CHAPTER 2

EXPERIMENTAL

2.1 Apparatus and Instruments

1. Voltammograph, PGSTAT 10, Autolab, Netherlands.
2. Voltammograph cell, 633 VA Stand, Metrohm, Switzerland.
3. Digital pH meter, model 667 420, Leybold, Germany.
4. Magnetic bar and Magnetic stirrer, Combination, Scotland.
5. Atomic Absorption Spectrophotometer, model AA-680, Shimadzu, Japan.
6. Ultrapure water system, model D4745, Barnstead, U.S.A.
7. Weighing machine, model AA-200DS, Denver Instrument, U.S.A.
8. Glassware, Pyrex, U.S.A.

2.2 Chemicals

1. Gracial acetic acid, AR grade, Fuka, Switzerland.
2. Sodium acetate, AR grade, Fuka, Switzerland.
3. Standard lead solution, AR grade, Merck, W. Germany.
4. Hydrochloric acid, AR grade, Merck, W. Germany.
5. Sodium hydroxide, AR grade, Ajax Chemicals, Australia.
6. Potassium hydroxide, AR grade, Ajax Chemicals, Australia.
7. Epichlorohydrin, AR grade, Ajax Chemicals, Australia.
8. Acetone, AR grade, Ajax Chemical, Australia.
9. Ether, AR grade, Ajax Chemical, Australia.

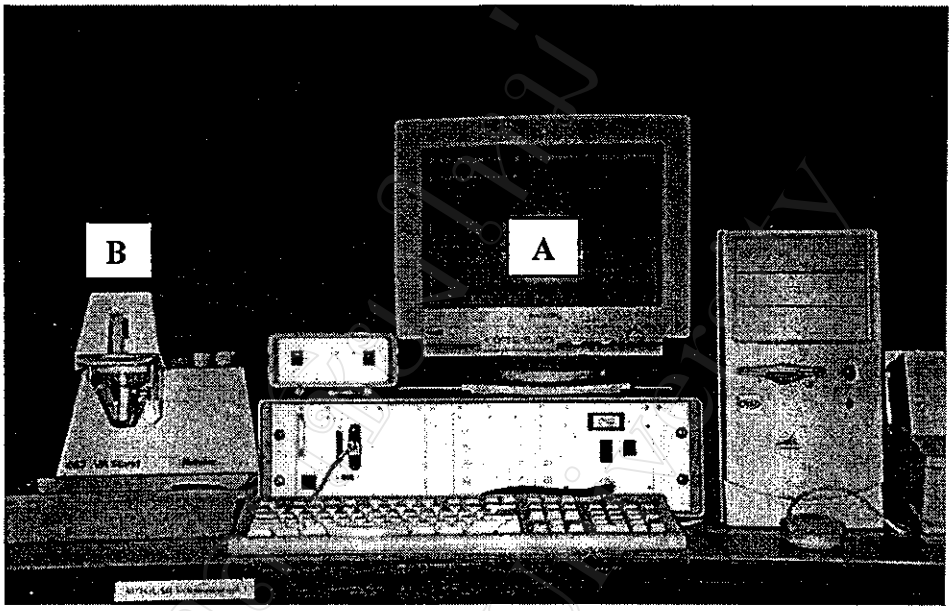

Figure 2.1 Electrochemical analyzer set (A) PGSTAT 10 (B) Metrohm stand for voltammetric.

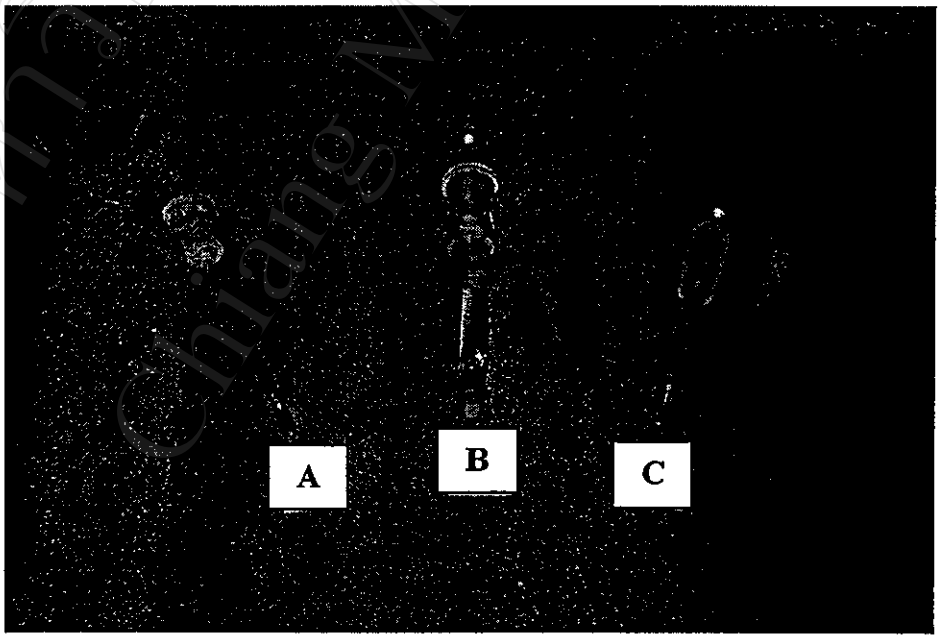

Figure 2.2 Three-electrode system used for analysis (A) Carbon paste electrode as working electrode (B) saturated calomel electrode as reference electrode (C) Platinum wire electrode as auxiliary electrode.

2.3 Preparation of Solutions

2.3.1 Preparation of 0.6 M Acetic acid solution

This solution was prepared by dissolving 17.10 ml of gracial acetic acid in 500 ml double deionized water in a 500 ml volumetric flask.

2.3.2 Preparation of 0.6 M Sodium acetate solution

This solution was prepared by accurately weighing 40.82 g of sodium acetate dissolving with double deionized water into a 500 ml volumetric flask and making up to the mark with double deionized water.

2.3.3 Preparation of 0.6 M Acetate buffer for controlling pH and ionic strength

The 0.6 M acetate buffer at any pH was prepared by mixing appropriate volumes of 0.6 M acetic acid and 0.6 M sodium acetate solutions.

2.3.4 Preparation of 0.1 M Hydrochloric acid

Appropriate volume of 4.15 ml of 37% hydrochloric acid was transferred into a 500 ml volumetric flask and then the volume of the solution was made up to the mark with double deionized water.

2.3.5 Preparation of 1 ppm lead(II) solution

This solution was prepared from standard lead(II) solution.

2.4 Preparation of treated-*Pennisetum*

Pennisetum setosum had modified by crosslink-xanthate method [85]. In order to improve sorption capacity of *Pennisetum setosum*. It can enhance the sorption capacity of *Pennisetum setosum*. The procedure is as follows:

In the first step *Pennisetums* were washed with water and dried at 80°C for 24 hrs. After that ground and sieved for 1 mm particle size then 50 g of the ground *Pennisetums* were weighed, placed into a beaker, followed by 75 ml of 0.2 M sodium chloride, and 2.75 ml of epichlorohydrin were added and mixed for 10 min. The beaker was placed on a hotplate and 20 ml of 2 M potassium hydroxide was added and then slowly stirred at 50 °C for 30 min. The beaker was then removed from the hot plate. After cooling to room temperature, the mixed solution of 1ml epichlorohydrin and 25 ml of deionized water were added and stirred for 16 hr. After that 125 ml of 5 M sodium hydroxide and 7.5 ml of carbondisulfide were added and stirred for 2 hr. Finally the mixture was washed with water, acetone and ether. Allow to dry in a desiccator for 72 hr.

2.5 Electrode preparation

The modified electrode carbon paste electrode (15% treated-*Pennisetum* by weight) were prepared by mixing 0.0500 g of graphite power of spectroscopic quality with 0.0150 g of treated-*Pennisetum*, the *Pennisetum* having been previously modified by crosslink-xanthate method. After that 0.03 g of mineral oil was then added to form a paste and thoroughly mixed for 15 minutes to ensure uniform distribution of the treated-*Pennisetum* within the carbon paste. Finally the modified paste was packed into one end of a glass tube (3 mm i.d.) were a copper wire was inserted through the opposite end to establish electrical contact. The carbon paste surface was smoothed on watch glass.

Activation of electrode was achieved by subjecting it to cyclic high rate scans between –1.0 and +1.0 for 30 min and then to measuring and regenerating processes (between 5 and 10 cycle) until reproducible behavior was observed.

2.6 Optimization of system

2.6.1 The study pH of electrolyte solution.

The effect of varying the electrolyte pH on peak current for the determination of Pb(II) at the treated-*Pennisetum* modified (15% w/w) carbon paste electrode was studied by varying the pH of electrolyte solution in the range of 3.5-70. The experiments are as follow:

1. The treated-*Pennisetum* modified (15% w/w) carbon paste electrode was rinsed with water and placed in 1 ppm lead(II) solution contained in the accumulation cell for 2 min. The accumulation was carried out under constant stirring with an open circuit.

2. The modified electrode was then taken out of the accumulation solution, rinsed with water and transferred into the measurement cell containing 20 ml of acetate buffer pH 3.5 with an ionic strength of 0.6. Voltammograms were obtained by differential pulse voltammetry, by scanning between potential –0.700 and 0.350 V with 5 mV/sec scan rate and 40 mV modulation amplitude after purging with nitrogen for 15 sec.

3. Once the voltammogram had been obtained, the electrode was rinsed with water and transferred to regeneration cell, containing 0.05 M hydrochloric acid , thus eliminating any lead(II) still remained on the electrode surface , which was then ready for next measuring cycle.

4. Similarly, other pH of acetate buffer solutions in measurement cell were measured under the same conditions. The pH values of acetate buffer solution tested were 4, 4.5, 5, 5.5, 6, 6.5, 7 respectively.

2.6.2 The study of preconcentration times

The effect of varying the preconcentration time for 0.05, 0.1 and 1 ppm Pb(II) at the treated-*Pennisetum* modified (15% w/w) carbon paste electrode was studied by the following procedure:

1. The treated-*Pennisetum* modified (15% w/w) carbon paste electrode was rinsed with water and placed in 1 ppm lead(II) solution contained in the accumulation cell for 1 min. The accumulation was carried out under constant stirring with an open circuit.

2. The modified electrode was then taken out of the accumulation solution, rinsed with water and transferred into the measurement cell containing 20 ml of acetate buffer pH 5.0 solution with an ionic strength of 0.6. Measurements were made by differential pulse voltammetry, by scanning between potential –0.700 and 0.350 V with 5 mV/sec scan rate and 40 mV modulation amplitude after purging with nitrogen for 15 sec.

3. Once the voltammogram had been obtained, the electrode was rinsed with water and transferred to regeneration cell, containing 0.05 M hydrochloric acid, which was then ready for next measuring cycle.

4. Similarly, other accumulation time in accumulation cell was measured under the same conditions. The accumulation times studied were 2, 3, 4, 5, 6, 8 and 10 min respectively.

5. The above procedure from steps 1-4 was repeated for other concentrations of lead(II) solutions in the accumulation cell under the same conditions. The concentrations of lead(II) solution tested were 0.1 and 0.05 ppm respectively.

2.6.3 Effect of ionic strength in electrolyte solution

The effect of various ionic strengths on peak current for the determination of 0.05 ppm Pb(II) at treated-*Pennisetum* modified (15% w/w) carbon paste electrode was studied by the following steps :

1. The treated-*Pennisetum* modified (15% w/w) carbon paste electrode was rinsed with water and placed in 0.05 ppm lead(II) solution contained in the accumulation cell for 10 min. The accumulation was carried out under constant stirring with an open circuit.

2. The modified electrode was then taken out of the accumulation solution, rinsed with water and transferred into the measurement cell containing 20 ml of acetate buffer pH 5.0 solution with an ionic strength of 0.6. The differential pulse voltammogram was scanned between potential –0.700 and 0.350 V with 5 mV/sec scan rate and 40 mV modulation amplitude after purging with nitrogen for 15 sec.

3. Once the voltammogram had been obtained, the electrode was rinsed with water and transferred to regeneration cell, containing 0.05 M hydrochloric acid, which was then ready for next measuring cycle.

4. Similarly, other ionic strengths of acetate buffer solutions in measurement cell were measured under the same conditions. The ionic strengths of acetate buffer solutions studied were 0.2, 0.4, 0.8 and 1.0 respectively.

2.6.4 The study of paste composition

The effect of various paste composition on the peak current for the determination of 0.05 ppm Pb(II) at treated-*Pennisetum* modified carbon paste electrode was studied by following steps :

1. The treated-*Pennisetum* modified (15% w/w) carbon paste electrode was rinsed with water and placed in 0.05 ppm lead(II) solution contained in the accumulation

cell for 10 min. The accumulation was carried out under constant stirring with an open circuit.

2. The modified electrode was then taken out of the accumulation solution, rinsed with water and transferred into the measurement cell containing 20 ml of acetate buffer pH 5.0 solution with an ionic strength of 0.6. The differential pulse voltammogram was scanned between potential –0.700 and 0.350 V with 5 mV/sec scan rate and 40 mV modulation amplitude after purging with nitrogen for 15 sec.

3. Once the voltammogram had been obtained, the electrode was rinsed with water and transferred to regeneration cell, containing 0.05 M hydrochloric acid, which was then ready for next measuring cycle.

4. Similarly, other compositions of paste in the treated-*Pennisetum* modified carbon paste electrode were measured under the same conditions. The treated-*Pennisetum* contents studied were 0, 5, 10 and 20 %(w/w) respectively.

2.6.5 The study of modulation amplitude

To obtain the best sensitivity of this method, various modulation amplitude on peak current for the determination of 0.05 ppm Pb(II) at treated-*Pennisetum*-modified (10% w/w) carbon paste electrode were studied according to the following steps :

1. The treated-*Pennisetum*-modified (10% w/w) carbon paste electrode was rinsed with water and placed in 0.05 ppm lead(II) solution contained in the accumulation cell for 10 min. The accumulation was carried out under constant stirring with an open circuit.

2. The modified electrode was then taken out of the accumulation solution, rinsed with water and transferred into the measurement cell containing 20 ml of acetate buffer pH 5.0 solution with an ionic strength of 0.6. The differential pulse voltammogram was scanned between potential –0.700 and 0.350 V with 5 mV/sec scan rate and 20 mV modulation amplitude after purging with nitrogen for 15 sec.

3. Once the voltammogram had been obtained, the electrode was rinsed with water and transferred to regeneration cell, containing 0.05 M hydrochloric acid, which was then ready for next measuring cycle.

4. Similarly, other modulation amplitudes were measured under the same conditions. The modulation amplitudes studied were 40, 60, 80 and 100 mV respectively.

2.6.6 The study of scan rate

The effect of varying scan rate on peak current for the determination of 0.05 ppm Pb(II) at treated-*Pennisetum* modified (10% w/w) carbon paste electrode was studied by following steps :

1. The treated-*Pennisetum* modified (10% w/w) carbon paste electrode was rinsed with water and placed in 0.05 ppm lead(II) solution contained in the accumulation cell for 10 min. The accumulation was carried out under constant stirring with an open circuit.

2. The modified electrode was then taken out of the accumulation solution, rinsed with water and transferred into the measurement cell containing 20 ml of acetate buffer pH 5.0 solution with an ionic strength of 0.6. Voltammograms were obtained by differential pulse voltammetry, by scanning between potential –0.700 and 0.350 V with 1 mV/sec scan rate and 80 mV modulation amplitude after purging with nitrogen for 15 sec.

3. Once the voltammogram had been obtained, the electrode was rinsed with water and transferred to regeneration cell, containing 0.05 M hydrochloric acid, which was then ready for next measuring cycle.

4. Similarly, other scan rates were measured under the same conditions. The scan rates studied were 5, 10, 15 and 20 mV/sec respectively.

2.7 Analytical characteristic of the method

The Analytical characteristics of the proposed method such as linear range, detection limit, reproducibility, interference and calibration curve were studied. Most experiments were performed using the preconcentration/medium exchange/voltammetry/regeneration scheme. For the preconcentration step, the modified electrode was immersed in the stirred sample solution for a given time (5 min); the accumulation proceeded with an open circuit. The electrode was then removed from the preconcentration cell. Washing with deionized water and placed in the electrochemical cell. The voltammogram was recorded. After scanning, the electrode was transferred to the cleaning cell for regenerating a lead-free surface, prior to the next cycle. The linear range of the proposed method was studied by measurement lead(II) standard solution in the concentration range of 0.02-0.14 ppm under the suitable conditions. The detection limit is defined as the lest concentration of analyte which gives the signal. The calibration curve of the proposed method was studied by measurement of various concentrations of lead(II) standard solutions (0.02-0.06 ppm) using treated-*Pennisetum* and untreated *Pennisetum* modified carbon paste electrode under the suitable conditions. The reproducibility of the system was determined by repeating measurement of 0.05 ppm lead(II) for 16 replicates. The effects of some possible interferences were studied by adding known amounts of each interference to 0.05 ppm lead(II) standard solution and measurements were made under optimum conditions.