

CHAPTER 2

Experimental

2.1 Chemicals, apparatus and instruments

2.1.1 Chemicals

All chemicals used are analytical reagent grade, and all standard and reagent solutions were prepared with ultrapure water (Milli Q water, Millipore, Sweden).

Chemicals used in this research are listed below:

1. Acetic acid 99.7% (w/v) : CH_3COOH (LabScan, Poland)
2. Ammonium molybdate : $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Carlo Erba, Italy)
3. Anion exchange resin AG 1-X8 Chloride form (BIO-RAD, USA)
4. Arsenic trioxide : As_2O_3 (Fluka, Switzerland)
5. Cupric chloride : $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (BDH, England)
6. Ethanol 99.5% (v/v) : $\text{C}_2\text{H}_5\text{OH}$ (Merck, Germany)
7. Hydrochloric acid 37% (w/v) : HCl (Merck, Germany)
8. Nitric acid 65% (w/v) : HNO_3 (Merck, Germany)
9. Potassium antimonyl tartrate : $\text{K}[\text{C}_4\text{H}_2\text{O}_6 \text{Sb}(\text{OH})] \cdot \frac{1}{2}\text{H}_2\text{O}$ (Merck, Germany)
10. Sodium acetate trihydrate : $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (Carlo Erba, Italy)
11. Sodium arsenate heptahydrate : $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Riedel–De Haen, USA)
12. Sodium diethyldithiocarbamate : $\text{NaS}_2\text{CN}(\text{C}_2\text{H}_5)_2 \cdot 3\text{H}_2\text{O}$ (BDH, England)
13. Sodium hydroxide : (NaOH) (Merck, Germany)
14. Sodium thiosulphate : $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (Fluka, Switzerland)
15. Sulfuric acid 98% (v/v) : H_2SO_4 (LabScan, Poland)

2.1.2 Software

1. Microsoft Excel 2007 (Microsoft, USA)
2. GPES software for control of the voltammograph (VA-757 computrace, Metrohm, Switzerland)

2.1.3 Material and instrument

1. Voltammetric analyzer (VA-757 computrace, Metrohm, Switzerland)
2. pH meter model 744 (Metrohm, Switzerland)
3. A glassy carbon electrode (3 mm diameter, Metrohm, Switzerland)
4. A platinum electrode (3 mm diameter, Metrohm, Switzerland)
5. Micropipette (Eppendorf, Germany)
6. Electrode polishing kit PK-4 MF-2060 (BASi, USA)

2.2 Preparation of solutions

2.2.1 Standard solutions

Stock standard solution of arsenite ($1000 \text{ mg L}^{-1} \text{ As}^{\text{III}}$) was prepared by dissolving 0.1320 g of arsenic trioxide with 1 mL of 25% w/v NaOH, then immediately acidified with 2 mL of conc. HCl and adjusted to the volume of 100 mL with water.

Stock standard solution of arsenate ($1000 \text{ mg L}^{-1} \text{ As}^{\text{V}}$) was prepared by dissolving 0.4249 g of sodium arsenate and adjusting the volume to 100 mL with water.

Stock standard solution of copper ($10000 \text{ mg L}^{-1} \text{ Cu}^{\text{II}}$) was prepared by dissolving 2.7101 g of cupric chloride dihydrate in 0.1 mol L^{-1} HCl 100 mL.

Stock standard solution of thiosulfate ($10000 \text{ mg L}^{-1} \text{ S}_2\text{O}_3^{2-}$) was prepared by dissolving 2.2130 g of sodium thiosulfate heptahydrate in boiling water and adjusting to 100 mL.

2.2.2 Working standard solution of As^{III} and As^{V}

The working standard solutions of As^{III} and As^{V} were daily prepared by diluting the stock standard solutions with water.

2.2.3 Sodium diethyldithiocarbamate solution (1000 mg L⁻¹ Na-DDTC)

A Na-DDTC solution was daily prepared by dissolving 0.1335 g of sodium diethyldithiocarbamate with 20 mL of ethanol and adjusted to the volume of 100 mL with water.

2.2.4 Ammonium molybdate solution (10% (w/v))

The solution was prepared by dissolving 2.50 g of ammonium molybdate and adjusting the volume to 25 mL with water.

2.2.5 Potassium antimonyl tartrate solution (1% (w/v))

The solution was prepared by dissolving 1.00 g of potassium antimonyl tartrate and adjusting the volume to 100 mL with water.

2.2.6 Hydrochloric acid solution (1 mol L⁻¹ HCl)

An aliquot of 21 mL of 37% (w/v) hydrochloric acid was added to water before adjusting the volume to 250 mL with water.

2.2.7 Sodium hydroxide solution (1 mol L⁻¹ NaOH)

The solution was prepared by dissolving 4.00 g of sodium hydroxide and adjusting the volume to 100 mL with water.

2.2.8 Acetate buffer solution

The solution was prepared by dissolving 2.41 g sodium acetate trihydrate with water. Acetic acid 2 mL was added into the sodium acetate solution. The pH of solution was measured, and adjusted to 4.5 by adding 1 mol L⁻¹ NaOH. Finally, the solution was made up to 500 mL with water to obtain acetate buffer 0.1 mol L⁻¹ and pH 4.5.

2.3 Preparation of electrode

2.3.1 Preparation of glassy carbon electrode (GCE)

The glassy carbon electrode was polished with water slurry of 1 μm alumina particles on a polishing pad for about 2 minutes to obtain a fresh surface. Then, the

electrode was rinsed well with water and sonicated to remove residual abrasive particles from its surface.

2.3.2 Preparation of platinum (Pt) electrode

The surface of platinum electrode was rinsed with water, followed by methanol and polished with water slurry of 1 μm diamond particles on the white nylon disk. After 2 minutes, rinsed away all remaining with methanol. Next, polished the electrode with water slurry of 1 μm alumina particles on a polishing pad for about 2 minutes. Then, it was rinsed well with water and sonicated to remove residual abrasive particles from its surface. Finally, rinse the electrode with methanol. The electrode is now ready to use.

2.4 Cathodic stripping voltammetry for inorganic arsenic determination

2.4.1 Square wave cathodic stripping voltammetric system for determination inorganic arsenic employing HMDE as working electrode in presence of Cu^{II} and Na-DDTC

Cathodic stripping voltammetry was performed on a Metrohm 757 VA computrace voltammograph. The instrument was controlled by a computer using VA Computrace software. A hanging mercury drop electrode (HMDE) working electrode, a Pt auxiliary electrode and a Ag/AgCl/3M KCl double junction reference electrode were used. The electrochemical cell was equipped with a nitrogen purge tube and a motor-driven PTFE stirrer. The system is shown in Figure 2.1.

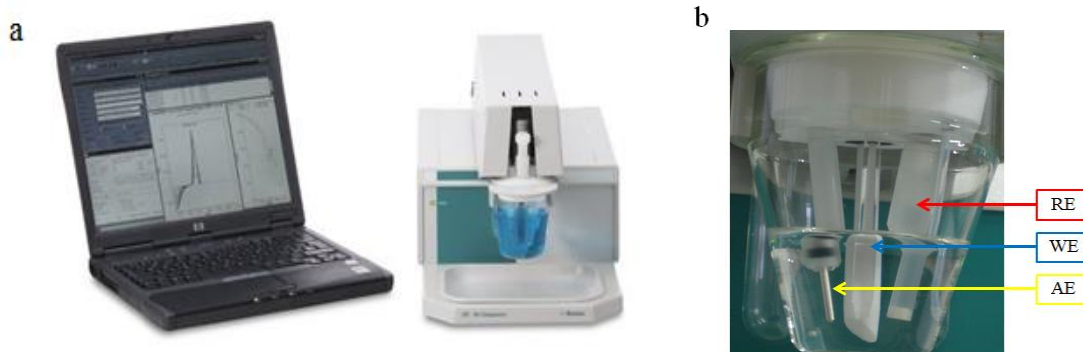


Figure 2.1 Cathodic stripping voltammetric system; (a) Metrohm 757 VA computrace voltammograph (b) HMDE: WE, Pt: AE, Ag/AgCl: RE

A milli-Q water (23 mL) was placed into a voltammetric cell and 2 mL of conc. HCl was added to obtain about 1 mol L⁻¹ HCl in a solution. Cu^{II} solution and Na-DDTC solution were added to obtain 30 mg L⁻¹ and 5 µg L⁻¹ of each, respectively. In case of As^V determination, thiosulfate solution was added into the vessel to get 10 mg L⁻¹ thiosulfate in the final solution. The same conditions of square wave CSV procedure was employed for both As^{III} and As^V determination by setting the operating parameters as follows: initial purging time: 300 s (sufficient period for complete reduction of As^V to As^{III} by thiosulfate), stirring rate: 2,000 rpm, deposition potential: -0.40 V, deposition time: 60 s, equilibration time: 10 s, end potential: -1.00 V, voltage step: 2 mV, amplitude: 20 mV, frequency: 140 Hz and sweep rate: 277.8 mV. After the potential scanning, a voltammogram was recorded and peak current (µA) at the peak potential of -0.82 V was measured.

2.4.2 Analytical characteristics of the system

Calibration curves and limit of detection

Under the optimum conditions of CSV system for determination of inorganic arsenic, from the voltammograms obtained, peak potentials and peak currents of As^{III} were determined. A linear calibration graph of As^{III} was constructed by plotting between concentration of As^{III} (µg L⁻¹) and peak current (µA).

LOD (limit of detection) is the concentration giving a signal three times the standard error plus the Y intercept divided by the slope of calibration curve.

Regression equation for peak currents of As^{III} with their concentrations is;

$$Y_i = mX + b \quad (2.1)$$

where; Y_i = peak currents

m = slope

b = Y intercept

Y value for calculation of standard error is $\hat{Y}_i = mX + b$ where X is the concentration of As^{III}.

Standard error is calculated based on following equation [58];

$$S_{Y/X} = \sqrt{\frac{\sum (Y_i - \hat{Y}_i)^2}{n-2}} \quad (2.2)$$

$$C_L = 3 \times \frac{S_{Y/X}}{m} \quad (2.3)$$

where; Y_i = response value from the instrument corresponding to the individual X- values

\hat{Y}_i = value of Y on the calculated regression line corresponding to the individual X - values

n = number of points on the calibration line

m = slope of the straight line

2.5 Cyclic voltammetry for arsenate determination

2.5.1 Cyclic voltammetric system for determination arsenate employing a GCE as a working electrode

The cyclic voltammetric system was carried out with Metrohm 757 VA computerized voltammograph, consisted of a glassy carbon electrode (GCE) as working electrode (3 mm diameter), a Pt auxiliary electrode and a Ag/AgCl/3M KCl double junction reference electrode.

A 10 mL milli-Q water was placed into a voltammetric cell and 200 μ L of conc. sulfuric acid was added to obtain 2.0% (v/v) H_2SO_4 in a solution. 10% (w/v) ammonium molybdate solution and potassium antimonyl tartrate solution were added to obtain 0.5% (w/v) ammonium molybdate and 0.0002% (w/v) potassium antimonyl tartrate, respectively. The operating parameters are as follows: scan potential between 0.10 to 0.55 V, stirring rate: 2,000 rpm, scan rate 100 mVs⁻¹. After the potential scanning, a voltammogram was recorded. Two peak potentials were observed at 0.34 and 0.39 V.

2.5.2 Analytical characteristics of the system

2.5.2.1 Calibration curves and limit of detection

Under the optimum conditions of CV system for determination of arsenate, from the voltammograms obtained, peak potentials and peak currents of As^V were determined. A linear calibration graph of As^V was constructed by plotting between concentration of As^V and peak current. LOD was calculated as the same as described above in section 2.4.2.

2.5.2.2 Precision

The precision of the system was examined by analysis of standard solution of As^V at $\mu\text{g L}^{-1}$ (ppb) and mg L^{-1} (ppm) levels for 11 replicates. The percentage of relative standard deviation (%RSD) values was used for evaluating the precision and can be calculated from the equation (2.4).

$$\%RSD = \frac{SD}{\bar{X}} \times 100 \quad (2.4)$$

where; %RSD = percentage relative standard

SD = standard deviation

\bar{X} = mean

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