CHAPTER III

EXPERIMENTAL

3.1 Chemicals

All chemicals employed were of reagent grade. No further purification of these compounds was attempted unless otherwise stated.

Millipore membranes and hygroscopic compounds were kept in a desiccator over the anhydrous silica gel.

The double deionized water used throughout this study was prepared by passing the distilled water through a set of three columns which were packed with anion exchange resins, Amberlite IR - 45(OH) and cation exchange resins, Amberlite IR - 120(H)(38) .

Purified nitrogen gas for deaerating test solutions in anodic stripping analyses was prepared by passing the nitrogen gas (obtained from the Royal Thai Army Chemical Department) through a vanadium (II) chloride solution and then through the double deionized water before entering the cell(39) .

The percentage of the metal ion species in the analar grade reagent was determined. Cadmium nitrate, zinc nitrate, copper nitrate solutions were potentiometrically titrated with EDTA.(40) Lead nitrate was standardized against potassium dichromate by amperometric titration(40).

3.2 Apparatus

Particulate matter was collected on a 37-mm diameter Millipore membrane (0.45 µm, pore size) by a Bendix Telematic Air Sampler Model 150A. The flow rate of this instrument was calibrated with a Precision Scientific West Test Meter.

Atomic absorption data for Cd, Cu, Pb, and Zn in airborne particulates were obtained with a Varian Techtron Atomic Absorption Spectrophotometer Model AA-5, and for Hg was obtained with a Coleman Model MAS-50 Mercury Analyzer.

Voltammograms were obtained with a Radiometer Copenhagen Polariter type PO4g. The cell employed in all analyses is a two compartment cell (H-shaped cell), one compartment served for the reference electrode, saturated calomel electrode (SCE), and another compartment for the test solution.

Glassy carbon electrode (GCE) with an area of 0.071 cm^2 was used as working electrode (41,42).

The pH values of the solutions were measured with a pH meter (Radiometer Copenhagen type PHM 28).

3.3 Procedure

3.3.1 Stock solutions

A 100.00 $\mu g/cm^3$ solution of each metal ion was prepared. The Cd(II), Cu(II), Pb(II), and Zn(II) solutions were prepared by dissolving the appropiate amounts of the nitrate salts of the corresponding metals with the double deionized water. The Hg(II) solution was prepared by dissolving $Hg(NO_3)_2$ in 0.1M HNO_3 .

3.3.2 Air particulate sampling

A piece of 37-mm-diameter Millipore membrane with filter paper (Whatman No 5) was dried in the desiccator, weighed, and filled in a plastic holder by facing the Millipore membrane for collecting air particulates. This collector was ready for air sampling. When an air particulate sampling was desired , the collector was connected to the Bendix Telmatic Air Sampler by means of a piece of rubber tubing (see Figure 1). The level of the collector was set. The plastic cover of the collector was opened, and the timer on the air sampler was set, this made the pump automatically turned on. The flow rate of ambient air drawn through the collector was maintained at 2 liters per minute. The sampling interval for this collection was 2 hours. After sampling, the piece of Millipore membrane with filter paper was dried in the desiccator for 1 day. Then, this piece of Millipore membrane with filter paper was weighed again, The difference between the weights of this piece of Millipore membrane with filter paper before and after sampling was the total weight of air particulates.

3.3.3 Preparation of sample solutions

The air particulate sample on the piece of Millipore membrane with filter paper was dissolved in 5 cm^3 of concentrated

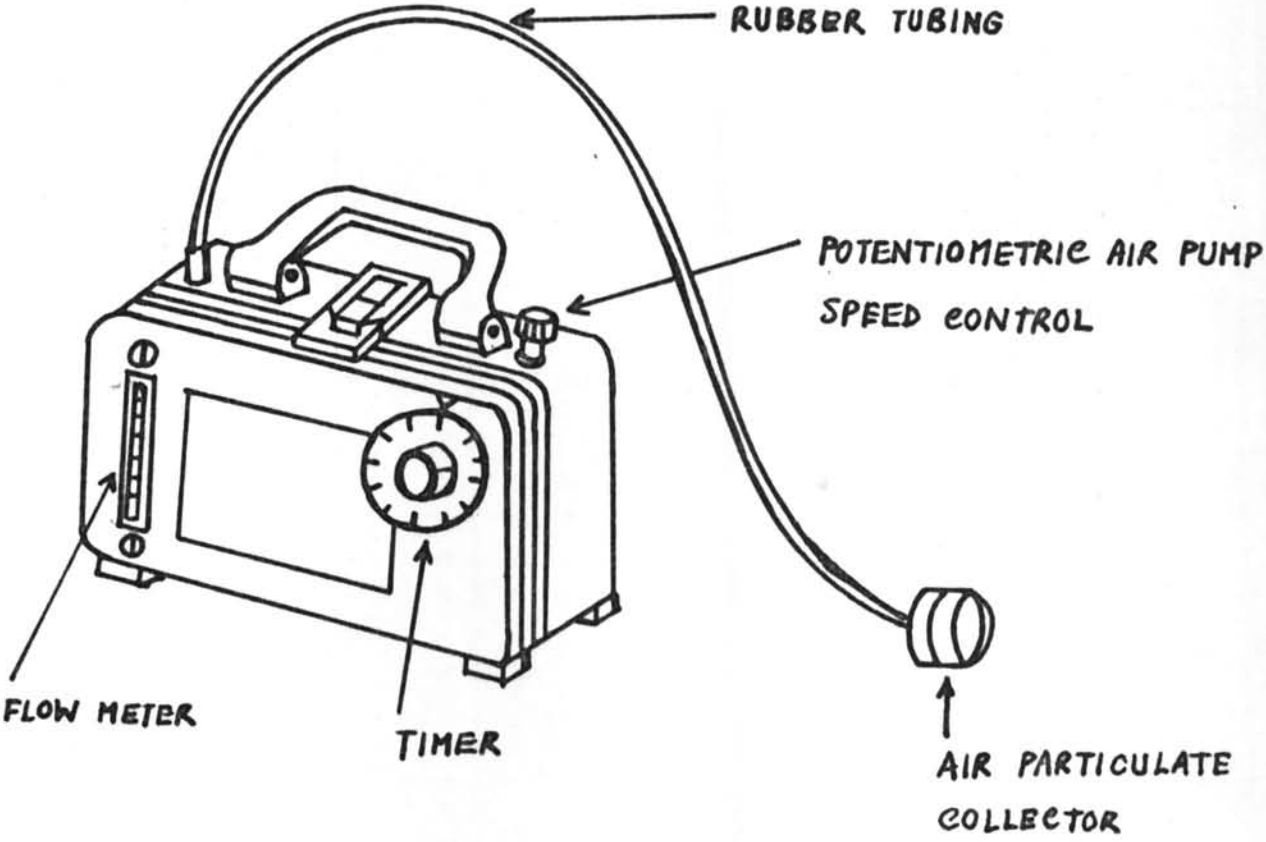

Figure 1. The Bendix Telmatic Air Sampler Model 150 A with an Air Particulate Collector.

nitric acid and heated to aid the dissolution and to decompose the organic matter. Further heating was performed to expel nitrogen oxides and 10 cm^3 of the double deionized water were added. The solution was heated for other 5 minutes. After cooling, the residue was filtered off and the washing was performed several times with the double deionized water. The volume of the filtrate was made up to 25.00cm^3 with the double deionized water in a volummetric flask. Blank solution was prepared in the same manner but a new piece of Millipore membrane with filter paper was used instead. These solutions were ready for determining Cd(II), Cu(II), Hg(II), Pb(II), and Zn(II) by atomic absorption spectrophotometric and anodic stripping voltammetric techniques.

3.3.4 Anodic stripping analyses

3.3.4.1 Standard and reagent solutions

Series of standard solutions of Zn(II), Cd(II), Pb(II), Cu(II), and Hg(II) were obtained by successive dilution of the 100.00 $\mu g/cm^3$ solution of each metal ion species with the double deionized water.

Acetate buffer pH 5.8 was prepared by mixing the dissolved sodium acetate trihydrate (12.92 g in the double deionized water) with 0.32 cm^3 of 99.7 % acetic acid and the solution was diluted to 100.00cm^3 with the double deionized water.

A 0.06830 g of $Ga(CLO_4)_3 \cdot 6H_2O$ was dissolved and diluted to 100.00cm^3 with 0.1M HNO_3 , this solution resulted in 100.00 µg Ga/cm^3

3.3.4.2 Blank solution

The blank solution was prepared as described in 3.3. 3

3.3.4.3 Fabrication of the glassy carbon electrode (40,41)

A piece of 10-mm glassy carbon rod (vitreous carbon rod, 3mm.dia, from Tokai Electrode Manufacturing Co.) was glued in a 4-mm (ID) soft glass tube with Araldit epoxy (Ciba-Geigy Limited, Basle, Switzerland). A fresh glassy carbon surface was always prepared for each run by polishing with a piece of silicon carbide paper, then washed with the double deionized water and gently rubbed with a piece of filter paper to get rid of dust and moisture.

3.3.4.4 Test solutions

The test solution for determining Cu(II), Pb(II), and Cd(II) was prepared by mixing 10.00 cm^3 of the sample solution with 1.25 cm^3 of 100.00 µg/cm^3 of Hg(II) and 2.50 cm^3 of M KNO_3. The mixture was pH adjusted to 2 and diluted with the double deionized water to the mark of the 25.00cm^3 volummetric flask.

For determination of Zn(II), the test solution was prepared by mixing 10.00 cm^3 of the sample solution with 1.25 cm^3 of 100.00 µg/cm^3 of Hg(II), 10.00 cm^3 of acetate buffer pH 5.8 , and 2.50 cm^3 of 100.00 $\mu g/cm^3$ of Ga(III). The solution was made up volume to 25.00cm^3 with the double deionized water.

For determination of Hg(II), the test solution was prepared by mixing 10.00 cm^3 of the sample solution with 2.50 cm^3 of M KNO_3. The solution was acidified with concentrated HNO_3 to pH 2 and was diluted with the double deionized water to 25.00cm^3

3.3.4.5 Voltammetric and stripping analyses

In order to obtain the deposition potential of any species, a cathodic voltammogram of the species interested was recorded and the peak potential was measured.

Before the test solution was placed in the cell for either voltammetric or stripping analysis, the test compartment was washed twice with the double deionized water and rinsed once with the test solution. A 10.00-cm^3 test solution was transferred to the cell. The purified nitrogen gas was bubbled through the solution for 5 minutes and was maintained above the solution during the analysis. The glassy carbon electrode was then inserted in the test compartment.

For deposition of metal species, the stirrer was turned on, the desired potential was set and the electrolysis was proceeded for 20 minutes.

For voltammetry, the desired potential range, current sensitivity, scan rate and polarity were set on the instrument and then the recorder was turned on.

3.3.5 Atomic absoption spectrophotometric analyses

3.3.5.1 Flame atomic absorption

3.3.5.1.1 Standard solutions

Series of standard solutions containing 0.10 µg/cm^3-3.00 µg/cm^3 of Zn(II), Cd(II) Pb(II) and Cu(II) were prepared by successive dilution of the 100.00 µg/cm^3 stock solutions with the double deionized water.

3.3.5.1.2 Blank solution

The blank solution which was prepared by the method as described in 3.3. 3 was used.

3.3.5.1.3 Calibration curves of metal ions

The calibration curves of metal ions were established by plotting the absorbance of the standard metal ion solution against its concentration in the range of 0.10 µg/cm^3-3.00 µg/cm^3

3.3.5.1.4 Analysis of sample

An aliquot of the sample and blank solution were subjected to atomic absorption analyses. The absorbances of sample and blank were measured, and the corrected absorbance was obtained by substracting the blank absorbance from the sample absorbance. The concentration of metal species in the sample solution was determined by comparing the corrected absorbance of the sample with the calibration curve of that metal ion species.

3.3.5.2 Flameless atomic absorption

3.3.5.2.1 Standard and reagent solutions

Mercury standard solution, 1.00 µg/100 cm^3, (cat. NO. 50-107, Coleman Instruments) was used for calibrating the the instrument.

A 10% (W/V) tin(II) chloride solution was prepared by dissolving 25.00 g of tin(II) chloride dihydrate in 50.0 cm^3 concentrated hydrochloric acid and the solution was made up to 250.0 cm^3 with the double deionized water. Then, the solution was heated until the precipitate completely dissolved(43).

3.3.5.2.2 Blank solution

The blank solution was prepared as described in 3.3.3

3.3.5.2.3 Test solution

The test solution was prepared by mixing 100.0 cm^3 of sample or blank solution with 5.00 cm^3 of 10% (W/V) tin(II) chloride solution.

3.3.5.2.4 Calibration of the instrument

The instrument was calibrated by using the average value of the percent transmittances of four samples of the mercury standard (3.3.5.2.1) of concentration 1.00 µg/100cm^3 (44).

3.3.5.2.5 Analysis of sample

A 105.0 cm^3 of the test solution was subjected to atomic absorption analysis. The amount of mercury in microgram in the test solution was obtained by reading from the meter scale. The corrected concentration of mercury in sample solution was determined by substracting the amounts of mercury in the blank solution from the sample solution.