na_2SO_3) was dissolved in 500 cm^3 of freshly boiled, cooled water. This solution contained the equivalent of 320 to 400 µg SO_2/cm^3. The actual concentration of the solution was determined by adding excess iodine solution and back titrating with 0.01 N sodium thiosulfate solution.

For back-titration, a 50 cm^3 of 0.01 N iodine solution was pipetted into each of the two 500 cm^3 flasks, A and B. A 25 cm^3 deionized water was added into flask A (Blank) and a 25 cm^3 sulfite solution was pipetted into flask B (sample). The flasks were closed with stoppers and allowed the contents to react for 5 minutes. These solutions were titrated with 0.01 N sodium thiosulfate solution to a pale yellow, then a 3 cm^3 starch indicator solution wad added to each flask and the titration was continued until the blue color disappeared. The concentration of sulfur dioxide in the sulfite standard solution was calculated by the following equation.

$$C = \frac{(A - B)(N)(3200)}{25}$$

where : C = concentration of sulfur dioxide, µg SO_2/cm^3

A = volume of 0.01 N sodium thiosulfate solution for blank, cm^3

B = volume of 0.01 N sodium thiosulfate solution for sample, cm^3

N = normality of 0.01 N sodium thiosulfate solution

32,000 = milliequivalent weight of sulfur dioxide, µg

25 = volume of sulfite standard solution, cm^3

Sulfite standard solution must be standardized every time before being used.

3.2.9 Reagent for Iodine method

Standard potassium iodate-iodide solution (0.025 N KIO_3-0.1 N KI). A 0.892 g potassium iodate, dried at 180°C for 2 hours, and 16.6 g potassium iodide were dissolved with water into a 1000 cm^3 volumetric flask. This solution was made up to the volume with freshly boiled, cooled water.

3.2.10 Reagents for Alkalimetric method.

3.2.10.1 Standard sulfuric acid solution (0.1 M)

A 5.6 cm^3 96 % w/w sulfuric acid was added into 1000 cm^3 of water. This solution was standardized with 0.1 N sodium hydroxide solution (as described in 3.2.1.1).

3.2.10.2 Methyl orange indicator.

A 0.1 g methyl orange was dissolved into 100 cm^3 of water.

3.2.10.3 Phenolphthalein indicator.

A 0.1 g phenolphthalein was dissolved into 100 cm^3 of ethanol.

3.2.11 Reagents for Aniline method

3.2.11.1 Aniline solution

A 0.1 cm^3 99 % w/w aniline solution was pipetted into a 50 cm^3 volumetric flask and the solution was made up to the volume with 1 M hydrochloric acid. A 10 cm^3 of this solution was pipetted into a 100 cm^3 volumetric flask. A 10 cm^3 of 3M phosphoric acid was added and the solution was diluted to the volume with 1M hydrochloric acid

3.2.11.2 4.5 M sodium hydroxide solution

A 18 g sodium hydroxide was dissolved into 100 cm^3 of water.

3.2.11.3 0.2 % Formaldehyde solution

A 5 cm^3 of formaldehyde solution (36 to 38 percent) was diluted to 1000 cm^3 with water. This solution was freshly prepared daily.

3.2.11.4 0.6 % Sulfamic acid solution

A 0.6 g sulfamic acid was dissolved with 100 cm^3 of water, freshly prepared daily.

3.2.12 Reagents for Pararosaniline method.

3.2.12.1 Pararosaniline reagent

A 20 cm^3 purified pararosaniline stock solution (0.2 percent nominal) (40) was pipetted to a 250 cm^3 volumetric flask. A 25 cm^3 of 3M phosphoric acid was added and diluted to the volume with water.

3.2.12.2 Working sulfite -TCM solution

A 2 cm^3 of the sulfite standard solution (as described in 3.2.8) was pipetted into a 100 cm^3 volumetric flask and made up to 100 cm^3 with 0.04 M TCM solution (as described in 3.2.14).

3.2.12.3 0.2 % Formaldehyde solution (as described in 3.2.11.3)

3.2.12.4 0.6 % Sulfamic acid solution (as described in 3.2.11.4)

3.3 Methods

3.3.1 Iodine method

A 6 cm^3 of the sulfite standard solution (as described in 3.2.8) was pipetted into a 100 cm^3 volumetric flask and made up to the volume with freshly boiled, cooled water. This sulfite solution (0-10 cm^3) was pipetted into 25 cm^3 of the absorbing reagent A, B or C. A 0.5 cm^3 concentrated hydrochloric acid and a 25 cm^3 standard potassium iodate-iodide solution were mixed gently. The excess iodine was back titrated with 0.01 N sodium thiosulfate solution to a pale yellow. A 3 cm^3 starch indicator was added and the titration was continued until the blue color disappeared.

3.3.2 Alkalimetric method

A series of the sulfite standard solution (as described in 3.2.8), volume 5-20 cm^3, was pipetted into 25 cm^3 of absorbing reagent A, B or C. A 25 cm^3 of this solution was pipetted into a 100 cm^3 flask. A 2 drops of phenolphthalein was added and the solution was titrated with standard sulfuric acid until the red color disappeared (sodium hydroxide was neutralized). Then 2 drops of methyl orange was added. The solution was titrated with standard sulfuric acid until red color

appeared.

3.3.3 Aniline method

3.3.3.1 Using Absorbing reagent B

A 6 cm^3 of the sulfite standard solution (as described in 3.2.8) was pipetted into a 100 cm^3 volumetric flask and made up to the volume with freshly boiled, cooled water. This sulfite solution (0-10 cm^3) was pipetted into a 50 cm^3 volumetric flask which contained 25 cm^3 of the absorbing reagent B. A reagent blank was prepared by adding absorbing reagent B to a 50 cm^3 volumetric flask. A 2 cm^3 of 2 % formaldehyde solution was added into the sample and blank. A 5 cm^3 of aniline solution (as described in 3.2.11.1) was pipetted into the solution and diluted to 50 cm^3 with water. Between 10 and 20 minutes later, the absorbance of the sample was measured at 242 nm. The reagent blank was used as reference.

3.3.3.2 Using Absorbing reagent C

A 6 cm^3 of the sulfite standard solution (as described in 3.2.8) was pipetted into a 100 cm^3 volumetric flask and made up to the volume with freshly boiled, cooled water. This working sulfite solution (0-10 cm^3) was pipetted into a 50 cm^3 volumetric flask which contained 25 cm^3 of the absorbing reagent C. A reagent blank was prepared by adding absorbing reagent C to a 50 cm^3 volumetric flask. A 1 cm^3 of 0.6 % sulfamic acid was added into the sample and blank. The solutions were stood for 10 minutes to destroy the nitrite from oxides of nitrogen. A 1 cm^3 of 4.5 M sodium hydroxide solution was pipetted into the sample and blank solution. Then a 5 cm^3 of aniline solution was added. The contents of these flasks were made up to 50 cm^3 with water and mixed throughly. Between 10 and 20 minutes later, the absorbance of the sample was measured at 242 nm. The reagent blank was used as reference.

3.3.3.3 Interferences

3.3.3.3.1 Heavy metals (Cu, Pb, Mn)

Copper (II) nitrate, Lead (II) nitrate or Manganese (II) nitrate (range 0-15 µg) were added into 3 cm^3 of the working sulfite solution in 25 cm^3 absorbing reagent C. Then the remaining reagents (as described in 3.3.2.2) were added. The absorbance was measured at 242 nm after a period of 10 minutes but not exceeding 20 minutes.

3.3.3.3.2 Oxides of nitrogen

A 0.011 g sodium nitrite ($NaNO_2$) was dissolved with 1000 cm^3 water. This solution contained the equivalent of 100 µg/cm^3 of nitrogen dioxide (1.0 mole NO_2 ≃ 0.072 mole $NaNO_2$)(62). This solution, volume 0-10 cm^3, was pipetted into 25 cm^3 of each absorbing reagent which contained 1 µg/cm^3 sulfur dioxide. Sulfamic acid solution (0.6 percent), volume 0-1 cm^3 was added. After 10 minutes, 1 cm^3 of 4.5 M sodium hydroxide solution and 5 cm^3 aniline solution were added; then the solution was diluted to 50 cm^3 with water. The absorbance was measured at 242 nm after 10 minutes but not exceeding 20 minutes.

3.3.4 Pararosaniline method (58)

The working sulfite-TCM solution (as described in 3.2.12.2), volume 0-5 cm^3, was pipetted into a 25 cm^3 of volumetric flask. Sufficient TCM solution was added to bring the volume to approximately 10 cm^3. A reagent blank was prepared by adding 10 cm^3 of TCM solution to a 25 cm^3 volumetric flask. A 1 cm^3 sulfamic acid was added into the sample and blank. The solution was allowed to react for 10 minutes to destroy the nitrite from oxides of nitrogen. A 2 cm^3 of 0.2 %

formaldehyde solution was pipetted into the solution. Then 5 cm^3 of pararosaniline reagent was added and diluted to volume with freshly boiled, cooled water and the solution was mixed thoroughly. Between 30 and 60 minutes later, the absorbance of the solution was determined at 548 nm. Deionized water, not the reagent blank, was used as the reference.

3.3.5 Sampling sulfur dioxide in inert gas and ambient air

3.3.5.1 Sampling sulfur dioxide in inert gas

3.3.5.1.1 Sampling

Sulfur dioxide gas from Dynacalibrator was drawn to the sampling train as shown in Figure 6. Absorber A contained 50 cm^3 TCM solution and absorber B contained 50 cm^3 buffered formaldehyde solution, The sample was collected at 0.4 liter/minute in the peroid of 2-4 hours.

3.3.5.1.2 Determination by Aniline method

a) Sample preparation

The entire sample was diluted to 50 cm^3 with buffered formaldehyde solution. This solution was remained for 20 minutes before analysis to allow any ozone decomposed. A 25 cm^3 of the sample was pipetted into a 50 cm^3 volumetric flask.

b) Determination

For each set of determinations, a reagent blank was prepared by adding 25 cm^3 unexposed buffered formaldehyde solution to a 50 cm^3 volumetric flask. The samples were determined as described in 3.3.3.2

c) Calibration curve

A series of the working sulfite solutions (such as 0, 0.5, 1, 2, 3 and 4 cm^3) was accurately pipetted into 50 cm^3 volumetric flask which contained 25 cm^3 buffered formaldehyde solution in each flask. The remaining reagents were added as described in 3.3.3.2 The absorbances were plotted against the total concentration in µg SO_2 for the corresponding solutions. The total µg SO_2 in solution equals to the concentration of the standard in µg SO_2/cm^3 times the volume (cm^3) of sulfite solution added.

3.3.5.1.3 Determination by Pararosaniline method

a) Sample preparation

The entire sample was diluted to 50 cm^3 with TCM absorbing reagent. A 5 cm^3 of this solution was pipetted into a 10 cm^3 volumetric flask and diluted to volume with TCM absorbing solution. This solution was remained 20 minutes before analysis to allow any ozone decomposed.

b) Determination

For each set of determinations, a reagent blank was prepared by adding 10 cm^3 of unexposed TCM solution to a 25 cm^3 volumetric flask. Control solution was prepared by adding 2 cm^3 of working sulfite-TCM solution and 8 cm^3 of TCM solution to another 25 cm^3 volumetric flask. These solution and the samples were determined as described in 3.3.4

c) Calibration Curve

A series of the working sulfite-TCM solution

(such as 0, 0.5, 1, 2, 3 and 4 cm^3) was pipetted into 25 cm^3 volumetric flask. Sufficient TCM solution was added to each flask to bring the volume to approximately 10 cm^3. The remaining reagents (as described in 3.3.4) were added. The absorbance of the solution was measured at 548 nm. The absorbances were plotted against the total concentration in µg SO_2 for the corresponding solutions. The total µg SO_2 in solution equals to the concentration of the standard in µg SO_2/cm^3 times the volume (cm^3) of sulfite solution added.

3.3.5.2 Sampling sulfur dioxide in ambient air

3.3.5.2.1. Station locations

The sampling stations were located in the Mae Moh Basin areas as shown in Figure 8.

Stations	Locations
1	Ban Hua Fai
2	Pump House at Power Plant units 4-7
3	Old Power Plant Housing
4	Huai Khing Dam

3.3.5.2.2 Sampling

Ambient air was collected in the period of 24 hours (midnight to midnight). A 50 cm^3 of TCM solution and 50 cm^3 of buffered formaldehyde solution were placed into each of the two absorbers. The sample was collected at 0.2 liter/minute and protected from direct sunlight throughout collection and storage.

3.3.5.2.3 Determination

Determination was as described in 3.3.5.1.2 and 3.3.5.1.3.

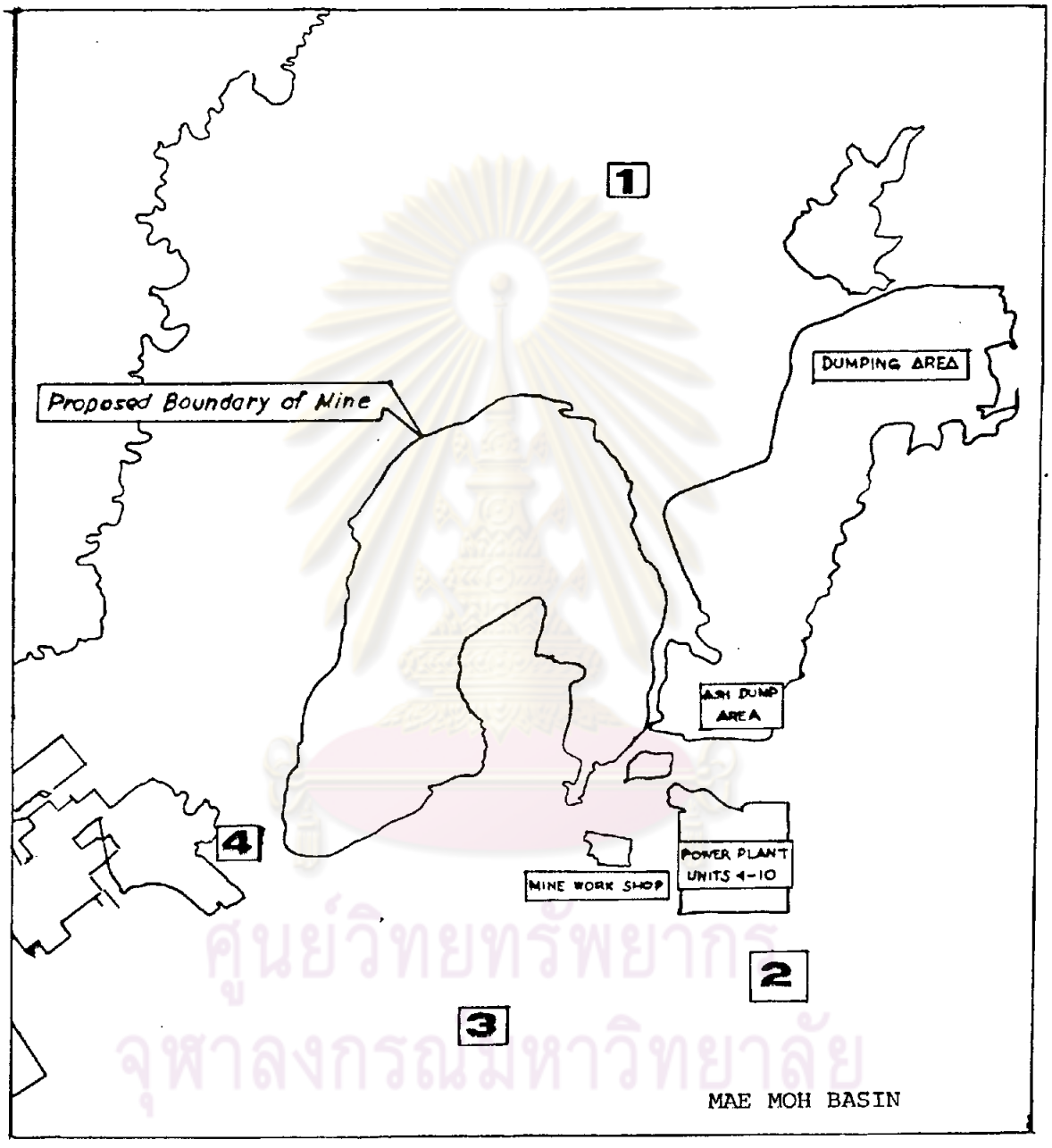

Figure 8. Location of ambient air sampling stations