CHAPTER 2
EXPERIMENTAL

2.1 Instrument and apparatus

1) Ion-meter model 5800-05 Solution Analyzer, Cole-Parmer Instrument Co.Ltd. , USA

2) Electrodes

- Working electrode :Iodide Coated Wire Ion selective electrode
- Reference electrode : saturated calomel electrode

3) Magnetic stirrer with magnetic bar

4) Thermostatic bath ; plastic box was covered by foam , size 22 x 32x 6 cm , which controls temperature of the analyte solution was simply made in the laboratory with thermometer[24].

5) Sieve 200 mesh, F. Kurt Retsch. GmbH & Co. KG. Germany

6) Orion Iodide Electrode, Orion Research Inc., USA

2.2 Chemical

1) Cu wire (∅ = 1.0 mm)

2) Epoxy adhesive, Selleys Chemical Company PTY. Limited, Australia

- 100% w/w liquid epoxy resin
- 92% w/w Polymercaptan, 8% w/w Polyamine

3) Silver nitrate, $AgNO_3$, A.R. , E Merck, Darmstadt, Germany

4) Potassium iodide , KI , A.R. , BDH Chemical Ltd., Poole, England

5) Sodium nitrate, $NaNO_3$, A.R. , BDH Chemical Ltd., Poole, England

6) Potassium dihydrogenphosphate, KH_2PO_4, A.R., Fluka AG., Busch, Switzerland

7) Disodium hydrogenphosphate, Na_2HPO_4, A.R., BDH Chemical Ltd., Poole, England

8) Poly(vinyl chloride), PVC , medium relative molecular weight, BDH Chemical Ltd., Poole, England

9) Cyclohexanone, $C_6H_{10}O$, E Merck, Darmstadt,Germany

10) Acetone, C_2H_6O, A.R., E Merck, Darmstadt,Germany

11) Sodium iodide, NaI, A.R., Fluka AG., Busch, Switzerland

12) Sodium sulfide, Na_2S, A.R., E Merck, Darmstadt, Germany
13) Sodium chloride, NaCl, A.R., E Merck, Darmstadt,Germany
14) Sodium fluoride, NaF, A.R., BDH Chemical Ltd., Poole, England
15) Sodium bromide, NaBr, A.R., Riedel de Haen, Germany
16) Dioctyl phthalate (DOP), BDH Chemical Ltd., Poole,England

2.3 Construction of the iodide coated wire ion selective electrode (CWISE)

2.3.1 Preparation of Silver iodide (AgI) [25]

1) 50.0 ml of 0.99 M KI was slowly dropped into 50.0 ml of 0.54 M $AgNO_3$ with vigorous stirring.

2) Yellow AgI precipitate was filtered by using sintered glass crucible.

3) AgI precipitate then was washed with distilled water for several times and was dried overnight in an oven, kept it in dry, clean amber bottle.

2.3.2 Preparation of Coating solution

2.3.2.1 Without solvent

About 0.10 g of polymer matrix and about 0.10 g of AgI were mixed together.

2.3.2.2 With solvent

About 0.10 g of polymer matrix and about 0.10 g of AgI were mixed together, and then added with acetone as solvent. If polymer matrix was PVC, solvent would be cyclohexanone. The mixture was then homogeneously stirred.

The polymer matrice used were;

1) Epoxy resin

2) Hardener of epoxy fixed; 92%w/w polymercaptan and 8%w/w polyamine

3) Epoxy resin mixed together with hardener

4) Poly(vinyl chloride)

The characteristics of coating solution were observed.

2.3.3 Preparation of electrodes

1) Cu wire was clean, about 6 inches long and 1.0 mm in diameter, with mechanical polishing and washed with distilled water and acetone, respectively.

2) The clean Cu wire was weighed, and about 5 pieces of wire was packed on plasticine as shown in figure 2.1, hence 5 electrodes could be prepared as the same time.

3) During the coating procedure, Cu wire must be in a vertical position so that a uniformed and symmetrical coat was obtained. This procedure was accomplished by clamping Cu wire as shown in figure 2.1.

4) The Cu wire set was quickly dipped about 1.0 cm of exposed Cu wire into coating solution several times and the solvent evaporated in air each time. A membrane was formed on the wire surface and the electrode allowed to set about one night.

5) Uncoated wire areas were then masked with parafilm [28] except the upper end of the wire about 3.0 cm. The finished electrode is shown in figure 2.2.

6) Finished electrode was conditioned by soaking in $1x10^{-5}$ M KI solution overnight. It may be stored dry after conditioning step, but should be preconditioned again before re-use.

7) Characteristics of electrodes were observed and results were shown on page .

2.4 A study of the effect of optimum ratio of silver iodide and epoxy resin

2.4.1 Preparation of stock solution of iodide; 1,000 ppm.

About 0.32 g of potassium iodide (M W 166.0) was weighed accurately, then dissolved with distilled water in 250 ml volumetric flask and diluted to volume with distilled water.

2.4.2 Preparation of Ionic strength adjustor (ISA) [24]

About 21.24 g of sodium nitrate (M W 84.99) was weighed accurately. It was dissolved with distilled water in 50 ml volumetric flask and diluted to volume with distilled water.

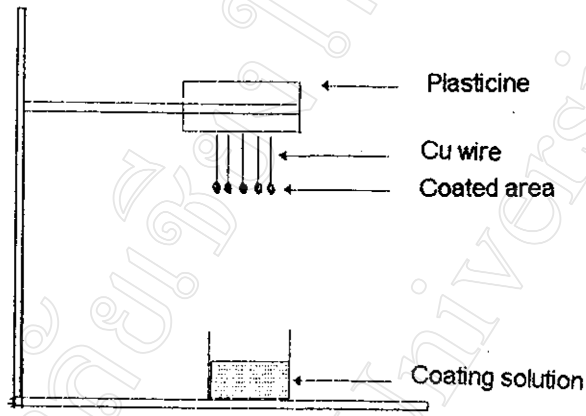

Figure 2.1 Cu wire set

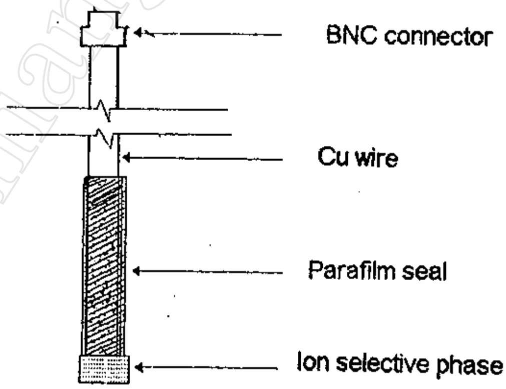

Figure 2.2 Finished coated wire ion selective electrode

2.4.3 Preparation of buffer solution pH 6.98 [27]

2.4.3.1 Solution A; 0.067 M Potassium dihydrogenphosphate, KH_2PO_4

About 2.26 g of potassium dihydrogenphosphate was weighed accurately. It was dissolved with distilled water in 250 ml volumetric flask and diluted to the volume with distilled water.

2.4.3.2 Solution B ; 0.053 M. Disodium hydrogenphosphate, Na_2HPO_4

About 2.33 g of disodium hydrogenphosphate was weighed accurately. It was dissolved with distilled water in 250 ml volumetric flask and diluted to the volume with distilled water.

Solution A and B were mixed together in the ratio 4:6 (solution A: solution B).

2.4.4 Preparation of electrodes

The iodide CWISE was prepared as in 2.3 with various ratios as in table 2.1.

Table 2.1 AgI and Epoxy resin in various ratios

Weight of AgI (g)	Weight of Epoxy resin (g)	AgI:Epoxy resin (w/w)
0.3542	0.1791	2:1
0.5457	0.1669	3:1
0.8087	0.1927	4:1
1.5010	0.2948	5:1
1.8300	0.3056	6:1

2.4.5 Measurement of electrode slope

1) The ion-meter was turned on and warmed about 1 hour.

2) The reference electrode and iodide-CWISE were connected to ion-meter.

3) 100.0 ml distilled water, 2.0 ml ISA, and 10.0 ml buffer solution of pH 6.98 were mixed together in 250 ml beaker.

4) The beaker containing the solution in (3) above was put down in the thermostatic bath which was simply made in laboratory. The temperature was controlled in the range of 25.0 ± 0.5 °C.

5) 1.00 ml of 1000 ppm iodide stock solution was pipetted into solution (3). The solution was stirred during the measurements. Potentials were recorded when steady readings were obtained.

6) 10.00 ml of 1000 ppm iodide stock solution was pipetted into solution (3). Potentials were recorded when stable readings were obtained.

7) All measurements were done while the solution was constantly stirred with a magnetic stirrer.

8) The electrode slope was obtained from different potentials of solutions (5) and (6).

2.5 Effect of the membrane thickness on electrode slope of iodide CWISE

Iodide CWISE was prepared as the procedure in 2.3 in the ratio of 3:1 (AgI:epoxy resin) w/w. The satisfying membrane thickness was observed and then was weighed accurately. The membrane thickness will be observed along with the weight of coating solution. The finished iodide CWISE was measured the electrode slope as the procedure in 2.4.5.

Table 2.2 Membrane thickness of iodide CWISE in the range of 0.0080-0.0100 g of weight of coating solution

Electrode number	Weight of Cu wire (g)	Weight of Cu wire and coating solution (g)	Weight of coating solution only (g)
E51	2.6422	2.6510	0.0088
E52	2.6244	2.6332	0.0088
E53	2.1586	2.1685	0.0099
E54	2.1086	2.1185	0.0099
E55	2.0401	2.0483	0.0082

Table 2.3 Membrane thickness of iodide CWISE in the range of 0.0150-0.0250 g of weight of coating solution

Electrode number	Weight of Cu wire (g)	Weight of Cu wire and coating solution (g)	Weight of coating solution only (g)
E56	2.1701	2.1901	0.0200
E57	1.8904	1.9099	0.0195
E58	2.2050	2.2250	0.0200
E59	2.0862	2.1097	0.0235
E60	2.2627	2.2781	0.0154

Table 2.4 Membrane thickness of iodide CWISE in the range of 0.0200-0.0270 g of weight of coating solution

Electrode number	Weight of Cu wire (g)	Weight of Cu wire and coating solution (g)	Weight of coating solution only (g)
E61	2.4196	2.4425	0.0229
E62	2.6507	2.6754	0.0247
E63	2.0494	2.0755	0.0261
E64	1.9674	1.9316	0.0242
E65	1.9230	1.9439	0.0209

The measurement of the electrode slope of these electrodes was carried out as in 2.4.5.

2.6 Effect of particle sizes of silver iodide precipitate on electrode slope

1) Silver iodide precipitate was prepared as in 2.3.1

2) Silver iodide precipitate was separated into two portions. One of AgI was ground and sieved through 200 mesh screen. The other was not.

3) Silver iodide precipitate was used to prepare iodide CWISE in the ratio of 3:1 (AgI:Epoxy resin) w/w.

4) The slope of electrode was determined as in 2.4.5.

2.7 Comparison of response time of conditioned and un-conditioned iodide CWISE

1) The ion-meter was turned on and warmed about 1 hour.

2) The reference electrode and un-conditioned iodide CWISE in the ratio of 3:1 (AgI:Epoxy resin) by weight were connected to ion-meter.

3) 100 ml distilled water, 2.0 ml ISA, and 10.0 ml buffer solution of pH 6.98 were mixed together in 250 ml beaker.

4) The solution (3) was put in the thermostatic bath and 10.0 ml of 1,000 ppm stock solution of iodide was pipetted into solution (3).

5) Potentials were recorded every 30 seconds.

6) Response time was determined from a graph between time and potential.

7) The same procedure was repeated again except the electrode used was conditioned by steeping in 10^{-5} M potassium iodide overnight before use.

2.8 The effect of concentration on response time of iodide CWISE

Iodide CWISE used was in the ratio of 3:1 (AgI:epoxy resin) by weight . The response time of iodide CWISE was measured semilarly to the procedure in 2.7. They were measured in 10^{-3}, 10^{-4}, and 10^{-5} M concentration of iodide.

2.9 Characteristics of iodide CWISE

2.9.1 Response time

The response time of the iodide CWISE and commercial electrode;Orion iodide electrode were measured similarly to the procedure in 2.7

2.9.2 Detection limit

1) To prepare 1 M stock solution of iodide, 16.6 g of potassium iodide were weighed accurately and then dissolved with distilled water in 100 ml volumetric flask. 1 M iodide stock solution was used to prepare 10^{-1} to 10^{-10} M of iodide by ten-fold dilution.

2) The ion-meter was turned on and warmed about 1 hour.

3) The reference electrode and iodide CWISE in the ratio of 3:1 (AgI:Epoxy resin) w/w were connected to ion-meter.

4) 100 ml. of 10^{-9} M iodide, 2.0 ml ISA, and 10.0 ml buffer solution of pH 6.98 were mixed together in 250 ml beaker.

5) The solution 4 was put in the thermostatic bath. Potentials were recorded when stable reading were obtained.

6) Repeated steps 4 and 5 with 10^{-9} to 1 M. iodide concentration.

7) Detection limit was determined from a graph between concentration and potential.

8) The same procedure was repeated again with commercial electrode; Orion Iodide Electrode.

2.9.3 Sensitivity of electrodes

The sensitivity of electrode was considered as electrode slope. The electrode used was iodide CWISE in ratio of 3:1 (AgI:Epoxy resin) w/w.The electrode slope was determined from different potentials of 1 decade concentration difference. The measurement of electrode slope was carried out similarly to the procedure in 2.4.5.

2.9.4 Calibration curve of iodide CWISE

The electrode used was in the ratio 3:1 (AgI:Epoxy resin) w/w.

1) 2.0 ml of 5 M $NaNO_3$ as ionic strength adjustor and 10.0 ml of KH_2PO_4/Na_2HPO_4 buffer solution of pH 6.98 were added into 100.0 ml of distilled water. Then this solution was put into waterbath which the temperature was controlled at 25.0±0.5°C

2) After immersion of the Iodide CWISE and the saturated calomel reference electrodes, solution was stirred at the constant rate, then known amounts of 1000 ppm Iodide standard solution were added.

3) The potential measurements were taken when steady reading were obtained after each addition.

4) The additions of iodide solution were made, so that the iodide concentration should cover a range of concentrations from 2.10×10^{-5} M to 3.72×10^{-3} M.

5) The calibration curve was constructed by plotting the potentials against $-\log C_{I^-}$ (C_{I^-} = iodide concentration).

6) The final iodide concentration in the solution after each addition can be calculated by the equation below ;

$$C_{I^-} = \frac{7.88\times10^{-3}\,(M)\times V_T\,(ml)}{112.0\,ml + V_T\,(ml)}$$

where

C_{I^-} = iodide concentration

V_T = total volume of 1000 ppm iodide solution added.

7) The same procedure was carried out again with commercial electrode; Orion Iodide Electrode.

2.9.5 Selectivity coefficient of iodide CWISE

1) Preparation of iodode solution

One molar concentration of iodide was made by dissolving 14.99 g of NaI with deionized water in 100.0 ml volumetric flask. Then 10^{-2} M of iodide was made by diluted 10.0 ml of 1 M iodide solution with deionized water in 1000.0 ml volumetric flask.

2) Preparation of chloride solution

One molar concentration of chloride was made by dissolving 5.84 g of NaCl with deionized water in 100.0 ml volumetric flask. Then 10^{-2} M of chloride was made by diluted 10.0 ml of 1 M chloride solution with deionized water in 1000.0 ml volumetric flask.

3) Preparation of bromide solution

One molar concentration of bromide was made by dissolving 10.25 g of NaBr with deionized water in 100.0 ml volumetric flask. Then 10^{-2} M of bromide was made by diluted 10.0 ml of 1 M bromide solution with deionized water in 1000.0 ml volumetric flask.

4) Preparation of fluoride solution

One molar concentration of fluoride was made by dissolving 5.84 g of NaF with deionized water in 100.0 ml volumetric flask. Then 10^{-2} M of fluoride was made by diluted 10.0 ml of 1 M fluoride solution with deionized water in 1000.0 ml volumetric flask.

5) Iodide CWISE use was in the ratio 3:1 (AgI:Epoxy resin) w/w.

6) 100.0 ml of 10^{-2} M NaBr, 2.0 ml of 5 M $NaNO_3$ as ionic strength adjustor and 10.0 ml of KH_2PO_4/Na_2HPO_4 buffer solution of pH 6.98 were mixed together in 250 ml beaker , then this solution was put in the thermostatic bath which the temperature was controlled at 25.0±0.5°C.

7) After immersion of the Iodide CWISE and the saturated calomel reference electrodes, solution was stirred at the constant rate, then known amounts of 10^{-2} M NaI standard solution were added.

8) The potential measurements were taken when steady reading were obtained after each addition.

9) The final iodide concentration in the solution after each addition can be calculated by the equation ;

$$C_{I^-} = \frac{1\times 10^{-2}\,(M)\times V_T\,(ml)}{112.0\,ml + V_T\,(ml)}$$

where

C_{I^-} = iodide concentration

V_T = total volume of 10^{-2} M iodide solution added.

10). The measured potential values were plotted against the $-\log C_{I^-}$ on a graph paper. And then the calculation of potentiometric selectivity coefficient $K^{pot}_{I,Br}$ was made.

11) For the estimation of $K^{pot}_{I,Cl}$ and $K^{pot}_{I,F}$, the process was repeated again except that the solution (6) in 250 ml beaker was 10^{-2}M of NaCl for $K^{pot}_{I,Cl}$ and 10^{-2} M of NaF for $K^{pot}_{I,F}$.

12) The $K^{pot}_{I,Br}$, $K^{pot}_{I,Cl}$ and $K^{pot}_{I,F}$ were estimated again by Orion iodide electrode as that same process.

Calculation [28,29,30]

According to the Nernst equation :

$$E = \text{constant} \pm \frac{2.303RT}{Z_A F} \log a_A \qquad (1)$$

The electrode selectivity to other ions is also studied and the potentiometric selectivity coefficient $K_{A,B}$ as defined by the modified Nernst equation [28]:

$$E = \text{constant} \pm \frac{2.303RT}{Z_A F} \log \left[a_A + K_{A,B}\,(a_B)^{z_A/z_B} \right] \qquad (2)$$

is determined. Because of its accuracy, a fixed interference method (mixed solution method) is utilized for the estimation of $K_{A,B}$ based on e.m.f. measurements in a solution of constant level of interfering ion, by a series of additions of knownamounts of the primary ion. The plot of the measured potential values versus $-\log C_A$, allows the calculation of the $K_{A,B}$, using the equation ;

$$K_{A,B} = \frac{a_A}{(a_B)^{Z_A/Z_B}} \qquad (3)$$

where a_B is the constant background activity of the interfering ion B and a_A is the primary ion activity, which corresponds to the point where the difference in potential between curve and extrapolation of the Nernstian response lines is $18/Z_A$ mV at 25°C.

In this experiment, the activities in the equation (3) can be replaced by the concentrations without significant error. This is true because,for the applied experiment conditions, all measurements were made under a constant background of ionic strength.(see appendix I)

2.10 Comparison of characteristics of electrode sets

1) Three electrode sets* were prepared as the same procedure in 2.3.in the ratio of 3:1(AgI:epoxy resin) by weight.

2) Response time, electrode slope, detection limit, and calibration curve of electrode were determined as in 2.9.

* = each set has 5 electrode samples which was prepared as the same time

2.11 Lifetime of iodide CWISE

Iodide CWISE used was in the ratio of 3:1 (AgI:Epoxy resin) w/w. Electrode slope of Iodide CWISE was measured to indicate lifetime of electrode. It was measured as the same procedure in 2.4.5 every week.

2.12 Percent yield of iodide CWISE preparation

1) The electrodes were constructed as the same procedure in 2.3 in the ratio of 3:1 (AgI:Epoxy resin) w/w.

2) The measurement of electrode slope was carried out as similarly to the procedure in 2.4.5.

3) Percent yield of iodide CWISE was obtained by equation below;

$$\%\,\text{yield} = \frac{\text{Nernstian} - \text{slope electrode}}{\text{Total electrode}} \times 100$$

2.13 Preparation of iodide CWISE with silver iodide in poly(vinyl chloride)

2.13.1. Preparation of electrodes

The preparation of coating solution was similarly to procedure in 2.3.2 and the electrode process was carried out as in 2.3, except conditioning step, with various ratio of AgI:epoxy resin as in the table 2.5. The conditioning step of iodide CWISE which was prepared with AgI in PVC may be more than one night

Table 2.5 The composition of coating solution in the various ratios of AgI:epoxy resin

Weight of AgI (g)	Weight of PVC (g)	Volume of cyclohexanone (ml)	%w/v of AgI in PVC solution [1]
0.15	0.25	5.0	3.0
0.25	0.25	5.0	5.0
0.35	0.25	5.0	7.0
0.50	0.25	5.0	10.0
0.75	0.25	5.0	15.0

1 : 5 % (w/v) PVC in cyclohexanone [26]
5.0 ml of this PVC solution were used in this experiment

2.13.2. Electrode potential measurement

1) The ion-meter was turned on and let warm up for 1 hour.

2) The reference electrode and Iodide CWISE were connected to the ion-meter.

3) 100.0 ml distilled water, 2.00 ml ISA and 10.00 ml buffer solution of pH 6.98 were mixed together in 250 ml beaker.

4) The solution in 3 was put in home made thermostatic bath. The temperature was controlled in the range of 25.0±0.5 °C.

5) 10.00 ml of 1000 ppm stock solution of iodide was pipetted onto solution (3). The solution was stirred during measurement. Potential were recorded when stable reading were obtained.

2.14 Preparation of iodide CWISE with AgI/Ag_2S in PVC

2.14.1 Preparation of AgI/Ag_2S

1) 1.00 M Na_2S was prepared by dissolving 7.800 g Na_2S in 100.0 ml distilled water. Then $1x10^{-3}$ M Na_2S was prepared from stock solution 1.00 M Na_2S.

2) 1.4990 g NaI was dissolved in 10.0 ml of solution of $1x10^{-3}$ M Na_2S and then 10.0 ml of 1.50 M $AgNO_3$, which was prepared by dissolving 2.5485 g $AgNO_3$ in 10.0 ml distilled water, was added slowly under vigorous stirring into the Na_2S.NaI mixture.

3) Coprecipitation AgI/Ag_2S was washed with hot water 5-6 times, then coprecipitation was filtrated and washed twice with acetone and dried over night at 105.5 °C. The dried AgI/Ag_2S precipitate was pulverized in a motar and kept in dried, cleaned bottle.

2.14.2 Preparation of electrode

The preparation of coating solution was carried out as in 2.3.2 and the electrode process was produced as in 2.3, except conditioning step, with various ratio of AgI/Ag_2S:PVC as in table 2.6. The conditioning step of iodide CWISE which was prepared with AgI/Ag_2S in PVC solution might be more than one night

Table 2.6 The composition of coating solution in various ratios of AgI/Ag_2S:PVC

Weight of AgI/Ag_2S (g)	Weight of PVC (g)	Volume of cyclohexanone (ml)	%w/v of AgI/Ag_2S in PVC solution [1]
0.15	0.25	5.0	3.0
0.25	0.25	5.0	5.0
0.35	0.25	5.0	7.0
0.50	0.25	5.0	10.0
0.75	0.25	5.0	15.0
1.00	0.25	5.0	20.0

1 : 5 % (w/v) PVC in cyclohexanone [26]
5.0 ml of this PVC solution were used in this experiment

2.14.3 Electrode potential measurement in various length of conditioned methods

After soaking the electrode in 10^{-5} M KI at least one night, the electrode potential was measured, as previous the procedure in 2.13.2, everyday about 10 days.

2.14.4 Response time

The response time of iodide CWISE in various ratios of AgI/Ag_2S in 5% w/v PVC in cyclohexanone was determined as previous the procedure in 2.9.1.

2.14.5 Study of the effect of optimum ratio of AgI/Ag_2S and PVC solution

The iodide CWISE in the ratio of 3, 5, 7, 10, 15, and 20 % w/v AgI/Ag_2S in 5 % w/v PVC in cyclohexanone were prepared and then the electrode slopes were established as similarly to procedure in 2.4.5.

2.15 Preparation of iodide CWISE with AgI/Ag_2S in plasticized PVC

1) The plasticized PVC solution was prepared by dissolving PVC with cyclohexanone in the ratio of 5% w/v. Then plasticizer (dioctyl phthalate;DOP) was added in the ratio of 7, 25, 50, 90% w/v DOP in PVC.

2) The plasticized PVC solution was used to prepared iodide CWISE in the ratio of 10% w/v AgI/Ag_2S in plasticized PVC solution.

3) The response time and the electrode slope were determined as in 2.9.1 and 2.4.5, respectively.