

CHAPTER 2

EXPERIMENTALS

2.1 Chemicals

The chemicals for the experiments were the high purity commercially available and were used without further purification. They are all shown in Table 2.

Table 2 Sources of chemicals.

Entry	Chemicals	Source	Grade	Remarks
1	Anthraquinone	BDH	Laboratory	England
2	1, 2-Dihydroxyanthraquinone	Aldrich	Laboratory	Purris ~97% (USA)
3	1, 4-Dihydroxyanthraquinone	Aldrich	Laboratory	Purris 96% (USA)
4	1, 5-Dihydroxyanthraquinone	Fluka	HPLC	Assay ~90 % Switzerland
5	1, 8-Dihydroxyanthraquinone	Aldrich	Laboratory	Puriss 97 % (USA)
6	Acetonitrile	LAB-SCAN	Analytical Reagent	Ireland
7	Ammonium chloride	UNIVAR	Analytical Reagent	Assay 99.5 %
8	Silver nitrate	MERCK	Pro analysi	Switzerland
9	Silicone oil	APS	Laboratory	Australia
10	Nitric acid	J.T. Baker	ACS	Assay 69-70% (USA)

Table 2 (Continued)

Entry	Chemicals	Source	Grade	Remark
11	Sodium nitrate	BDH	Laboratory	Assay 96% England
12	Sodium acetate	Carlo ERBA	ACS	Assay 99.5%
13	Sodium hydroxide	L A B - SCAN	Analytical Reagent	Ireland
14	Potassium dihydrogen phosphate	Fluka	Analytical Reagent	Puriss >99.5% Switzerland
15	Di-sodium hydrogen orthophosphate	APS	Analytical Reagent	Assay 99-102% Australia
16	4, 5-Dihydroxyanthraquinone-2- carboxylic acid	Fluka	Laboratory	Assay 90% Switzerland
17	4-Dodecylbenzenesulfonic acid	Fluka	Chemika	Assay 90% Switzerland
18	Calcium nitrate	Fluka	Chemika	Assay 99.5% Switzerland
19	1, 4-Benzoquinone	Fluka	HPLC	Assay \geq 99.5% Switzerland
20	Ammonium acetate	APS	Analytical Reagent	Assay 97% Australia
21	Sodium perchlorate monohydrate	Fluka	Chemika	Puriss 98 % Switzerland
22	Sodium carbonate	APS	Analytical Reagent	Puriss \geq 99.5% Australia
23	Boric acid	Merck	ACS	Germany
24	Potassium nitrate	APS	Analytical Reagent	Assay 99.5% Australia

Table 2 (Continued)

Entry	Chemicals	Source	Grade	Remark
25	Nickel nitrate	C a r l o ERBA	Laboratory	Assay 99% England
26	Bismuth nitrate pentahydrate	Fluka	Chemika	Assay \geq 98.0% Switzerland
27	Cobalt nitrate hexahydrate	Fluka	Chemika	Assay \geq 98.0% Switzerland
28	Lithium nitrate	Fluka	Biochemika	Assay \geq 99.0% Switzerland
29	Cesium nitrate	Fluka	Chemika	Assay \geq 99.0% Switzerland
30	Copper nitrate trihydrate	Fluka	Chemika	Assay 98-103% Switzerland
31	Lead nitrate	MERCK	Pro analysi	Assay 99.5% Germany
32	Cadmium nitrate-4- hydrate	MERCK	Pro analysi	Assay 99.5% Germany
33	Mercury nitrate	MERCK	Pro analysi	Germany
34	Potassium chloride	BDH	Laboratory	England
35	Potassium iodide	JT Baker	A C S Reagent	Assay 99.5% USA
36	Arsenic nitrate	Fluka	Biochemika	Assay \geq 99.0% Switzerland
37	Manganese nitrate	Aldrich	Laboratory	Puriss 99.99% USA
38	Sodium nitrite	Fluka	Chemika	Assay $>$ 98% Switzerland

Table 2 (Continued)

Entry	Chemicals	Source	Grade	Remark
39	Perchloric acid	MERCK	Pro analysi	Assay 70.0% Germany
40	Phosphoric acid	C a r l o ERBA	ACS	Assay 85%
41	Acetic acid	L A B - SCAN	Analytical Reagent	Assay 99.8% Ireland
42	Silver atomic spectroscopy standard solution	Fluka	S t a n d a r d solution	1000 ppm Switzerland
43	Sodium hydrogen carbonate	MERCK	AR Grade	Germany
44	Hydrochloric acid	BDH	AR Grade	England
45	Potassium hydroxide	BDH	AR Grade	England
46	Buffer solution pH 4	JT Baker	AR Grade	USA
47	Buffer solution pH 7	JT Baker	AR Grade	USA
48	Mineral oil	Fluka	AR Grade	Switzerland
49	Liquid paraffin	BDH	AR Grade	England
50	Alumina powder	Buehler	0.05 micron diameter	USA
51	Sodium tetraborate	MERCK	AR Grade	Germany
52	T e t r a b u t y l a m m o n i u m hexafluorophosphate (C ₁₆ H ₃₆ F ₈ NP)	Fluka	Electroche- mical Grade	Switzerland
53	Ferric nitrate	MERCK	Pro analysi	Germany
54	Magnesium nitrate	MERCK	Pro analysi	Germany

2.2 Instruments and apparatus

2.2.1 AUTOLAB PGSTAT 100 (Metrohm, Switzerland)

AUTOLAB PGSTAT 100 combined with the GPES software is a computer controlled electrochemical measurement system. It consists of a data acquisition system and a potentiostat/galvanostat shown in Figure 2.

2.2.2 Electrochemical cell and electrodes

- Glassy carbon electrode (2 millimeter diameter) served as the working electrode (Metrohm, Switzerland)
- Platinum wire served as the auxiliary electrode (Metrohm, Switzerland)
- Ag/AgCl (3 M KCl) served as the reference electrode (Metrohm, Switzerland)
- Ag/AgCl double junction (inner solution, 3 M KCl; outer solution, 3 M NaNO₃) served as reference electrode (Metrohm, Switzerland)
- Stirrer (number 6.1204.080, Metrohm, Switzerland)
- 15 mL of electrochemical cell (Metrohm, Switzerland)
- 50 mL of electrochemical cell (Metrohm, Switzerland)

2.2.3 Apparatus

- Teflon rod (0.8 and 2 centimeter of diameter) from Thai Saeng Trading, Hatyai, Songkhla, Thailand.
- Copper wire (2 millimeter of diameter) from Department of Physics, Faculty of Science, Prince of Songkla University.
- pH meter (Denver Instrument, Model 225, USA)
- Microlitre pipet 1, 000 µl (Gilson , France)
- Transparent paper
- Filter paper (Whatman, No. 42)
- Tissue paper (Kimberly Clark, 280-ply White Wipers)

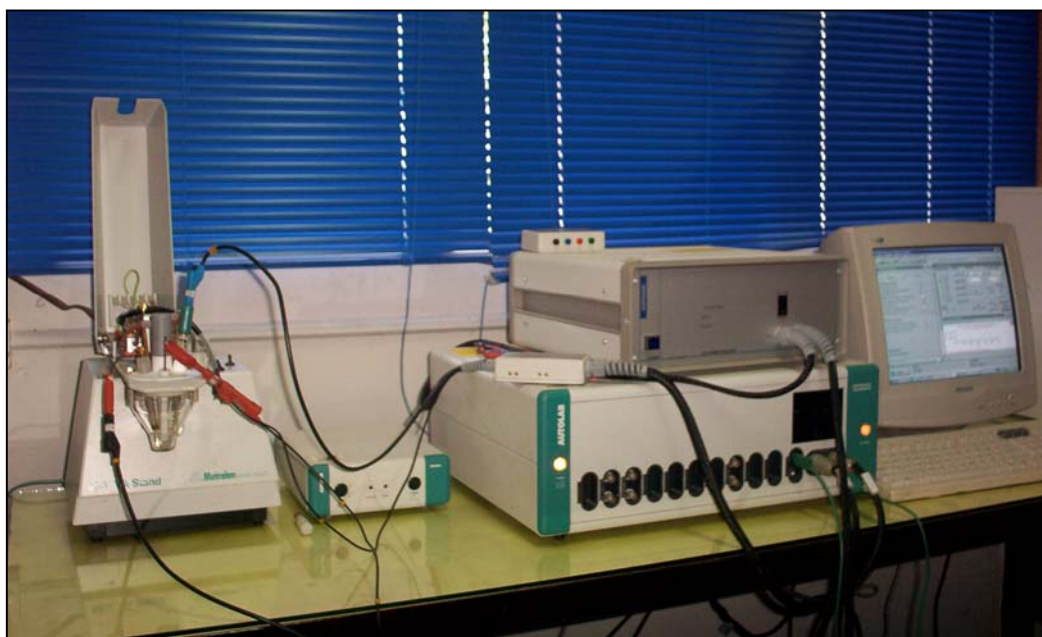


Figure 2 AUTOLAB PGSTAT 100 (Metrohm, Switzerland)



Figure 3 The cell with three electrode system

2.3 Procedure

2.3.1 Working electrode preparation

The configuration of the carbon paste electrode was a Teflon rod. The electrode body consists of two parts due to the fact that it can be compatible with the Metrohm system. The first part, the Teflon was cut to obtain a 5 centimetre piece and drilled to have the inside diameter 2 millimetre and drilled again at one end to expand the inside diameter to 6 millimetre (Motta and Guadalupe, 1994) with the depth of 5 millimetre. The copper with the diameter of 2 millimetre and 13 centimeter length was inserted into the other end through the centre of the rod to obtain a body of working electrode. The second part, the Teflon holder of working electrode was prepared as follows. Teflon rod with diameter 2 centimetre was cut to obtained a 3 centimetre piece as Teflon holder and then drilled to have the inside diameter 2 millimetre and making its has shape trapeze cylindrical, one end has the outside diameter 1.5 centimetre and the other end has the outside diameter 0.8 millimetre. After that the second part was inserted in the first part to obtain the main probe.

The chemically modified carbon paste electrode was prepared from three component: graphite powder, modifier and binder. From previous work (Hunag *et al.*, 1994), the sensitive of modified carbon paste electrode has been found to consist of 0.55 g graphite powder and 0.35 g modifier. The first carbon paste was prepared by adding a 0.55 g quantity of graphite powder in a mortar and grind with the pestle, then adding quinone compounds; after additional grinding of the mixture, a 0.15 mL of liquid paraffin (measured by glass dropper drops) was added to the carbon paste mixture and thoroughly mixed until obtaining a homogeneous paste. The paste was then packed at the end of the electrode framework with a spatula. The surface of carbon paste electrode was smoothed with filter paper (Labar and Lamberts, 1997) followed transparent paper (Hu *et al.*, 2003) until shiny. The blank carbon paste was prepared in the same way without adding quinone compounds. Figure 4 shows the complete chemically modified carbon paste electrode. A fresh carbon paste electrode was activated (Kalcher *et al.*, 1995) before using for preconcentration/stripping/regeneration cycle by dipping in 0.01 M HClO₄ for 30 min followed by dipping in 0.1 M HClO₄ for 2 min and rinsed with ultrapure water.



Figure 4 The complete chemically modified carbon paste electrode

2.3.2 General procedure

All electrochemical measurements were performed with a conventional three electrode cells as in Figure 3 and carried out with a AUTOLAB PGSTAT 100 controlled by commercial software package of GPES for Windows. Before voltammetric measurement the solution was purged with oxygen free nitrogen gas (99.99%) and during the measurement nitrogen gas was passed over the solution to prevent interference from oxygen. Glassy carbon electrode was polished by alumina powder on a wet pad (by dissolving in distill water) before any experiments.

For the cyclic voltammetry technique, The important parameter in cyclic voltammogram are the cathodic peak potential E_{pc} , the anodic peak potential E_{pa} , the cathodic peak current I_{pc} , and the anodic peak current I_{pa} . The following parameters are used to characterize the cyclic voltammogram of a reversible process (Wang, 2000):

1. *Reversible system*, The peak current for a reversible couple is given by the Randle Sevcik equation (Wang, 2000):

$$I_p = 2.69 \times 10^5 n^{3/2} ACD^{1/2} \nu^{1/2}$$

When n = number of electrons transferred/molecule

U = square root of scan rate ($V s^{-1}$)

A = electrode surface area (cm^2)

C = concentration ($mol cm^{-3}$)

D = diffusion coefficient ($cm^2 s^{-1}$)

Accordingly, the current is directly proportional to concentration and increases with the square root of the scan rate. The ratio of the reverse-to-forward peak currents is unity for a simple reversible couple.

2. The position of the peak on the potential axis is related to the formal potential of the redox process. The formal potential for a reversible couple is centered between E_{pa} and E_{pc} which $E^{\circ'} = (E_{pa} + E_{pc})/2$. The separation between the peak potentials (for a reversible couple) is given by $\Delta E_p = (E_{pc} - E_{pa}) = 59/n$ mV. Therefore, the peak separation can be used to determine the number of electron transferred and as a criterion of a Nernstian behavior. Accordingly, a fast one electron process exhibits a ΔE_p of about 59 mV. Both the cathodic and anodic peak potential are independent of the scan rate (Wang, 2000).

2.3.3 Blank cyclic voltammetry experiment

All blank cyclic voltammetry experiments were carried out with deoxygenated solution in 0.1 M TBAP (Zon *et al.*, 2003) and 50 mL CH_3CN solution at room temperature in a three electrode measuring cell. Before recording individual current-potential (i - E curve), the working electrode as glassy carbon electrode was polished by alumina powder followed by cleaning with tissue paper (Kimberly Clark). A platinum wire was used as a counter electrode and an $Ag/AgCl$ 3 M KCl was used as a reference electrode. All potentials given in the present work refer to this reference electrode.

2.3.4 Cyclic voltammetry of quinone compounds

After the blank cyclic voltammogram (50 mL of CH_3CN containing 0.1 M TBAP) were recorded, quinone compounds (0.001 M) was added. The cyclic voltammogram were then run after purging the solution for 3 min with nitrogen gas to eliminate interfering oxygen. Then cyclic voltammograms of the each quinone compounds solution were carried out at 120 $mV s^{-1}$

scan rate. The potential was recorded by scanning from positive potential to negative potential between 0.000 and -2.000 V vs Ag/AgCl reference electrode using 3 potential cycles.

2.3.5 Cyclic voltammetry of silver ions in acetonitrile

Silver(I) 0.001 M in 50 mL CH₃CN containing 0.1 M TBAP as electrolyte was added in electrochemical cell. The cyclic voltammogram was then run after purging the solution for 3 min with nitrogen gas to eliminate interfering oxygen. The potential was recorded by scanning from positive potential to negative potential with 120 mV s⁻¹ scan rate between 1.000 and -1.000 V vs Ag/AgCl using 2 potential cycles. Cyclic voltammogram was run compared with the blank solution.

2.3.6 Cyclic voltammetry of mercury ions in acetonitrile

Mercury(II) 0.001 M in 50 mL CH₃CN containing 0.1 M TBAP as electrolyte was added in electrochemical cell. The cyclic voltammogram was then run after purging the solution for 3 min with nitrogen gas to eliminate interfering oxygen. The cyclic voltammogram were run starting from -1.500 to 2.000 V and back with 120 mV s⁻¹ scan rate. Cyclic voltammogram was run compared with the blank solution.

2.3.7 Cyclic voltammetry of copper ions in acetonitrile

Copper(II) 0.001 M in 50 mL CH₃CN containing 0.1 M TBAP as electrolyte was added in electrochemical cell. The cyclic voltammogram was then run after purging the solution for 3 min with nitrogen gas to eliminate interfering oxygen. The potential was recorded by scanning from positive potential to negative potential between -1.750 and 2.000 V vs Ag/AgCl using 2 potential cycles. Cyclic voltammogram was run compared with the blank solution.

2.3.8 Cyclic voltammetry of silver(I), mercury(II), and copper(II) by carbon paste electrode modified with quinone compounds

The modified carbon paste electrode (graphite powder: quinone compounds; 0.55:0.35 g and 0.30 mL liquid paraffin) was immersed in 15 mL solution of 1.0×10^{-4} M Ag(I) containing 0.2 M HNO₃. The solution was stirred for 5 min after purging the solution for 3 min

with nitrogen gas, during which it was held at -0.200 V vs Ag/AgCl. After the preconcentration step, the stirring was stopped, this require 5 s equilibrate time for stable current to achieved before the scan and the accumulated ion measured by cycling the potential between 0.000 and 0.600 V with 80 mV s^{-1} . During all the measurements nitrogen gas was passed over the solution. After each electrochemical measurement, the regeneration step is necessary. The electrode was dipped in 0.2 M HNO_3 (Hunage *et al.*, 1994) and electrolyses with stirring at a potential of +0.500 V (vs Ag/AgCl) for 2 min, then rinsed with 0.2 M HNO_3 and ultrapure water. These should be no wave in the potential scan range. The optimum renewal of the working electrode will be study in the topic of optimum condition for analysis. Cyclic voltammograms of silver(I) for each quinone compounds modified electrode was run compared with the blank carbon paste electrode.

Cyclic voltammogram of Hg(II) 0.001 M was run compared with the blank carbon paste electrode. Hg(II) 0.001 M was prepared in 0.001 M HNO_3 (Tonle *et al.*, 2005). All conditions for cyclic voltammogram was set as in condition of Ag(I) but the potential scan was set between -0.200 to 0.800 V vs Ag/AgCl.

In the case of Cu(II), cyclic voltammogram of Cu(II) 0.100 M in 0.1 M HNO_3 (Etienne *et al.*, 2001) was performed and comparison the peak current with the blank carbon paste electrode. All conditions for cyclic voltammogram was set as in condition of Ag(I) but the potential scan was set between -0.200 to 0.600 V vs Ag/AgCl.

2.3.9 Comparison stripping voltammogram of silver(I) in differential pulse and square wave mode

For differential pulse anodic stripping voltammetric measurement, the carbon paste electrode modified with 1,8-dihydroxyanthraquinone was immersed in 15 mL solution of 0.2 M HNO_3 containing 1.0×10^{-4} M of Ag(I) and the solution was stirred (3000 rpm) for 5 min after purging the solution for 3 min with nitrogen gas (99.99%), during which it was held at -0.200 V vs Ag/AgCl. After the accumulation step, the stirring was stop, then required 5 s for equilibrate time. Following the differential pulse anodic stripping voltammogram was recorded by applying a positive going potential scan from 0.000 to 0.600 V at step potential 5 mV with modulation amplitude of 25 mV and modulation time of 0.01 s.

For square wave anodic stripping voltammetric measurements, stripping voltammogram of silver(I) 1.0×10^{-4} M was obtained with the same condition in differential pulse mode. The parameter of square wave mode was set at step potential 5 mV, the frequency 100 Hz, and pulse amplitude 50 mV (Etienne *et al.*, 2001). The regeneration of electrode after each electrochemical measurement was performed with the same way in 2.3.8.

2.3.10 Simultaneous voltammogram of Cu(II) and Ag(I) on carbon paste electrode modified with 1,8-dihydroxyanthraquinone

A mixture solution of 0.001 M of Cu(II) and Ag(I) were prepared by dissolving 0.085 g of silver nitrate [AgNO₃] and 0.121 g of copper nitrate [Cu(NO₃)₂·2H₂O] in 500 mL of 0.2 M HNO₃. The mixture solution 15 mL was transferred to the electrochemical cell. In accumulation step, the mixture solution was stirred for 5 min at the potential of -0.200 V vs Ag/AgCl and kept quiet for 5 s. the stripping voltammogram in the range of -0.200 to 0.600 V were recorded in the square wave mode (Etienne *et al.*, 2001) for which the step potential 5 mV, the pulse amplitude is 50 mV, and the frequency is 100 Hz. The stripping voltammogram of the mixture metal ions was compared between blank carbon paste electrode and carbon paste electrode modified with 1,8-dihydroxyanthraquinone. The regeneration of working electrode after each electrochemical measurement was performed with the same procedure in 2.3.8.

2.3.11 Comparison SWASV of Ag(I) between Ag/AgCl and Ag/AgCl double junction

The solution of silver(I) 0.50×10^{-4} M in 0.2 M HNO₃ was transferred 15 mL to electrochemical cell. CPE modified with 1,8-DHAQ (graphite:1,8-DHAQ, 0.55:0.35, 0.30 mL liquid paraffin) was used as working electrode and platinum wire as auxiliary electrode. The solution was stirred for 5 min at the potential of -0.200 V (vs Ag/AgCl 3 M KCl) and then kept quiet for 5 s. Following the record of stripping voltammogram in the range of 0.000 to 0.600 V in square wave mode with the pulse amplitude is 50 mV, the frequency is 100 Hz and the step potential 5 mV. The same conditions and parameter was applied to record stripping voltammogram of Ag(I) which used Ag/AgCl double junction (inner 3 M KCl, outer 3 M NaNO₃) reference electrode. The regeneration of working electrode after each electrochemical measurement was performed with the same procedure in 2.3.8.

2.3.12 Cyclic voltammetry of Ag(I) at various scan rates

Carbon paste electrode modified with 1,8-DHAQ (graphite 0.55 g, 1,8-DHAQ 0.35 g and 0.30 mL liquid paraffin) was used as working electrode, platinum wire as auxiliary electrode and Ag/AgCl double junction as reference electrode. The solution of silver(I) 1.0×10^{-3} M in 0.2 M HNO_3 was transferred 15 mL to electrochemical cell and purging to solution for 3 min with nitrogen gas (99.99%) to eliminated interfering oxygen. The cyclic voltammogram of Ag(I) were carried out at various scan rate as 25, 50, 100, 200, 400, 600, 800 mV s^{-1} respectively. The potential was recorded by scanning between 0.000 V and 0.600 V. Furthermore, the stripping voltammogram of Ag(I) 0.5×10^{-3} M was performed in the same procedure. The regeneration of working electrode after each electrochemical measurement was performed with the same procedure in 2.3.8.

2.4 Optimization condition for analysis

Initially the condition were tested using the chemically modified carbon paste electrode with 1,8-DHAQ by square wave anodic stripping voltammetry. All conditions and parameters for voltammetric analysis and electrode systems were optimized to obtain a maximum signal. To optimize the conditions which may effect the result, uniparameter variation was used. This was done by changing a single variable while the others are kept constant. While obtained the optimum of first condition, the optimization of next conditions is using all optimum condition which was studied before.

The optimized variables of voltammetric system include the paste composition, electrolyte solutions, pH, activated procedure of carbon paste electrode, preconcentration time, instrumental parameters, convection rate, equilibrate time, renewal of the working electrode, reproducibility, linear range, calibration graph, detection limit, interferences.

All the electrochemical cell contains a CPE modified with 1,8-DHAQ, a platinum wire as auxiliary electrode and a Ag/AgCl double junction as reference electrode (inner: 3 M KCl, outer: 3 M NaNO_3). Silver(I) solution was prepared daily by diluting atomic absorption standard solution from Fluka ($1,000 \text{ mg L}^{-1}$). The general procedure involved three steps. Firstly, the working electrode was immersed into a cell, which was filled with 15 mL of

Ag(I) solution and purging the solution for 1 min with nitrogen gas (99.99%) to eliminate interfering oxygen. Following the stirring solution for 5 min at the potential of -0.200 V of accumulation step. Secondly, the stripping voltammogram was recorded in square wave mode with 50 mV pulse amplitude, 5 mV step potential and 100 Hz frequency (Etienne *et al.*, 2001). During the voltammetric measurement, the flow of gas was passed over solution. After silver ion peak were detected, a regeneration of the working electrode was performed by applied a positive potential as 0.600 V to the electrode for 2 min while it was immersed in 0.2 M HNO₃ under stirred conditions.

2.4.1 The paste composition

The composition of carbon paste electrode modified with 1,8-DHAQ was studied with 1.0×10^{-4} and 0.5×10^{-4} of silver(I) in 0.2 M HNO₃. Firstly, graphite powder and liquid paraffin were used constantly at 0.275 g and 0.15 mL respectively. The amount of 1,8-DHAQ were 0.025, 0.050, 0.075, 0.100, 0.125, 0.150 and 0.175 g. The silver solution was stirred for 5 min at the potential of -0.200 V and then kept quiet for 5 s. Following the stripping voltammograms in the range of 0.000 to 0.600 V were recorded in the square wave mode with the step potential is 5 mV, pulse amplitude is 50 mV, and frequency is 100 Hz. The stripping voltammogram of Ag(I) were run three time of each case. The regeneration of working electrode after each electrochemical measurement was set as in 2.4. Secondly, the varies of pasting medium, graphite powder and 1,8-DHAQ were used constantly at 0.275 and 0.050 g (*vide infra*) respectively. The amount of liquid pasting were liquid paraffin, mineral oil and silicone oil as 0.15, 0.20, 0.25, and 0.30 mL. The sample for condition was measured three times with the same procedure above.

2.4.2 Electrolyte solution

Different electrolysis and stripping electrolytes were investigated with an electrode composed of 0.275 g graphite powder, 0.050 g 1,8-DHAQ, and 0.15 mL of liquid paraffin. Various electrolytes and concentrations, including KH₂PO₄, Na₂HPO₄, HNO₃, NH₄C₂H₃O₂, CH₃COONa, NaNO₃, NaClO₄, H₃PO₄, Na₂B₄O₇, HClO₄, and NH₄C₂H₃O₂ + NaClO₄ were evaluated fore their suitability in accumulating and stripping Ag(I) at modified electrode.

The experiments were performed at conditions as follows: 1.0×10^{-4} M Ag(I), 5 min preconcentration time, -0.200 V accumulation potential, 5 s equilibrate time, 5 mV step potential, 50 mV pulse amplitude and 100 Hz frequency. The stripping voltammogram was recorded in the range of 0.00 to 0.60 V. The concentration of electrolytes was investigated in the range of 0.3 to 1.2 M for NaNO₃, 0.05 to 0.3 M for HNO₃ and 0.0001 to 0.1 M for HClO₄ with the same procedure and parameter above. Each concentration of electrolyte was run three times.

2.4.3 Effect of pH

Throughout the process of accumulation, the pH of the solution plays crucial role because of its direct effect on modifier-silver interaction. This important variable was studied for 0.8 M NaNO₃ (optimum electrolyte) solution in the pH range 1.00-9.00 with the concentration of silver(I) as 0.5×10^{-4} M, and 1.0×10^{-4} M M in 0.8 M NaNO₃. pH was adjusted with 0.5 and 1.0 M HNO₃ and 0.1 M KOH. Carbon paste electrode composed of 0.275 g graphite powder, 0.050 g 1,8-DHAQ and 0.15 mL of liquid paraffin (optimum paste). Stripping voltammogram was run in square wave mode with the same conditions and parameters in 2.4.2.

2.4.4 Activation of carbon paste electrode

To obtain a maximum analytical signal, at first, the working electrode was activated before voltammetric detection. The carbon paste electrode composed of 0.275 g graphite powder, 0.050 g 1,8-DHAQ, and 0.15 mL of liquid paraffin (optimum paste). The activation of carbon paste was performed with the different methods:

- Preanodization in electrolyte (0.8 M NaNO₃) at 0.600 V for 5 min followed by cathodization for 10 s at -0.200 V (Ravichandran and Baldwin, 1984).
- Carbon paste electrode was dipped in 0.01 M HClO₄ for 30 min followed by dipping in 0.1 M HClO₄ for 2 min (Kalcher *et al.*, 1995).
- Carbon paste electrode was dipped in 0.001 M Ag(I) for 3 min followed by washed with ultrapure water. Repeat three times. (Won *et al.*, 2003).
- Carbon paste electrode was activated by applying cyclic voltammetry varying potential between 0.6 and 2.0 V at 5 V s^{-1} for 10 min for unstirred solution of 0.5 M NaHCO₃ (Motta and Guadalupe, 1994).

- The electrode was oxidized at 1.0 V for 3 min in 0.8 M NaNO₃ solution, then scanned to -0.2 V at 20 mV s⁻¹ and reduced at this potential for 3 min. repeat three times (Zhang *et al.*, 2001.)

After the activation of carbon paste electrode finished, the stripping voltammogram of Ag(I) 1.0 x 10⁻⁴ M in 0.8 M NaNO₃ (pH 2.00) as electrolyte was recorded in square wave mode with the same conditions and parameter in 2.4.2.

2.4.5 Preconcentration time

The preconcentration time was studied for three difference concentration of silver(I) under carefully controlled condition with optimization before. The carbon paste electrode was prepared with the optimum ratio as in 2.4.2. The activation was followed by applying cyclic voltammetry with varying potentials between 0.2 and 0.6 V at 5 V s⁻¹ for 10 min in stirred solution of 0.5 M NaHCO₃ (Motta and Guadalupe, 1994). The concentration of Ag(I) was used as 0.5 x 10⁻⁴, 1.0 x 10⁻⁴ and 1.5 x 10⁻⁴ M in 0.8 M NaNO₃, pH 2.00. The concentration time was studied from 2 to 12 min with accumulation potential of -0.200 V. The stripping voltammogram of silver(I) was recorded in the square wave mode with the same condition and parameter in 2.4.2. and repeat three time. The regeneration of working electrode was set as in 2.4.

2.4.6 Instrumental parameters

a) Accumulation potential

The accumulation potential on the on the current was investigated in the range of -0.300 to 0.100 V. the concentration of Ag(I) was used as 0.5 x 10⁻⁴, and 1.0 x 10⁻⁴ M in 0.8 NaNO₃ (pH 2.00). The optimum of preconcentration time was 8 min (2.4.5). The others conditions and parameter of square wave mode set as in 2.4.2. The stripping voltammogram of Ag(I) was recorded repeat three times of each potential. The regeneration of working electrode was set as in 2.4.

b) Equilibrating time

The equilibrating time was tested in the range of 5 to 30 s. The stripping voltammogram of 1.0 x 10⁻⁴ M Ag(I) was run with the optimum condition as described in previous section. The convection rate was set at 3000 rpm. The parameter of square wave mode

was used as in 2.4.2. The electrode was activation/preconcentration/stripping/regeneration for three times of each equilibrating time.

c) Convection rate

The optimum convection rate was tested with 1.0×10^{-4} M of Ag(I) in 0.8 NaNO₃. The convection rate was set as 1000, 1500, 2000, 2500 and 3000 rpm. Each convection rate was run three times with the optimum condition and the parameter of square wave mode is performed with a pulse amplitude 50 mV, step potential 5 mV and frequency 100 Hz.

d) Step potential and pulse amplitude

The step potential is related with the scan rate of square wave mode. The effect of step potential and pulse amplitude on peak current were studied by varying them in the following range: 0.150-0.900 mV and 25-200 mV respectively. The concentration of Ag(I) was used as 1.0×10^{-4} M in 0.8 NaNO₃ (pH 2.00). A similar pattern of the peak current was observed upon increasing the individual parameter, step potential keeping any two of the three parameters constant (100 Hz frequency). The stripping peak of Ag(I) was performed with the optimum condition and the accumulation time was set as -0.25 V. The regeneration of the working electrode was set as in 2.4.

2.4.7 Regeneration of the working electrode

Different chemical and electrode cleaning techniques were tested to restore the electrode surface to its pre-accumulation state after each voltammetric determination. The solution of Ag(I) was used for regeneration of the electrode as 1.0×10^{-4} M in 0.8 M NaNO₃ (pH 2.00). The parameters of square wave mode was set at deposition potential -0.250 V for 8 min, pulse amplitude 75 mV, step potential 0.3 mV, and frequency 100 Hz. After activation of carbon paste electrode with optimum procedure (Motta and Guadalupe, 1994), the preconcentration, stripping, and regeneration was performed. The chemical solution was used for the regeneration of electrode as NaNO₃ (0.1 M), HNO₃ (0.2 M), HCl (0.1 M), NaAc (0.2 M) and H₂O (ultrapure). After recording stripping voltammogram, the regeneration of electrode was performed in square wave mode with the potential applying at +0.600 V (2 min under stirring). The peak current before regeneration and the residual current after regeneration were then compared.

2.5 Reproducibility

The carbon paste electrode was prepared with optimum ratio (0.550 g graphite powder, 0.100 g 1,8-DHAQ, and 0.30 mL of liquid paraffin). The concentration of Ag(I) was used as 0.5×10^{-4} M and 1.0×10^{-4} M in 0.8 M NaNO₃ (pH 2.00). Other optimum conditions and parameters were used for studying the reproducibility. For a single electrode surface after preconcentration/stripping/regeneration for 8 times of 0.5×10^{-4} M of Ag(I), the %R.S.D. was calculated. For five new electrode surface after surface activation/preconcentration/stripping/regeneration, the %R.S.D. of the current responses for 0.5×10^{-4} M Ag(I) was calculated after 8 min preconcentration. Furthermore, the stripping peak of Ag(I) 0.5×10^{-4} M was performed in the same way. The precision was expressed as relative standard deviation.

2.6 Calibration graph and linear range

The Ag(I) standard working solution was prepared at concentration in the range of 8.0×10^{-7} – 9.0×10^{-4} M. 15 mL aliquot of each concentration was transferred into voltammetric cell equipped with a three electrode system which performed at optimum condition and parameters obtained from previous sections. Linearity of Ag(I) analysis was determined from the calibration curve by plotting the peak heights versus concentrations. The linearity was reflected using the linear regression. The preconcentration/stripping/ regeneration was performed after activated the new electrode surface. Sensitivity is defined as the slop of calibration graph, provided the plot is linear (Miller and Miller, 1993).

2.7 Limit of detection

The blank solution containing in 0.8 NaNO₃ (pH 2.00) was prepared. 15 mL aliquot of solution was transferred to voltammetric cell system which performed at optimum condition and parameters obtained from previous sections. Limit of detection was considered as the concentration that the CPE modified with 1,8-DHAQ could provide the signal on the

voltammogram. The detection limit was calculated as based on the signal corresponding to three times the noise of the response current (Wang and Bonakdar, 1988).

2.8 Effects of interferences

The effect of various common ions was evaluated with respect to their interference in the stripping peak of Ag(I) by adding appropriate amounts of foreign ions to 15 mL of solution containing 3.0×10^{-5} M of Ag(I) solution during preconcentration. The interfering ion was added with 3.0×10^{-3} M in silver solution. The chemicals were used as interfering ions such as $\text{As}(\text{NO}_3)_3$, KNO_3 , NaClO_4 , $\text{Zn}(\text{NO}_3)_2$, $\text{Hg}(\text{NO}_3)_2$, $\text{Cd}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, CH_3COONa , Na_2HPO_4 , $\text{Na}_2\text{B}_4\text{O}_7$, $\text{NH}_4\text{C}_3\text{H}_3\text{O}_2$, KH_2PO_4 , LiNO_3 , Na_2CO_3 , $\text{Ni}(\text{NO}_3)_2$, $\text{Bi}(\text{NO}_3)_3$, $\text{Pb}(\text{NO}_3)_2$, NaNO_2 , $\text{Co}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Fe}(\text{NO}_3)_3$, $\text{Mg}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2$. The preconcentration/stripping/regeneration were performed after activated the new electrode surface.

2.9 Determination of silver in photographic developer

The analytical procedure evaluated previous sections was applied for the determination of silver(I) in photographic developer water samples from Nakhon-Sinl Digital Lab:sample A (Hatyai, Songkha, Thailand), 07 Digital Services Ltd.:sample B (Hatyai, Songkha, Thailand), and Yindee-Silp:sample C (Hatyai, Songkha, Thailand). To certify the reliability of the analytical method, the photographic developer water samples were also analyzed by ICP-AES (see APPENDIX A). The results obtained with the stripping voltammetric method by CPE modified with 1,8-DHAQ and ICP-AES are evaluated and compared. The photographic developer solution sample were collected in polytetrafluoroethylene bottle. The studies showed (Sukawara *et al.*, 1998) that the concentration of silver(I) in photographic developer was at high level. Therefore, the sample solution was diluted 10 fold before voltammetric measurement. The measurement were carried out by the standard addition method. Each standard solution of Ag(I) was added into 1.5 mL of sample solution and volume adjusted to 15 mL with 0.8 M NaNO_3 (pH 2.00). Four concentrations of silver were added to sample solution as show in Table 3.

The stripping voltammogram was performed at optimum conditions and parameters. The results were plotted between current (i) and concentration. The concentration of silver(I) in the original samples can then be determined.

Table 3 The concentrations of silver(I) for standard addition method

Sample	Silver added (M)	Concentration of each stand solution (M)			
		1 st	2 nd	3 rd	4 th
A	0	3.0×10^{-5}	5.0×10^{-5}	7.0×10^{-5}	9.0×10^{-5}
B	0	1.0×10^{-5}	3.0×10^{-5}	5.0×10^{-5}	7.0×10^{-5}
C	0	3.0×10^{-6}	5.0×10^{-5}	7.0×10^{-5}	9.0×10^{-5}
A	1.0×10^{-5}	2.0×10^{-5}	4.0×10^{-5}	6.0×10^{-5}	8.0×10^{-5}
C	2.0×10^{-5}	3.0×10^{-5}	5.0×10^{-5}	7.0×10^{-5}	9.0×10^{-5}

The CPE-1,8-DHAQ for Ag(I) analysis was validated by comparing the results to those from the ICP-AES method. Two methods for determining Ag(I) in photographic developer waste water were applied to the same samples, focusing on the differences evaluated by the *t* test. The *t* test (Skoog *et al.*, 2004) statistic value is

$$t = \frac{\bar{d} \times \sqrt{N}}{s_d}$$

$$s_d = \sqrt{\frac{\sum (d_i - \bar{d})^2}{N-1}}$$

Where \bar{d} is the average difference equal to $\sum d_i / N$

d_i is the value of data

N is the number of data

s_d is the standard deviation of the mean difference

$N - 1$ is the number of degrees of freedom

The value of *t* test is calculated at 95% confidence level with the degrees of freedom of 2. If *t* calculated is less than *t* critical value, there is no significant difference.