CHAPTER 2

EXPERIMENTS

2.1 Chemicals and reagents

The chemicals was used without any purification or pretreament unless specified otherwise. The sources are shown in Table 1.

Table 1 Sources of chemicals

Number	Chemicals	Sources	Grade	Remarks
1	Cyclohexanone	Fluka	Chemika	Puriss ≥ 97%
2	*p*-Benzoquinone	Fluka	Chemika	Puriss ≥ 99.5% (Switzerland)
3	Tetrahydroxybenzoquinone	Fluka	Chemika	Switzerland
4	Benzophenone	Aldrich	Laboratory	Puriss 96% (USA)
5	α-Tetralone	Fluka	Chemika	Puriss 97%
6	1,4-Naphthoquinone	Fluka	Chemika	Puriss ≥ 99.5%
7	Anthrone	Aldrich	Laboratory	Puriss 97% (USA).
8	9-Xanthone	Fluka	Chemika	Puriss ≥ 97% (Switzerland)
9	Anthraquinone	BDH	Laboratory	England

Table 1 Sources of chemicals (Continued)

Number	Chemicals	Sources	Grade	Remarks
10	1,2-DHAQ	Aldrich	Laboratory	Puriss 97% (USA)
11	1,4-DHAQ	Aldrich	Laboratory	Puriss 96% (USA)
12	1,8-DHAQ	Aldrich	Laboratory	Puriss 97% (USA)
13	Dammacanthal	Dr.wilawan's research group which extracted from air-dried stems of *Morinda elliptica Ridl*	-	Prince of Songkla University, Thailand
14	Tetrabutylammo-niumhexafluoro phosphate	Fluka	Electrochemical grade	Switzerland
15	Tetraethylammo-nium perchlorate	GFS Chemicals LAB-SCAN Asia Co	Reagent grade	Ireland
16	Acetonitrile	LAB-SCAN Asia Co	Analytical Reagent	Ireland
17	Silver nitrate	MERCK	Pro analysi	Switzerland

Table 1 Sources of chemicals (Continued)

Number	Chemicals	Sources	Grade	Remark
18	Graphite powder	Central scientific supply	Laboratory chemical	Thailand
19	Liquid paraffin oil	BDH	Laboratory chemical	England
20	Nitric acid	MERCK	Pro analysi	Germany
21	Dimethylsulphoxide	LAB-SCAN	Analytical Reagent	Ireland
22	Alumina powder	Buehler	0.05 micron diameter	USA

The reagents were prepared according to the method and calculations specified in details in the appendix.

2.2 Instruments

2.2.1 Electrochemical apparatus and electrodes

All the measurements were performed with a conventional three-electrode configuration. Glassy carbon electrode (1 mm diameter) were used as the working electrode and a platinum wire served as the auxiliary electrode for cyclic voltammetry. A $Ag/AgCl/KCl_{sat}$ electrode was used as the reference electrode. Cyclic voltammetric data were recorded using a computer-controlled potentiostat/galvanostat (AUTOLAB PGSTAT 100, Metrohm). All electrodes are from Metrohm (Figure 10).

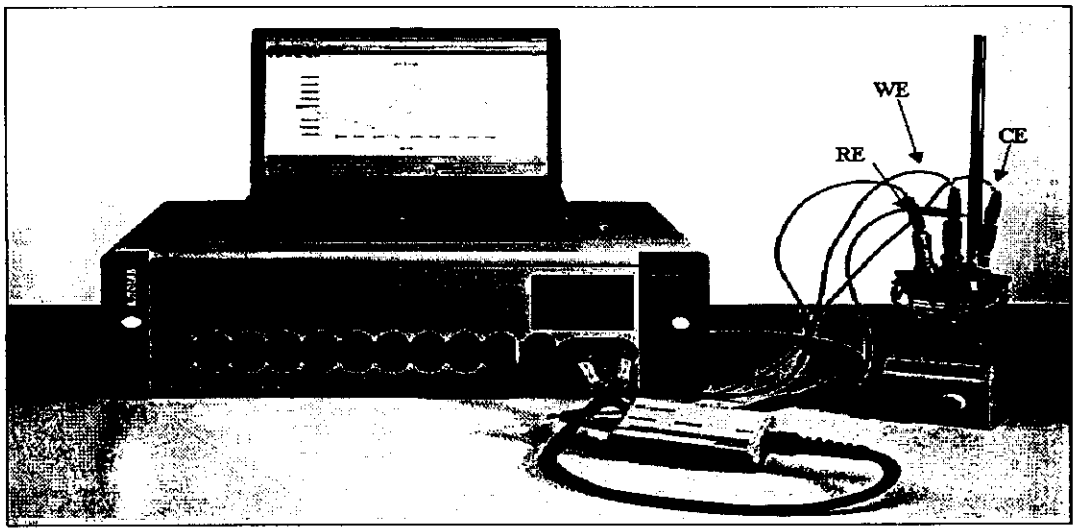

Figure 10 AUTOLAB PGSTAT 100 instrument (Metrohm)

2.2.2 UV-Visible apparatus

UV-Visible absorption measurement were carried out with a double beam spectrophotometer (Varian Cary 50, USM) and UV-Visible spectrometer of Perkin Elmer (PSU) in the wavelength range of 190-700 nm. A quartz cuvette (path length of 1 cm) which and micropipette was used in the work.

2.3 Procedure

2.3.1 Blank cyclic voltammetry experiments

All blank CV experiments were carried out under nitrogen gas for 3 min in 0.1 M of TBAP or TEAP (Appendix 1) in 50 ml CH_3CN solution at 25°C in a three-electrode measuring all. Glassy carbon electrode with 0.78 mm diameter was used as a working electrode and a platinum wire was used as a counter electrode. The electrode was polished by using Al_2O_3 powder (0.05 micron diameter) before recording individual current-potential (i-E) curves.

2.3.2 Cyclic voltammetry of ketones and quinones

After blank cyclic voltammograms were recorded, ketones and quinones (1 x 10^{-3} M in 50 ml of CH_3CN, Appendix 2.1 to 2.13) was added. The cyclic voltammogram was then run after purging the solution for at least 3 min with nitrogen gas (99.99%) eliminate interfering oxygen. Then the cyclic voltammograms of the test solution were carried out at various of scan rates i.e. 100 mV/s, 200 mV/s, 300 mV/s, 400 mV/s, 500 mV/s and 600 mV/s respectively. The potential was recorded by scanning from positive potential to negative potential between 0.500 and -3.000 V vs Ag/AgCl electrode using 2 potential cyclies.

2.3.3 CV of silver in CH_3CN

$AgNO_3$ 0.8494 g (0.1 M, Appendix 3) was put in the solution of 0.1 M TEAP in 50 ml CH_3CN. The cyclic voltammogram was then run after purging the solution for at least 3 min with nitrogen gas (99.99%) to eliminate interfering oxygen. The potential was recorded by scanning from positive potential to negative potential between 1.000 and -1.500 V vs Ag/AgCl using 2 potential cycles. CV was run compared with the blank solution.

2.3.4 The mole ratio method of ketone and quinone compounds with silver ion

2.3.4.1 UV-visible of Cyclohexanone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. In this work, the acetonitrile solution was used as blank solution. The concentration of 1 x 10^{-2} M Cyclohexanone was prepared by adding 103.64 µl of Cyclohexanone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN as a 1 x 10^{-2} M of Cyclohexanone (Appendix 4.1.1). Silver solution (0.1 M) was prepared by weighing 0.894 g of $AgNO_3$ and dissolved in 50 ml CH_3CN as a 0.1 M (Appendix 3.2). After

that the blank solution was run first to confirm clear background. The mole ratio method was then performed and the results are shown in Table 2.

Table 2 The mole ratio method for Cyclohexanone with silver solution

Mole ratio of Cyclohexanone and silver ion	Volume of silver (I) ion 0.1 M (μl)	Volume of Cyclohexanone 1.0×10^{-2} M (ml)
0.6 : 1.0	500.00	3.00
0.8 : 1.0	375.00	3.00
1.0 : 1.0	300.00	3.00
1.5 : 1.0	200.00	3.00
2.0 : 1.0	150.00	3.00
3.0 : 1.0	100.00	3.00
4.0 : 1.0	75.00	3.00
5.0 : 1.0	60.00	3.00
6.0 : 1.0	50.00	3.00

2.3.4.2 UV-visible of *p*-Benzoquinone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. *p*-Benzoquinone (1.0×10^{-2} M) was prepared by weighing 0.1081 g of *p*-Benzoquinone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN as a 1.0×10^{-2} M of *p*-Benzoquinone (Appendix 4.1.2). Silver solution (0.1 M) was prepared by weighing 0.8494 g of $AgNO_3$ and dissolved in 50 ml CH_3CN as a 0.1 M (Appendix 3.2). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 3.

Table 3 The mole ratio method for *p*-Benzoquinone with silver solution

Mole ratio of *p*-Benzoquinone and silver ion	Volume of silver (I) ion 0.1 M (µl)	Volume of *p*-Benzoquinone 1.0×10^{-2} M (ml)
0.25 : 1.0	1,200.00	3.00
0.50 : 1.0	600.00	3.00
0.90 : 1.0	333.33	3.00
1.30 : 1.0	230.70	3.00
2.00 : 1.0	150.00	3.00
2.50 : 1.0	120.00	3.00
3.00 : 1.0	100.00	3.00
4.00 : 1.0	75.00	3.00
5.00 : 1.0	60.00	3.00

2.3.4.3 UV-visible of Tetrahydroxybenzoquinone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. Tetrahydroxybenzoquinone solution (7.0×10^{-5} M) was prepared by weighing 1.456 mg of Tetrahydroxybenzoquinone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.3). Silver solution (1.0×10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in CH_3CN 50 ml (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 4.

Table 4 The mole ratio method for Tetrahydroxybenzoquinone with silver solution

Mole ratio of Tetrahydroxy-benzoquinone and silver ion	Volume of silver (I) ion 1.0 x 10^{-4} M (µl)	Volume of Tetrahydroxyben-zoquinone 7.0 x 10^{-5} M (ml)
1.2 : 1.0	1,750.00	3.00
1.4 : 1.0	1,500.00	3.00
1.7 : 1.0	1,235.30	3.00
2.0 : 1.0	1050.00	3.00
2.5 : 1.0	840.00	3.00
3.0 : 1.0	700.00	3.00
4.0 : 1.0	525.00	3.00
5.0 : 1.0	420.00	3.00

2.3.4.3 UV-visible of Benzophenone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. Benzophenone solution (2.0 x 10^{-5} M) was prepared by weighing 0.3644 mg of Benzophenone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.4). Silver solution (1.0 x 10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in CH_3CN 50 ml (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 5.

Table 5 The mole ratio method for Benzophenone with silver solution

Mole ratio of Benzophenone and silver ion	Volume of silver (I) ion 1.0×10^{-4} M (µl)	Volume of Benzophenone 2.0×10^{-5}M (ml)
0.5 : 1.0	1,200.00	3.00
0.6 : 1.0	1,000.00	3.00
0.8 : 1.0	750.00	3.00
0.9 : 1.0	666.66	3.00
1.5 : 1.0	400.00	3.00
2.0 : 1.0	300.00	3.00
3.0 : 1.0	200.00	3.00
4.0 : 1.0	150.00	3.00
5.0 : 1.0	120.00	3.00
6.0 : 1.0	100.00	3.00

2.3.4.5 UV-visible of α-Tetralone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. α-Tetralone solution (3.0×10^{-5} M) was prepared by pipetting 400.18 µl of α-Tetralone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.5). Silver solution (1.0×10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in CH_3CN 50 ml (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 6.

Table 6 The mole ratio method for α-Tetralone with silver solution

Mole ratio of α-Tetralone and silver ion	Volume of silver (I) ion 1.0×10^{-4} M (μl)	Volume of α-Tetralone 3×10^{-5} M (ml)
0.6 : 1.0	1,500.00	3.00
0.8 : 1.0	1,125.00	3.00
0.9 : 1.0	1,000.00	3.00
1.0 : 1.0	900.00	3.00
1.5 : 1.0	600.00	3.00
2.0 : 1.0	450.00	3.00
3.0 : 1.0	300.00	3.00
4.0 : 1.0	225.00	3.00
5.0 : 1.0	180.00	3.00
6.0 : 1.0	150.00	3.00

2.3.4.6 UV-visible of 1,4-Naphthoquinone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. 1,4-Naphthoquinone (5.0×10^{-5} M) was prepared by weighing 0.791 mg of 1,4-Naphthoquinone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.6). Silver solution (1.0×10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in 50 ml CH_3CN (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 7.

Table 7 The mole ratio method for 1,4-Naphthoquinone with silver solution

Mole ratio of 1,4-Naphthoquinone and silver ion	Volume of silver (I) ion 1.0×10^{-4} M (μl)	Volume of 1,4-Naphthoquinone 5×10^{-5} M (ml)
1.0 : 1.0	1,500.00	3.00
1.2 : 1.0	1,250.00	3.00
1.5 : 1.0	1,000.00	3.00
1.8 : 1.0	833.30	3.00
2.0 : 1.0	750.00	3.00
2.5 : 1.0	600.00	3.00
3.0 : 1.0	500.00	3.00
3.5 : 1.0	428.50	3.00
4.0 : 1.0	375.00	3.00
5.0 : 1.0	300.00	3.00
6.0 : 1.0	250.00	3.00

2.3.4.7 UV-visible of Anthrone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. Anthrone (1.0×10^{-5} M) was prepared by weighing 0.1942 mg of Anthrone into volumetric flask 100 ml then was dissolved in CH_3CN 100 ml (Appendix 4.1.7). Silver solution (1.0×10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in 50 ml CH_3CN (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 8.

Table 8 The mole ratio method for Anthrone with silver solution

Mole ratio of Anthrone and silver ion	Volume of silver (I) ion 1.0×10^{-4} M (µl)	Volume of Anthrone 1.0×10^{-5} M (ml)
0.3 : 1.0	1,000.00	3.00
0.4 : 1.0	750.00	3.00
0.5 : 1.0	600.00	3.00
0.6 : 1.0	500.00	3.00
0.8 : 1.0	375.00	3.00
1.0 : 1.0	300.00	3.00
1.5 : 1.0	200.00	3.00
2.0 : 1.0	150.00	3.00
3.0 : 1.0	100.00	3.00
4.0 : 1.0	75.00	3.00
5.0 : 1.0	60.00	3.00
6.0 : 1.0	50.00	3.00

2.3.4.8 UV-visible of 9-Xanthone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. 9-Xanthone solution (2.0×10^{-5} M) was prepared by weighing 0.3924 mg of 9-Xanthone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.8). Silver solution (1.0×10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in 50 ml CH_3CN (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 9.

Table 9 The mole ratio method for 9-Xanthone with silver solution

Mole ratio of 9-Xanthone and silver ion	Volume of silver (I) ion 1.0×10^{-4} M (µl)	Volume of 9-Xanthone 2.0×10^{-5} M (ml)
0.4 : 1.0	1,500.00	3.00
0.5 : 1.0	1,200.00	3.00
0.6 : 1.0	1,000.00	3.00
0.8 : 1.0	750.00	3.00
1.0 : 1.0	600.00	3.00
1.5 : 1.0	400.00	3.00
2.0 : 1.0	300.00	3.00
3.0 : 1.0	200.00	3.00
4.0 : 1.0	150.00	3.00
5.0 : 1.0	120.00	3.00
6.0 : 1.0	100.00	3.00

2.3.4.9 UV-visible of Anthraquinone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. Anthraquinone solution (9.0×10^{-6} M) was prepared by weighing 0.1874 mg of Anthraquinone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.9). Silver solution (1.0×10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in 50 ml CH_3CN (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 10.

Table 10 The mole ratio method for Anthraquinone with silver solution

Mole ratio of Anthraquinone and silver ion	Volume of silver (I) ion 1.0×10^{-4} M (µl)	Volume of Anthraquinone 9×10^{-6} M (ml)
0.50 : 1.0	540.00	3.00
0.75 : 1.0	360.00	3.00
1.00 : 1.0	270.00	3.00
1.25 : 1.0	216.00	3.00
1.50 : 1.0	180.00	3.00
2.00 : 1.0	135.00	3.00
2.25 : 1.0	120.00	3.00
2.50 : 1.0	108.00	3.00
3.00 : 1.0	90.00	3.00
6.00 : 1.0	45.00	3.00

2.3.4.10 UV-visible of 1,2-Dihydroxyanthraquinone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. 1,2-Dihydroxyanthraquinone solution (4.0×10^{-5} M) was prepared by weighing 0.9608 mg of 1,2-Dihydroxyanthraquinone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.10). Silver solution (1.0×10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in 50 ml CH_3CN (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 11.

Table 11 The mole ratio method for 1,2-Dihydroxyanthraquinone with silver solution

Mole ratio of 1,2-Dihydro-xyanthraquinone and silver ion	Volume of silver (I) ion 1.0 x 10^{-4} M (µl)	Volume of 1,2-Dihydroxy-anthraquinone 4 x 10^{-5} M (ml)
0.7 : 1.0	1,714.00	3.00
1.0 : 1.0	1,200.00	3.00
1.2 : 1.0	1,000.00	3.00
1.7 : 1.0	705.00	3.00
3.0 : 1.0	400.00	3.00
4.0 : 1.0	300.00	3.00
5.0 : 1.0	240.00	3.00
6.0 : 1.0	200.00	3.00

2.3.4.11 UV-visible of 1,4-Dihydroxyanthraquinone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. 1,4-Dihydroxyanthraquinone solution (1.0 x 10^{-5} M) was prepared by weighing 0.2402 mg of 1,4-Dihydroxyanthraquinone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.11). Silver solution (1.0 x 10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in 50 ml CH_3CN (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 12.

Table 12 The mole ratio method for 1,4-Dihydroxyanthraquinone with silver solution

Mole ratio of 1,4-Dihydro-xyanthraquinone and silver ion	Volume of silver (I) ion 1.0×10^{-4} M (µl)	Volume of 1,4-Dihydroxyanthraquinone 1×10^{-5} M (ml)
0.6 : 1.0	500.00	3.00
0.8 : 1.0	375.00	3.00
0.9 : 1.0	333.00	3.00
1.0 : 1.0	300.00	3.00
1.5 : 1.0	200.00	3.00
2.0 : 1.0	150.00	3.00
3.0 : 1.0	100.00	3.00
4.0 : 1.0	75.00	3.00
5.0 : 1.0	60.00	3.00
6.0 : 1.0	50.00	3.00

2.3.4.12 UV-visible of 1,8-Dihydroxyanthraquinone and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. 1,8-Dihydroxyanthraquinone solution (1.0×10^{-5} M) was prepared by weighing 0.2402 mg of 1,8-Dihydroxyanthraquinone into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.12). Silver solution (1.0×10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in 50 ml CH_3CN (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 13.

Table 13 The mole ratio method for 1,8-Dihydroxyanthraquinone with silver solution

Mole ratio of 1,8-Dihydro-xyanthraquinone and silver ion	Volume of Silver (I) ion 1.0×10^{-4} M (µl)	Volume of 1,8-Dihydroxyanthraquinone 1×10^{-5} M (ml)
0.6 : 1.0	500.00	3.00
0.8 : 1.0	375.00	3.00
0.9 : 1.0	333.00	3.00
1.0 : 1.0	300.00	3.00
1.5 : 1.0	200.00	3.00
2.0 : 1.0	150.00	3.00
3.0 : 1.0	100.00	3.00
4.0 : 1.0	75.00	3.00
5.0 : 1.0	60.00	3.00
6.0 : 1.0	50.00	3.00

2.3.4.13 UV-visible of Damnacanthal and silver ion

All the UV-Visible experiments were scan from 190 nm to 700 nm. Acetonitrile solution was used as blank solution. Damnacanthal solution (2.0×10^{-5} M) was prepared by weighing 0.5880 mg of Damnacanthal into volumetric flask 100 ml then was dissolved in 100 ml CH_3CN (Appendix 4.1.13). Silver solution (1.0×10^{-4} M) was prepared by weighing 1.699 mg of $AgNO_3$ and dissolved in 50 ml CH_3CN (Appendix 3.3). After that the blank solution was run first to confirm clear background. The mole ratio method was performed and the results are shown in Table 14.

Table 14 The mole ratio method for Damnacanthal with silver solution

Mole ratio of Damnacanthal and silver ion	Volume of silver (I) ion 1.0×10^{-4} M (µl)	Volume of Damnacanthal 2×10^{-5} M (ml)
0.75 : 1.0	800.00	3.00
1.00 : 1.0	600.00	3.00
1.25 : 1.0	480.00	3.00
1.50 : 1.0	400.00	3.00
2.00 : 1.0	300.00	3.00
2.50 : 1.0	240.00	3.00
3.00 : 1.0	200.00	3.00
4.00 : 1.0	150.00	3.00
5.00 : 1.0	120.00	3.00
6.00 : 1.0	100.00	3.00

2.3.5 The modified carbon paste electrode

To determine the complexation of ketone and quinone compounds be used in the analysis silver ion, the chemically modified carbon paste electrodes were prepared as follows:

Preparation of working electrode

The teflon rod from Thai Saeng Trading, Hatyai, Songkla, Thailand with the diameter of 9 mm was cut to obtain a 4.7 cm piece and then drilled to have the inside diameter 2 mm and drilled again at one end to expand the inside diameter to 4.5 mm with the depth of 1 cm. The copper wire with the diameter of 2 mm and 8.8 cm length (Department of Physics, Faculty of Science, Prince of Songkla University, Thailand) was inserted into the other end to obtain a working electrode.

Modified carbon pastes were prepared by mixing 0.275 g of carbon powder and 0.060 g of modified chemicals in the mortar and ground with the pestle. The liquid paraffin (0.2 mL) was added and ground again. The paste was then packed at the end of the electrode framework with spatula. The electrode was polished with clean paper until shiny. The blank electrode was prepared in the same way without adding chemicals (Runurak *et al.*, 2004).

The reference electrode was contained in a Pyrex tube with a softened glass cracked tip, filled with aqueous Tetramethylammonium chloride at a concentration to give a potential of 0.00 V vs SCE and placed inside a Luggin capillary. The platinum-wire auxiliary electrode was placed inside a glass frit (ACE GLASS, NJ, USA).

To investigate the potential of ketones and quinones for the analysis silver ion, the modified carbon paste electrode was prepared and immersed in a 10 ml solution of 0.2 M nitric acid containing 1 x 10^{-3} M of silver ion and the solution was stirred for 30 s. The Cyclic voltammograms were run starting from 0.000 to +0.500 V and back (with a 180 mVs^{-1} scan rate). All measurements were carried out at room temperature (22 ± 2 °C).