CHAPTER 5

RESULTS AND DISCUSSION

(5) RESULTS AND DISCUSSION

5.1 Determination of the half-wave for metals (lead, cadmium, and zinc) in the four different types of the supporting electrolytes by using the DPP mode.

The Figure 5.1 to5.8 shows the peak currents for lead, cadmium, and zinc in 4 different types of supporting electrolytes. The Table 5.1, 5.2, 5.3, and 5.4 show the peak current for metals (lead, cadmium, and zinc) in the four different types of supporting electrolytes by using the DPP mode.

Table 5.1: Peak current for lead, cadmium, and zinc with various concentrations in 0.1 M potassium nitrate, KNO_3 solution (DPP).

Concentration of lead (ppm)	Peak current, X 10^{-7} (A)	Concentration of cadmium (ppm)	Peak current, X 10^{-7} (A)	Concentration of zinc (ppm)	Peak current, X 10^{-7} (A)
1.00	+1.483	1.00	+1.965	0.25	+1.201
1.99	+2.308	1.99	+2.979	0.50	+1.811
2.49	+2.739	3.98	+4.575	0.75	+2.708
3.48	+3.482	4.98	+5.534	1.24	+4.187
3.98	+3.865	5.22	+5.845		

From the above data, a calibration graph (Graph 5.1) was plotted.

Table 5.2: Peak current for lead, cadmium, and zinc with various concentrations in 0.1 M potassium chloride, KCl solution (DPP).

Concentration of lead (ppm)	Peak current, X 10^{-7} (A)	Concentration of cadmium (ppm)	Peak current, X 10^{-7} (A)	Concentration of zinc (ppm)	Peak current, X 10^{-7} (A)
1.00	+1.206	1.00	+1.673	0.50	+1.787
1.99	+1.864	1.99	+2.953	0.75	+2.648
2.99	+2.386	2.99	+4.190	1.24	+3.566
4.48	+3.300	3.98	+5.376	1.49	+4.262
5.72	+4.031	4.48	+6.101		

From the above data, a calibration graph (Graph 5.2) was plotted.

Table 5.3: Peak current for lead, cadmium, and zinc with various concentrations in 0.1 M ammonium hydroxide-ammonium chloride, NH_4OH-NH_4Cl solution (DPP).

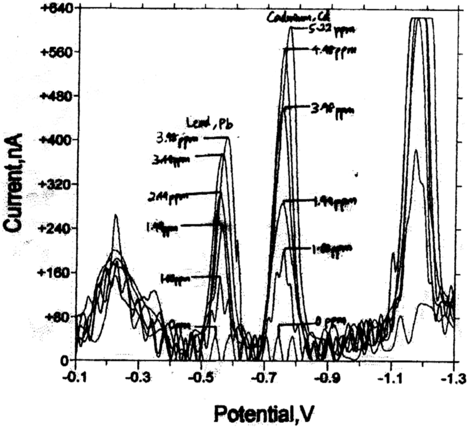
Concentration of lead (ppm)	Peak current, X 10^{-7} (A)	Concentration of cadmium (ppm)	Peak current, X 10^{-7} (A)	Concentration of zinc (ppm)	Peak current, X 10^{-7} (A)
1.74	+1.210	1.00	+2.374	1.99	+4.549
1.99	+1.237	2.49	+3.826	2.73	+5.711
7.96	+2.029	3.98	+5.206	2.99	+6.003
		4.73	+5.965		
		4.98	+6.269		

From the above data, a calibration graph (Graph 5.3) was plotted.

Table 5.4: Peak current for lead, cadmium, and zinc with various concentrations in o.1 M nitric acid, HNO_3 solution (DPP).

Concentration of lead (ppm)	Peak current, X 10^{-7} (A)	Concentration of cadmium (ppm)	Peak current, X 10^{-7} (A)	Concentration of zinc (ppm)	Peak current, X 10^{-7} (A)
1.00	+1.023	0.75	+1.636	0.25	+1.522
1.99	+1.698	1.99	+2.821	0.50	+2.396
2.99	+2.428	2.99	+3.823	1.00	+3.941
3.98	+3.107	3.98	+4.556	1.24	+4.992
4.98	+3.713	4.98	+5.521		

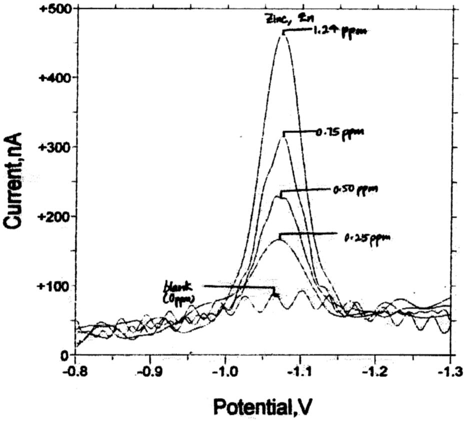
From the above data, a calibration graph (Graph 5.4) was plotted.



Mode: DPP
Supporting electrolyte: KNO_3(0.1M)
Drop size: 5

General parameters:	i) Initial E:	-100mV
	ii) Final E:	-1300mV
	iii) Sensitivity:	1μA/V
Specific parameters:	i) Scan rate:	2mV/s
	ii) Pulse amplitude:	50mV
	iii) Sample width:	17ms
	iv) Pulse width:	50ms
	v) Drop time:	1000ms
	vi) Quiet time:	5s

Figure 5.1: Peak current for Lead and Cadmium with various concentrations in 0.1M KNO_3 solution.

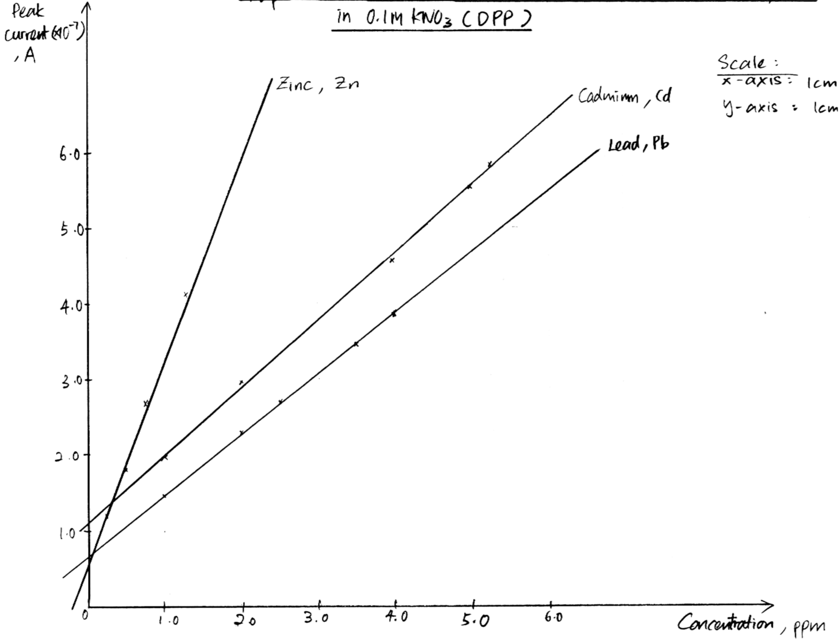


Mode: DPP
Supporting electrolyte: KNO_3(0.1M)
Drop size: 5

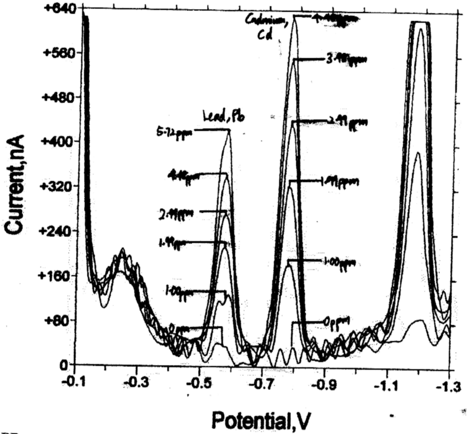
General parameters:	i) Initial E:	-800mV
	ii) Final E:	-1300mV
	iii) Sensitivity:	1µA/V
Specific parameters:	i) Scan rate:	2mV/s
	ii) Pulse amplitude:	50mV
	iii) Sample width:	17ms
	iv) Pulse width:	50ms
	v) Drop time:	1000ms
	vi) Quiet time:	5s

Figure 5.2: Peak current for Zinc with various concentration in 0.1M KNO_3 solution.

Graph 5.1 : Peak current versus concentration for Lead, Cadmium, Zinc in 0.1M KNO_3 (DPP)



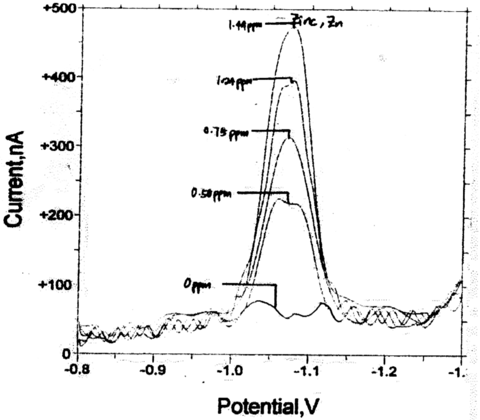
Scale :
x-axis : 1cm : 0.5ppm
y-axis : 1cm : 0.5×10^{-7}A



Mode: DPP
Supporting electrolyte: KCl (0.1M)
Drop size: 5

General Parameters:	i) Initial E:	-100mV
	ii) Final E:	-1300mV
	iii) Sensitivity:	1µA/V
Specific parameters:	i) Scan rate:	2mV/s
	ii) Pulse amplitude:	50mV
	iii) Sample width:	17ms
	iv) Pulse width:	50ms
	v) Drop time:	1000ms
	vi) Quiet time:	5s

Figure 5.3: Peak current for Cadmium and Lead with various concentration in 0.1M KCl solution.



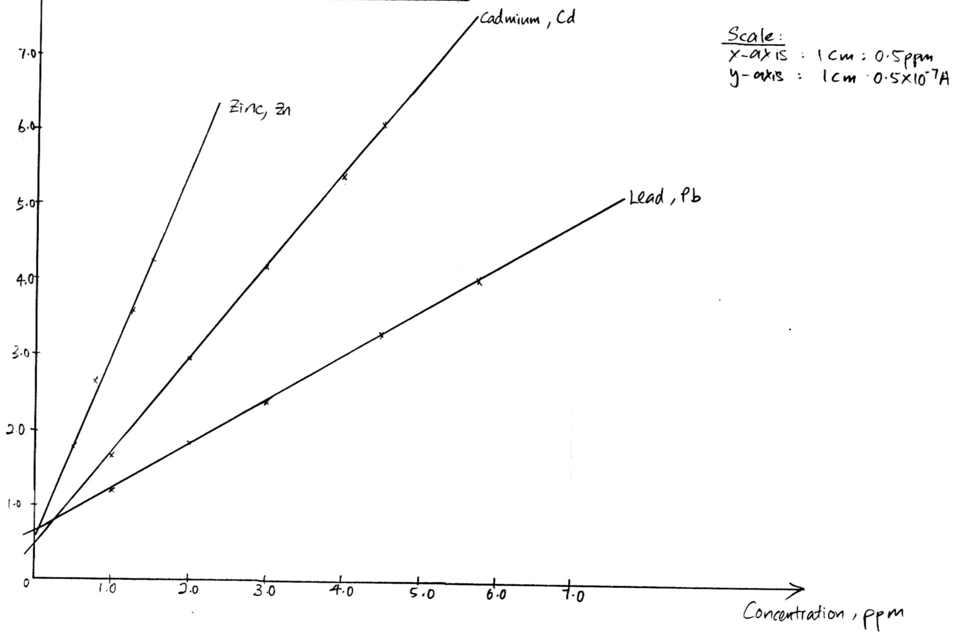
Mode: DPP
Supporting electrolyte: KCl (0.1M)
Drop size: 5

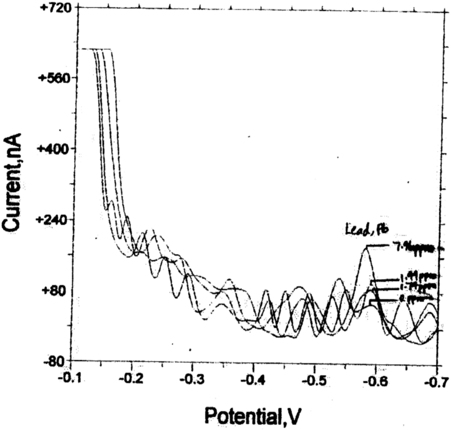
General Parameters:	i) Initial E:	-800mV
	ii) Final E:	-1300mV
	iii) Sensitivity:	1μA/V

Specific parameters:	i) Scan rate:	2mV/s
	ii) Pulse amplitude:	50mV
	iii) Sample width:	17ms
	iv) Pulse width:	50ms
	v) Drop time:	1000ms
	vi) Quiet time:	5s

Figure 5.4: Peak current for Zinc with various concentration in 0.1M KCl solution.

in 0.1M KCl (DPP)





Mode: DPP
Supporting electrolyte: NH_4OH-NH_4Cl(0.1M)
Drop size: 5

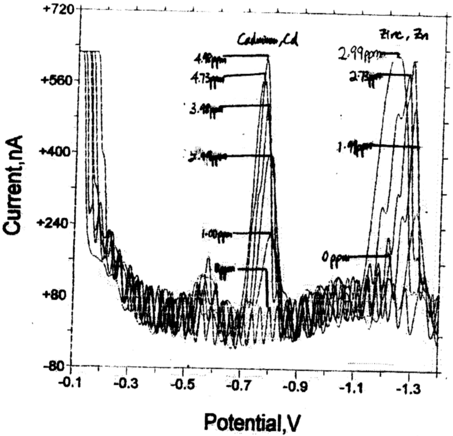
General Parameters:

i)	Initial E:	-100mV
ii)	Final E:	-700mV
iii)	Sensitivity:	1μA/V

Specific parameters:

i)	Scan rate:	2mV/s
ii)	Pulse amplitude:	50mV
iii)	Sample width:	17ms
iv)	Pulse width:	50ms
v)	Drop time:	1000ms
vi)	Quiet time:	5s

Figure 5.5: Peak current for Lead with various concentration in 0.1M NH_4OH-NH_4Cl solution.

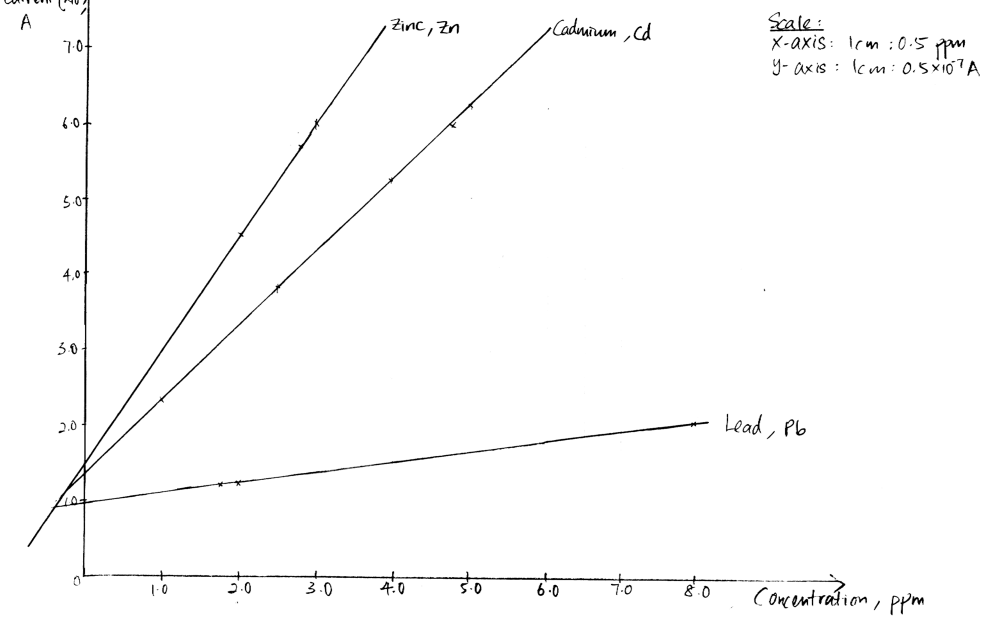


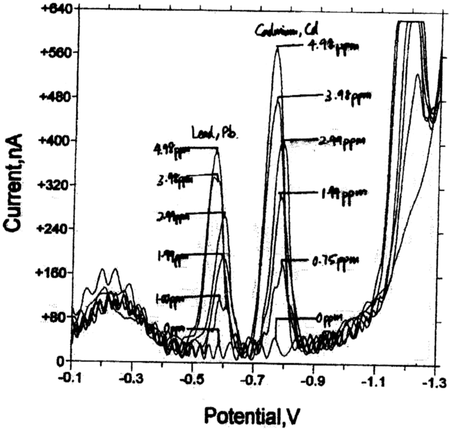
Mode: DPP
Supporting electrolyte: NH_4OH-NH_4Cl (0.1M)
Drop size: 5

General Parameters:	i) Initial E:	-100mV
	ii) Final E:	-1400mV
	iii) Sensitivity:	1μA/V
Specific parameters:	i) Scan rate:	2mV/s
	ii) Pulse amplitude:	50mV
	iii) Sample width:	17ms
	iv) Pulse width:	50ms
	v) Drop time:	1000ms
	vi) Quiet time:	5s

Figure 5.6: Peak current for Cadmium and Zinc with various concentration in 0.1M NH_4OH-NH_4Cl solution.

Graph 3.3 Peak current versus concentration for Lead, Cadmium, Zinc in 0.1M NH_4OH-NH_4Cl (DPP)

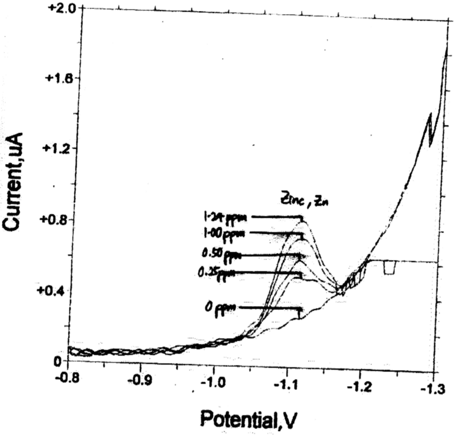




Mode: DPP
Supporting electrolyte: HNO_3 (0.1M)
Drop size: 5

General Parameters:	i) Initial E:	-100mV
	ii) Final E:	-1300mV
	iii) Sensitivity:	1μA/V
Specific parameters:	i) Scan rate:	2mV/s
	ii) Pulse amplitude:	50mV
	iii) Sample width:	17ms
	iv) Pulse width:	50ms
	v) Drop time:	1000ms
	vi) Quiet time:	5s

Figure 5.7: Peak current for Lead and Cadmium with various concentration in 0.1M HNO_3 solution.



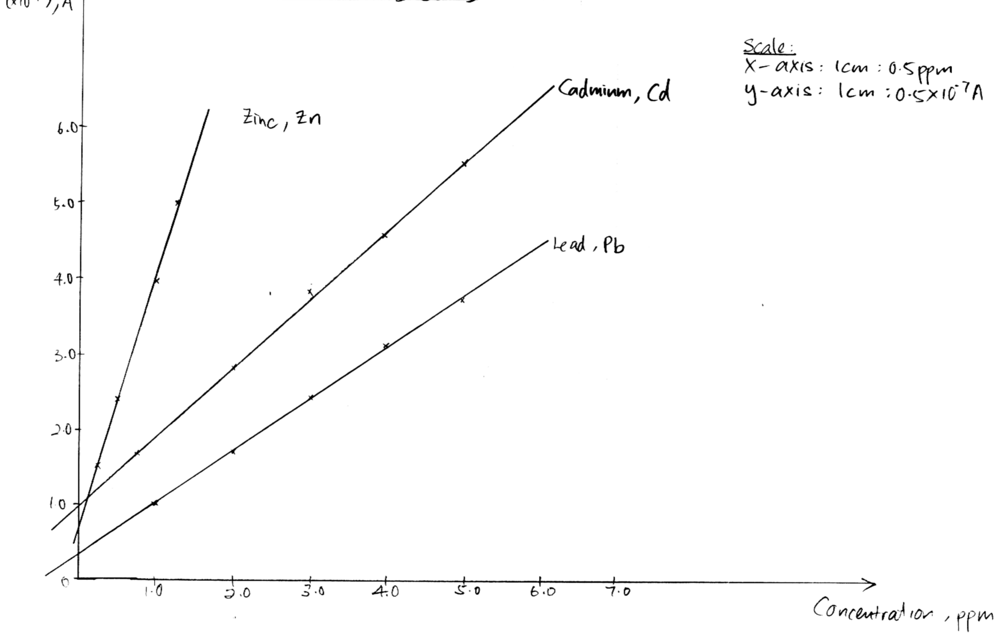
Mode: DPP
Supporting electrolyte: HNO_3 (0.1M)
Drop size: 5

General Parameters: i) Initial E: -800mV
ii) Final E: -1300mV
iii) Sensitivity: 1μA/V

Specific parameters: i) Scan rate: 2mV/s
ii) Pulse amplitude: 50mV
iii) Sample width: 17ms
iv) Pulse width: 50ms
v) Drop time: 1000ms
vi) Quiet time: 5s

Figure 5.8: Peak current for Zinc with various concentration in 0.1M HNO_3 solution.

in 0.1M HNO_3 (DPP)



Scale:
X-axis: 1cm : 0.5ppm
y-axis: 1cm : 0.5×10^{-7} A

As we know that, each of the metals (lead, cadmium, and zinc) has own half-wave potential, $E_{1/2}$. But, the different supporting electrolytes will produce different half-wave potential. From the Figure 5.1 to 5.8, all these polarograms show that each of the metals has own range of half-wave potential for each supporting electrolyte. The following table (Table 5.5) shows the range of the peak potential for metals (lead, cadmium, and zinc) in four different supporting electrolytes.

Table 5.5: The peak potential, $E_{1/2}$ for metals (lead, cadmium, and zinc) in four different supporting electrolytes (DPP).

Supporting electrolyte	Peak potential for lead (mV)	Peak potential for cadmium (mV)	Peak potential for zinc (mV)
KNO_3	-554 to -576	-750 to -770	-1066 to -1074
KCl	-572 to -588	-774 to -780	-1060 to -1078
NH_4OH-NH_4Cl	-564 to -590	-760 to -798	-1240 to -1300
HNO_3	-558 to -596	-756 to -790	-1104 to -1112

From the Table 5.5, it shows that the half-wave potentials for metals in different supporting electrolytes don't have so much different among them.

From the Graph 5.1 to 5.4, it is found that the peak current of metals is proportional to the concentration of the metals if all the parameters are constant.

The selectivity and sensitivity of the analysis are controlled by the types of the supporting electrolytes are used. The most suitable supporting electrolyte will be liked that:

(a) It produces well-separated peaks for the metals;

(b) It produces well-shaped peaks for the metals;

(c) It provides good linearity.

5.2 Determination of the detection limits for the metals (lead, cadmium, and zinc) by using the DPP mode.

The Figure 5.9, 5.10, and 5.11 show the polarograms of the determination of the detection limits for the lead, cadmium, and zinc by the DPP mode. The following tables (Table 5.6, 5.7, and 5.8) show the peak current for lead, cadmium, zinc in 0.1 M potassium chloride with different concentration, which are obtained from the Figure 5.9, 5.10, and 5.11.

Table 5.6: The concentrations of the lead and their peak currents in 0.1 M KCl (DPP).

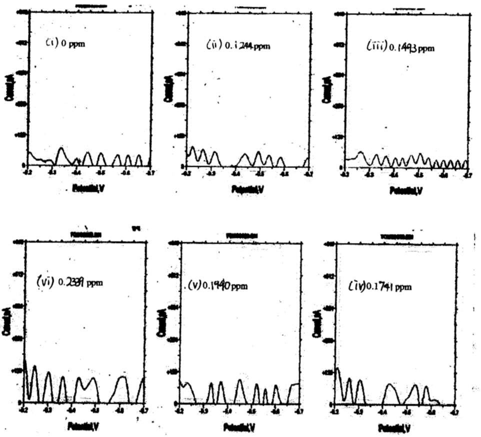
Concentration (ppm)	Peak current for lead, X 10^{-8} (A)
0	+5.660
0.1244	+4.861
0.1493	+5.774
0.1741	+10.56
0.1990	+11.05
0.2339	+11.20

Table 5.7: The concentrations of the cadmium and their peak currents in 0.1 M KCl (DPP).

Concentration (ppm)	Peak current for cadmium, X 10^{-8} (A)
0	+3.596
0.0498	-
0.0746	+4.841
0.0995	+5.536

Table 5.8: The concentrations of the zinc and their peak currents in 0.1 M KCl (DPP).

Concentration (ppm)	Peak current for zinc, X 10^{-8} (A)
0	-
0.0498	-
0.0597	+6.667
0.0697	+6.918

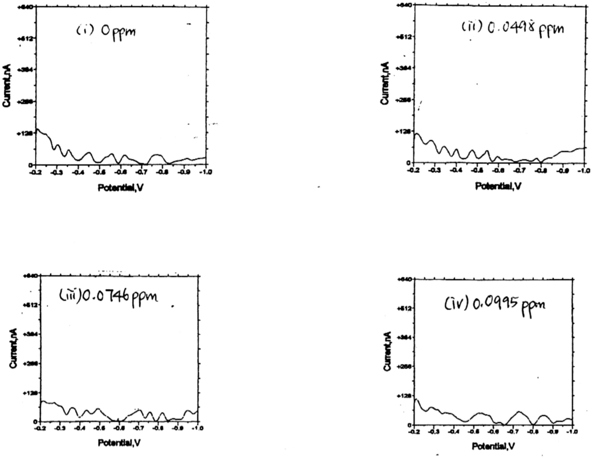


Mode: DPP
Supporting electrolyte: KCl (0.1M)
Drop size: 5

General Parameters: i) Initial E: -200mV
ii) Final E: -700mV
iii) Sensitivity: 1μA/V

Specific parameters: i) Scan rate: 2mV/s
ii) Pulse amplitude: 50mV
iii) Sample width: 17ms
iv) Pulse width: 50ms
v) Drop time: 1000ms
vi) Quiet time: 5s

Figure 5.9: Determination of detection limit for Lead using the DPP mode.

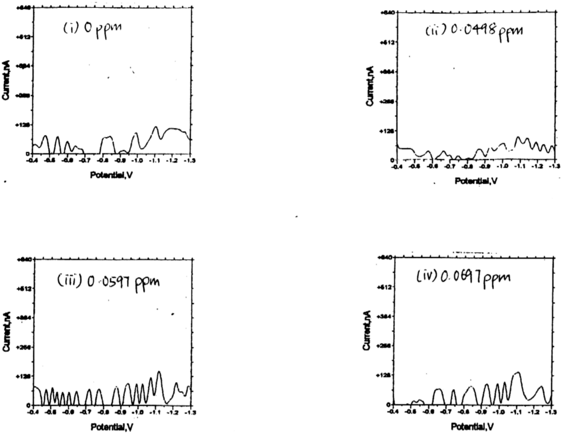


Mode: DPP
Supporting electrolyte: KCl (0.1 M)
Drop size: 5

General Parameters: i) Initial E: -200 mV
ii) Final E: -1000 mV
iii) Sensitivity: 1 μA/V

Specific Parameters: i) Scan rate: 2 mV/s
ii) Pulse amplitude: 50 mV
iii) Sample width: 17 ms
iv) Pulse width: 50 ms
v) Drop time: 1000 ms
vi) Quiet time: 5 s

Figure 5.10: Determination of detection limit for cadmium using the DPP mode.



Mode: DPP
Supporting electrolyte: KCl (0.1 M)
Drop size: 5

General Parameters:	i) Initial E:	-400mV
	ii) Final E:	-1300 mV
	iii) Sensitivity:	1 μA/V
Specific Parameters:	i) Scan rate:	2 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Drop time:	1000 ms
	vi) Quiet time:	5 s

Figure 5.11: Determination of detection limit for zinc using the DPP mode.

Detection limit is the smallest value that can be distinguished from a blank and there are various ways to calculate this (Reference 1). The detection limits of the DPP for the metals (lead, cadmium, and zinc) are quite low, about 10^{-7} to 10^{-8} M (Reference 52). The following table (Table 5.9) shows the detection limits for metals (lead, cadmium, and zinc) in 0.1 M potassium chloride by using the DPP mode.

Table 5.9: The detection limit for lead, cadmium, and zinc in 0.1 M KCl by using the DPP mode.

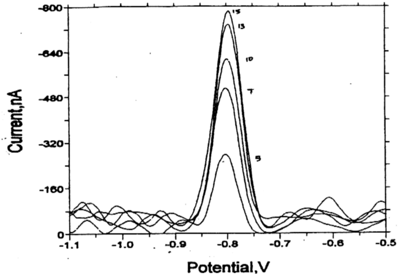
Metal	Detection limit (ppm)
Lead	0.1493
Cadmium	0.0746
Zinc	0.0597

5.3 Determination of optimum conditions for DPSV mode.

The parameters of the DPSV mode are liked the drop size of the mercury, scan rate, stir rate, deposition time, and quiet time. In this part all these parameters are being experimented, in order to obtain the optimum conditions for the DPSV mode.

5.3.1 Drop size of mercury

The Figure 5.12 shows the peaks for the different drop size of the mercury.



Mode: DPSV
Supporting electrolyte: NH_4OH-NH_4Cl (0.1 M)
Drop size: 5, 7, 10, 13, 15
Metal: cadmium (0.0498 ppm)

General Parameters: i) Initial E: -1100 mV
ii) Final E: -500 mV
iii) Rotation rate: 100 rpm
iv) Sensitivity: 10 μA/V
v) Deposition time: 300 s

Specific Parameters: i) Scan rate: 5 mV/s
ii) Pulse amplitude: 50 mV
iii) Sample width: 17 ms
iv) Pulse width: 50 ms
v) Pulse period: 200 ms
vi) Quiet time: 30 s

Figure 5.12: The effects of different drop size to the peak current.

The drop size of the mercury has used in this experiment for the DPSV mode is 5, 7, 10, 13, and 15. From the voltamogram (Figure 5.12), it shows that the bigger of the drop size of the mercury, the bigger the value for the peak current. This is because the bigger of the drop size of the mercury, the bigger of the surface area of the electrode. Hence, the peak current will be higher. This relationship is agreed with the equation as below (Reference 52).

$$i_l = \frac{n\,F\,A\,D_A\,C_A}{\delta}$$

But, the drop size of the mercury can not increase until too big because it will occur a few problems like the following:

(i) The peak broadening will happen. The bigger of the size drop will cause the metal diffuse more into the mercury. So, there is longer time for the metal to diffuse from the interior of the mercury. Hence, the resolution of the adjacent peaks will decrease.

(ii) The bigger drop size makes the mercury easier to drop from the electrode. It is because the heavier drop is pulled even more force by the gravity force.

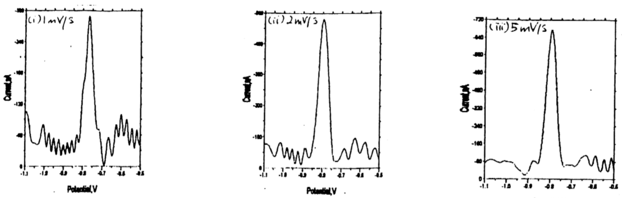
From the Figure 5.12, the best drop size is 13. It is because it can give a nice and sharp peak.

5.3.2 ***Scan rate***

The Figure 5.13 shows the different types of the scan rates are used to produce the peak current. The scan rates have chosen are 1 mV/s, 2 mV/s, 5 mV/s, 10 mV/s and 20 mV/s.

The slow scan rate makes the analysis time too long and not efficiently. Meanwhile, the fast scan rate can provide the faster analysis time. However, the fast scan rate can provide the incomplete stripping process happens, so not all the metals have deposited at the surface of mercury and strip from the electrode. Subsequently, there will loss some of the information because the peak is too smooth.

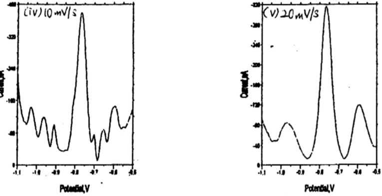
From the voltamogram (Figure 5.13), we can observe that 1 mV/s and 2 mV/s are not smooth. But, the scan rate of the 10 mV/s and 20 mV/s are too smooth. So, the best scan rate is 5 mV/s.



i) Pulse period: 1000ms
Pulse width: 50ms

(ii) Pulse period: 500ms
Pulse width: 50ms

(iii) Pulse period: 200ms
Pulse width: 50ms



(iv) Pulse period: 100ms
Pulse width: 50ms

(v) Pulse period: 50ms
Pulse width: 25ms

Mode: DPSV
Supporting electrolyte: NH_4OH-NH_4Cl (0.1 M)
Drop size: 13
Metal: cadmium (0.0373 ppm)

General Parameters:
i) Initial E: -1100 mV
ii) Final E: -500 mV
iii) Rotatio 100 rpm
iv) Sensitivity: 1µA/V
v) Deposition time: 300 s

Specific Parameters:
i) Scan rate: 2 mV/s
ii) Pulse amplitude: 50 mV
iii) Sample width: @
iv) Pulse width: 17 ms
v) Pulse period: *
vi) Quiet time: 30 s

@ *Pulse period is the time required for 1 potential cycle, and must be at least twice the Pulse width.*

* *The product of the Pulse period and Scan rate must be less than the Pulse amplitude, and greater than 1 mV.*

Figure 5.13: Determination of the best scan rate.

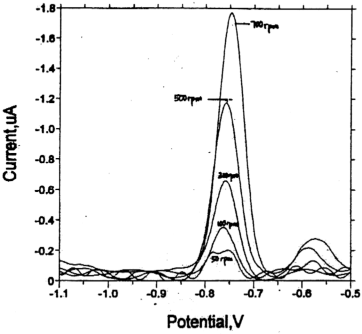
5.3.3The effects of the stir rate

The Figure 5.14 (a) shows the effects of the different stir rate to the peak current of the metal. Meanwhile, the Figure 5.14 (b) shows the effects of the different stir rate to the peak current of the metal without turning off the stirrer during the stripping process. Both of them show that the faster the stir rate will produce the bigger value of the peak current.

There are three types of ways the metal ions are traveled to the surface of the electrode, such as (i) diffusion, (ii) convection, and (iii) migration. The stirring process can use to assist the convection transport for the metals. The stirring process can decrease the thickness of the diffusion layer at the surface of the electrode and then the concentration polarization (Reference 52). In this case, the faster the stir rates, the higher the concentration of the metal in the electrode. But, if the stir rate is too fast, the electrode will become mechanically unstable.

From the Figure 5.14 (b), I found that if the stirrer is not switched during the stripping process, the peak current is higher. In addition, the voltamogram of the Figure 5.14 (a) is smoother than Figure 5.14 (b). It may be due to the stirring action during the stripping process can provide the extra convention process to help to strip the metal from the electrode.

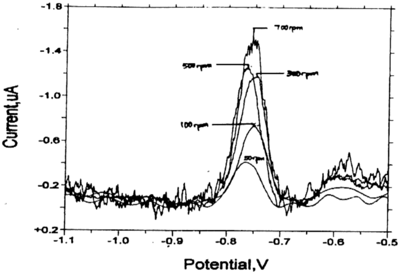
From the Figure 5.14 (a) and (b), the best stir rate is 100 rpm. It is because it can produce the nice, sharp, well-defined peak than the lower stir rate.



Mode: DPSV
Supporting electrolyte: NH_4OH-NH_4Cl (0.1 M)
Drop size: 13
Metal: cadmium (0.0249 ppm)

General Parameters:	i) Initial E:	-1100 mV
	ii) Final E:	-500 mV
	iii) Rotation rate:	50,100, 300, 500, 700 rpm
	iv) Sensitivity:	10 µA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.14 (a): The effects of stir rate to the peak current.



Mode: DPSV
Supporting electrolyte: NH_4OH-NH_4Cl (0.1 M)
Drop size: 13
Metal: cadmium (0.0249 ppm)

General Parameters:	i) Initial E:	-1100 mV
	ii) Final E:	-500 mV
	iii) Rotation rate:	50,100, 300, 500, 700 rpm
	iv) Sensitivity:	1 μA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.14 (b): The effects of stirring process during stripping step to the peak current.

5.3.4 Deposition time

The Figure 5.15 shows the effects of the different deposition times to the peak currents. The deposition times are experimented, including 100 s, 150 s, 300 s, 400 s, and 600 s.

Generally, the metal ion with concentration of 10^{-9}, 10^{-8}, and 10^{-7} with deposition time about 12, 5, and 2 minutes are quite sufficient by using the DPSV mode (Reference 52). However, if the deposition time is too long, there will be occurred a few problems, such like:

(a) The reduced species will travel into the electrode, but not just residing on the surface. Thus, there will happen no more metal for the re-oxidation or stripping process.

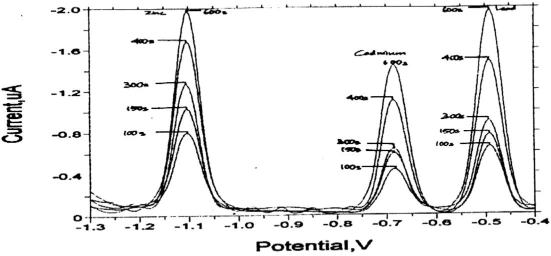
(b) The longer deposition time, the longer the analysis time.

(c) The formation of intermetallic compounds between the metals will occur.

(d) The mercury will be saturated by too many metals.

From the Figure 5.15, it is quite clear that the longer of the deposition time, the higher of the peak current. It might because the longer the deposition time, there will be more electroactive species (metals) has been concentrated from the solution on the surface of the electrodes. Subsequently, there will be a relative large faradaic current flow during the stripping process and result in higher peak current.

In addition, from the Figure 5.15, I found that between the 100 s and 300 s deposition time, the peak currents are increased quite constantly. But, after the 300 s, the increment is suddenly increase quite a lot, such as 400 s and 600 s deposition time. So, the deposition time has chosen is 300 s (5 minutes).



Mode: DPSV
Supporting electrolyte: KNO_3 (0.1 M)
Drop size: 13
Metal: lead (0.0423), cadmium (0.0373 ppm), zinc (0.0274 ppm).

General Parameters:	i) Initial E:	-1300 mV
	ii) Final E:	-400 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	10 μA/V
	v) Deposition time:	100 s, 150 s, 300 s, 400 s, 600 s.
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

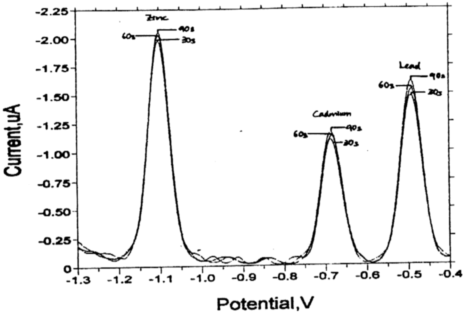
Figure 5.15: The effects of different deposition time to the peak current.

5.3.5 Quiet time

The Figure 5.16 shows the effects of the various quiet times to the peak current. The quiet time has experimented are liked 30 s, 60 s, and 90 s.

The quiet time (rest period) is the period between the deposition and stripping process (Reference 52). The quiet time is used to form the mercury drop with the uniform concentration of metal.

From the Figure 5.16, it is found that the longer of the quiet time, the higher of the peak current. But, the increment of the peak currents from 30 s to 90 s is just a little and not obvious. So, the rest period use in this project is 30 s.



Mode: DPSV
Supporting electrolyte: KNO_3 (0.1 M)
Drop size: 13
Metal: lead (0.0423 ppm), cadmium (0.0373 ppm), zinc (0.0274 ppm).

General Parameters:	i) Initial E:	-1300 mV
	ii) Final E:	-400 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	10 μA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s, 60 s, 90 s.

Figure 5.16: The effects of different quiet time to the peak current.

5.4 Determination of the half-wave potential for metals (lead, cadmium, and zinc) in the four different types of the supporting electrolytes by using the DPSV mode.

The Figure 5.17 to 5.21 show the peak currents for lead, cadmium, and zinc in 4 different supporting electrolytes. The following tables (Table 5.10, 5.11, 5.12, 5.13, and 5.14) show the various concentrations of the metals (lead, cadmium, and zinc) with their peak currents in four different types of supporting electrolytes by the DPSV mode.

Table 5.10: The concentrations of the lead, cadmium, zinc and the peak currents in 0.1M potassium nitrate, KNO_3 solution (DPSV).

Concentration of lead (ppm)	Peak current, X 10^{-7} (A)	Concentration of cadmium (ppm)	Peak current, X 10^{-7} (A)	Concentration of zinc (ppm)	Peak current, X 10^{-6} (A)
0.0124	-4.532	0.0124	-2.844	0.0100	-0.7634
0.0249	-6.161	0.0249	-4.956	0.0199	-1.084
0.0398	-8.121	0.0299	-5.816	0.0224	-1.185
0.0423	-8.543	0.0373	-7.369	0.0274	-1.367

From the above data, a calibration graph (Graph 5.5) was plotted.

Table 5.11: The concentrations of the lead, cadmium, zinc and the peak currents in 0.1 M potassium chloride, KCl solution (DPSV).

Concentration of lead (ppm)	Peak current, X 10^{-7} (A)	Concentration of cadmium (ppm)	Peak current, X 10^{-7} (A)	Concentration of zinc (ppm)	Peak current, X 10^{-6} (A)
0.0124	-1.887	0.0100	-3.448	0.0100	-1.110
0.0174	-2.156	0.0224	-4.980	0.0149	-1.382
0.0373	-3.388	0.0373	-7.037	0.0323	-2.172
0.0498	-3.957	0.0498	-8.763	0.0498	-2.917
0.0622	-4.633	0.0522	-9.033	0.0522	-3.007

From the above data, a calibration graph (Graph 5.6) was plotted.

Table 5.12: The concentration for the cadmium (lower concentration) and their peak currents in 0.1 M potassium chloride, KCl solution (DPSV).

Concentration for cadmium (ppm)	Peak current for cadmium, X 10^{-7} (A)
0.00373	-1.673
0.00647	-2.395
0.00796	-2.770
0.00945	-3.192
0.01194	-3.744

From the above data, a calibration graph (Graph 5.7) was plotted.

Table 5.13: The concentrations of the lead, cadmium, zinc and the peak currents in 0.1 M ammonium hydroxide-ammonium chloride, NH_4OH-NH_4Cl solution (DPSV).

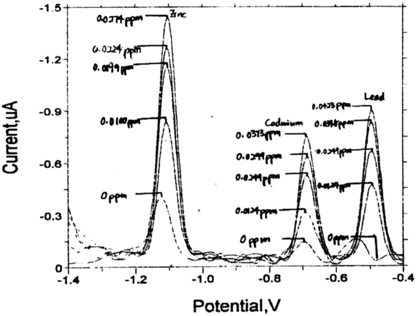
Concentration of lead (ppm)	Peak current, X 10^{-7} (A)	Concentration of cadmium (ppm)	Peak current, X 10^{-7} (A)	Concentration of zinc (ppm)	Peak current, X 10^{-7} (A)
0.0149	-0.4647	0.0249	-4.278	0.0100	-1.616
0.0373	-1.069	0.0373	-6.271	0.0124	-1.827
0.0498	-1.239	0.0498	-8.029	0.0299	-4.240
0.0622	-1.604	0.0622	-9.903	0.0398	-6.166
0.0746	-1.757	0.0721	-11.46	0.0498	-7.235
0.0846	-2.036			0.0597	-8.926
				0.0697	-10.29

From the above data, a calibration graph (Graph 5.8) was plotted.

Table 5.14: The concentrations of the lead, cadmium, zinc and the peak currents in 0.1 M nitric acid, HNO_3 solution (DPSV).

Concentration of lead (ppm)	Peak current, X 10^{-8} (A)	Concentration of cadmium (ppm)	Peak current, X 10^{-8} (A)	Concentration of zinc (ppm)	Peak current, X 10^{-7} (A)
0.0199	-2.618	0.0100	-2.445	0.0149	-0.5067
0.0398	-4.595	0.0124	-2.509	0.0299	-1.020
0.0498	-5.026	0.0323	-6.105	0.0572	-1.943

From the above data, a calibration graph (Graph 5.9) was plotted.

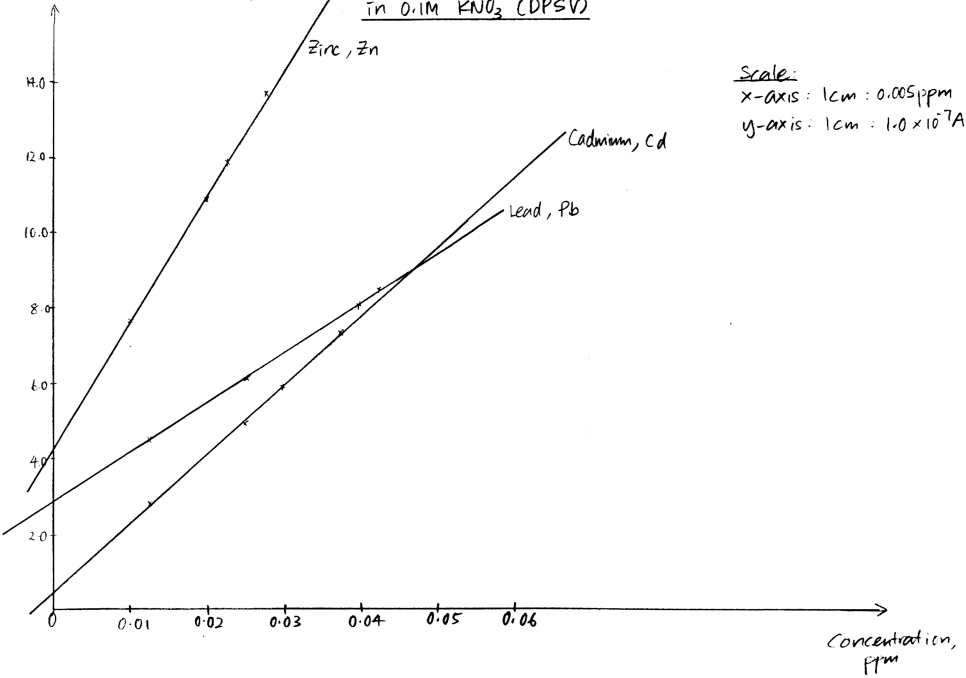


Mode: DPSV
Supporting electrolyte: KNO_3 (0.1 M)
Drop size: 13

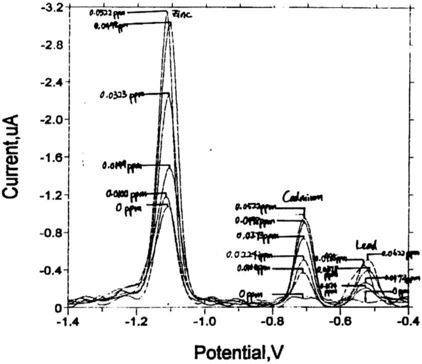
General Parameters:	i) Initial E:	-1400 mV
	ii) Final E:	-400 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	10 μA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.17: Peak current for lead, cadmium, zinc with various concentration in 0.1 M KNO_3 solution (DPSV).

in 0.1M KNO_3 (DPSV)



Scale:
x-axis : 1cm : 0.005ppm
y-axis : 1cm : 1.0×10^{-7}A

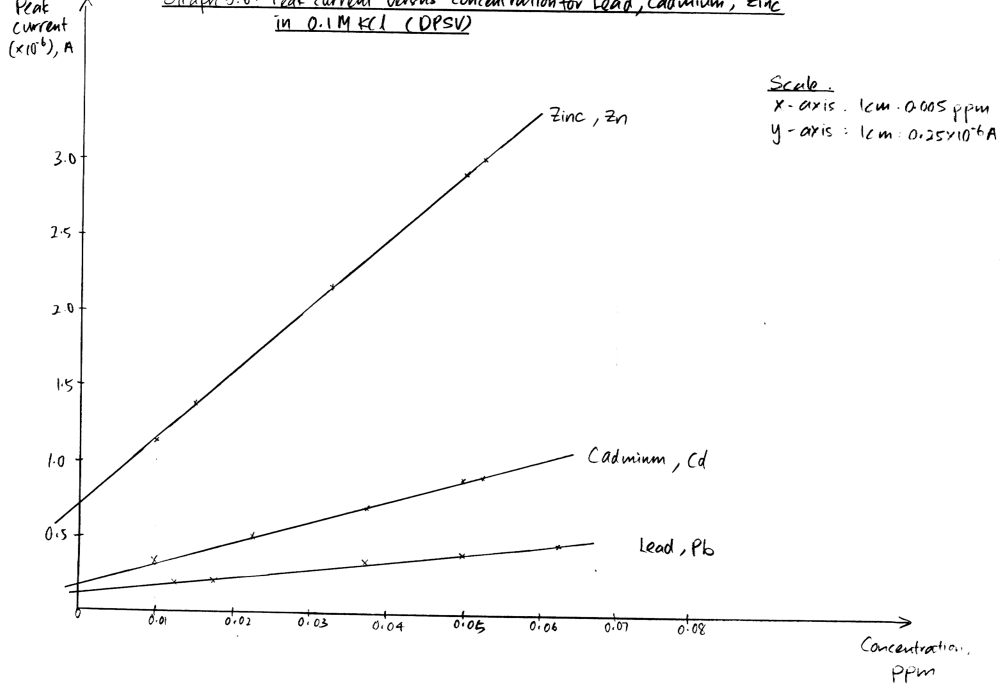


Mode: DPSV
Supporting electrolyte: KCl (0.1 M)
Drop size: 13

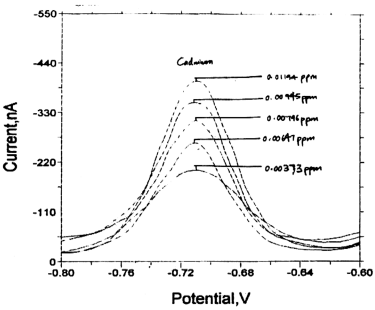
General Parameters:	i) Initial E:	-1400 mV
	ii) Final E:	-400 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	10 µA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.18: Peak current for lead, cadmium, zinc with various concentration in 0.1 M KCl solution (DPSV).

Graph [illegible] Peak current versus concentration for Lead, Cadmium, Zinc in 0.1M KCl (DPSV)



Scale.
x-axis. 1cm . 0.005 ppm
y-axis : 1cm : 0.25×10^{-6} A

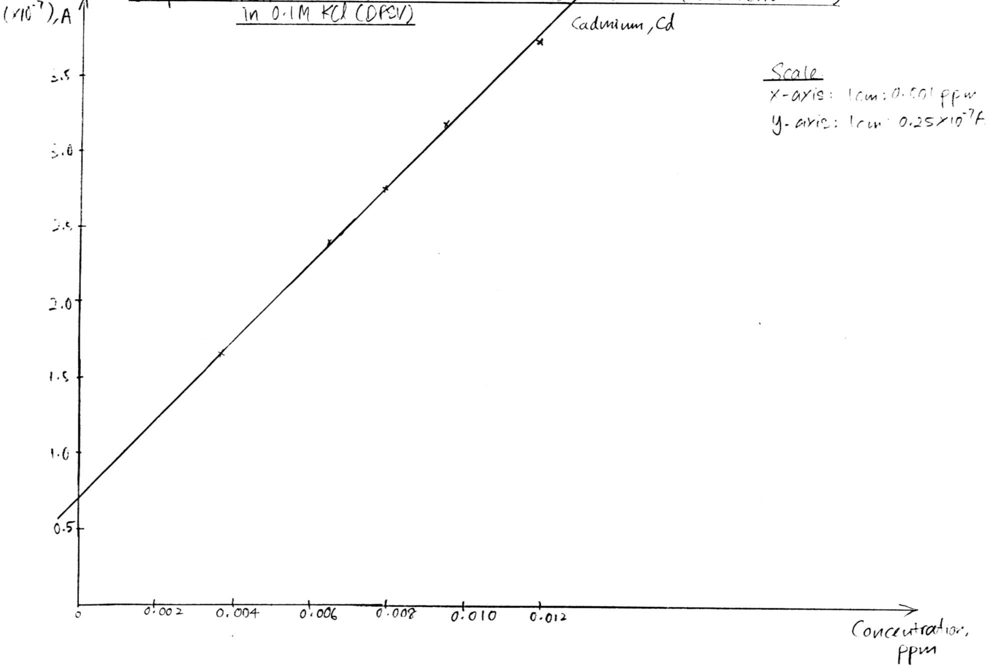


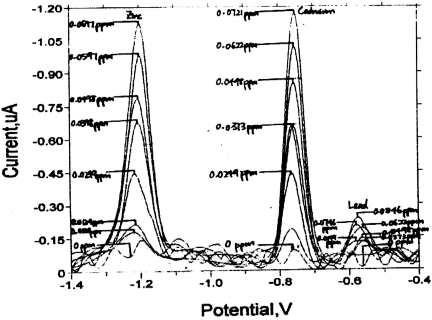
Mode: DPSV
Supporting electrolyte: KCl (0.1 M)
Drop size: 13

General Parameters:	i) Initial E:	-800 mV
	ii) Final E:	-600 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	10 μA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.19: Peak current for cadmium (lower concentration) in 0.1 M KCl solution (DPSV).

In 0.1M KCl (DPSV)



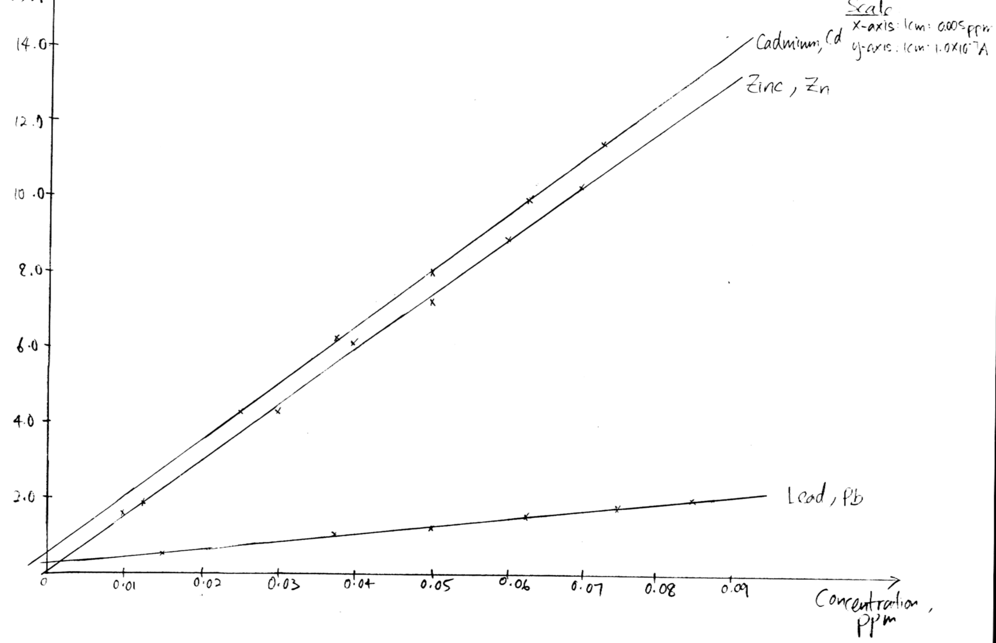


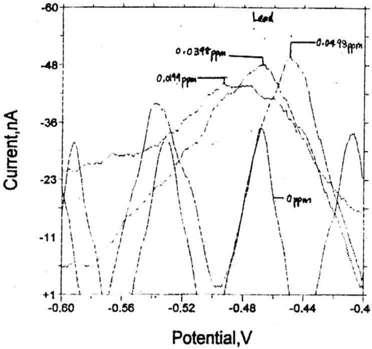
Mode: DPSV
Supporting electrolyte: NH_4OH-NH_4Cl (0.1 M)
Drop size: 13

General Parameters:	i) Initial E:	-1400 mV
	ii) Final E:	-400 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	10 μA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.20: Peak current for the lead, cadmium, zinc in 0.1 M NH_4OH-NH_4Cl solution (DPSV).

Graph 5.0 : Peak current versus concentration for Lead, Cadmium, Zinc in 0.1 M NH_4OH - NH_4Cl (DPSV)

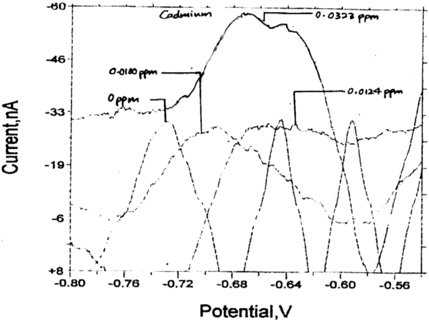




Mode: DPSV
Supporting electrolyte: HNO_3 (0.1 M)
Drop size: 13

General Parameters:	i) Initial E:	-600 mV
	ii) Final E:	-400 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	10 µA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

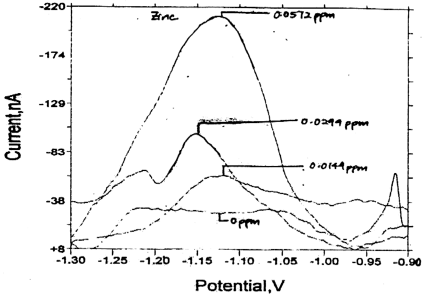
Figure 5.21 (a): Peak current for the lead in 0.1 M HNO_3 solution (DPSV).



Mode: DPSV
Supporting electrolyte: HNO_3 (0.1 M)
Drop size: 13

General Parameters:	i) Initial E:	-800 mV
	ii) Final E:	-520 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	10 μA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.21 (b): Peak current for the cadmium in 0.1 M HNO_3 solution (DPSV).

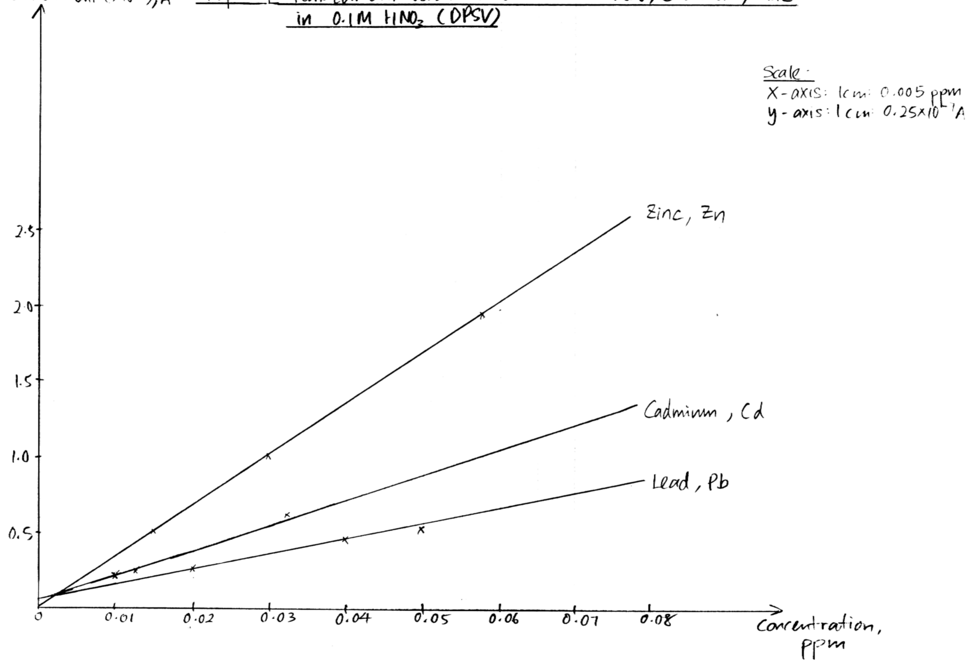


Mode: DPSV
Supporting electrolyte: HNO_3 (0.1 M)
Drop size: 13

General Parameters:	i) Initial E:	-1300 mV
	ii) Final E:	-900 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	10 μA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.21 (c): Peak current for the zinc in 0.1 M HNO_3 solution (DPSV).

Graph 5.1 : Peak current versus concentration for Lead, Cadmium, Zinc in 0.1M HNO_3 (DPSV)



Like the DPP, in the DPSV mode, each of the metal (lead, cadmium, and zinc) has their own half-wave potential, $E_{1/2}$. However, the different supporting electrolyte will produce different range of the half-wave potential. The following table (Table 5.15) shows the range of the peak potential for metals (lead, cadmium and zinc) in four different supporting electrolytes.

Table 5.15: The peak potential for metals (lead, cadmium, and zinc) in four different supporting electrolytes (DPSV).

Supporting electrolytes	Peak potential for lead (mV)	Peak potential for cadmium (mV)	Peak potential for zinc (mV)
KNO_3	-493 to -494	-686 to -692	-1102 to -1106
KCl	-519 to -531	-707 to -710	-1105 to -1115
NH_40H-NH_4Cl	-474 to -579	-752 to -762	-1199 to -1218
HNO_3	-450 to -493	-670 to -729	-1121 to -1154

As DPP, the Table 5.15 shows not much different for the peak potentials of the metals in different supporting electrolytes.

In the DPSV mode, sometimes there is a small peak when there is no metal in supporting electrolyte. But, it seldom happens to the DPP mode. It is due to the DPSV mode is a more sensitive technique. It detects any metals in the supporting electrolyte. It is due to the DPSV mode is more sensitive than the DPP mode. So, this experiment should carry out in a very clean condition.

From the Figure 5.17, 5.18, 5.19, 5.20, and 5.21, it is found that the higher the concentration of the metal, the higher the peak current in all these four supporting electrolyte. Furthermore, the concentration of the metal is also proportional to the peak current like DPP.

From the Figure 5.17, 5.18, 5.19, 5.20, and 5.21, the supporting electrolyte has chosen for determination metals in river water is potassium chloride, KCl. It is because it can produce well-separated and well-shaped peaks for each metal. Yet, it can provide good linearity compare to the others.

SUMMARY:

The optimum conditions for the DPSV mode is written as the following table (Table 5.16). All these conditions are used to determine the concentration of the metals (lead, cadmium, and zinc) in the river water.

Table 5.16: The optimum conditions for the DPSV mode.

Drop size of mercury	13
Scan rate	5 mV/s
Stir rate	100 rpm
Deposition time	300 s
Pulse amplitude	50 mV
Quiet time	30 s
Supporting electrolyte	0.1 M KCl solution

5.5Determination the detection limits for the metals (lead, cadmium, and zinc) by using the DPSV mode.

The polarograms (Figure 5.22, 5.23, and 5.24) show the various concentrations of the metals (lead, cadmium, and zinc) with their peak currents in the potassium chloride solution. The Figure 5.22, 5.23, and 5.24 are done to determine the detection limits for lead, cadmium, and zinc for the DPSV mode. The following tables (Table 5.17, 5.18, and 5.19) show the peak current for lead, cadmium, and zinc with different concentration in 0.1 M potassium chloride.

Table 5.17: The concentrations of the lead and their peak currents in 0.1 M KCl (DPSV).

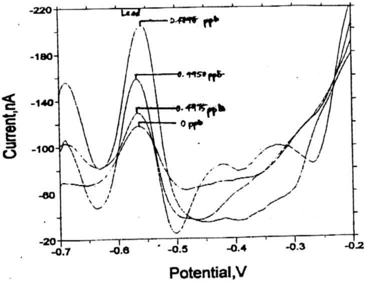
Concentration (ppb)	Peak current, X 10^{-8} (A)
0	-5.352
0.4975	-7.769
0.9950	-11.54
2.4876	-14.21

Table 5.18: The concentrations of the cadmium and their peak currents in 0.1 M KCl (DPSV).

Concentration (ppb)	Peak current, X 10^{-8} (A)
0	-5.159
0.4975	-5.110
1.9900	-6.640
2.0896	-6.775

Table 5.19: The concentrations of the zinc and their peak currents in 0.1 M KCl (DPSV).

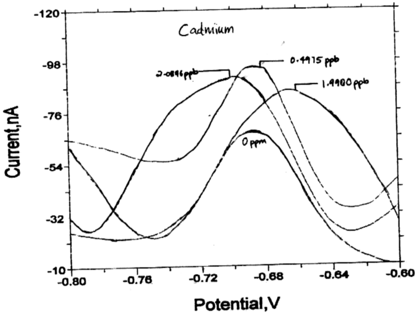
Concentration (ppb)	Peak current, X 10^{-8} (A)
0	-4.745
0.2985	-4.532
0.4975	-6.078
0.5970	-6.560



Mode: DPSV
Supporting electrolyte: KCl (0.1 M)
Drop size: 13

General Parameters:	i) Initial E:	-700 mV
	ii) Final E:	-200 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	1 µA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

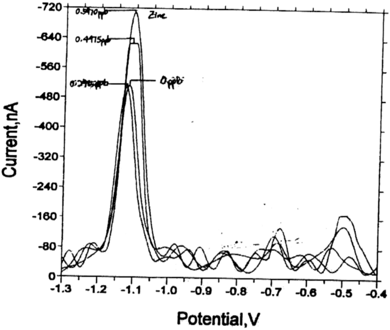
Figure 5.22: Determination of detection limit for lead using DPSV mode.



Mode: DPSV
Supporting electrolyte: KCl (0.1 M)
Drop size: 13

General Parameters:	i) Initial E:	-800 mV
	ii) Final E:	-600 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	1 μA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.23: Determination of detection limit for cadmium using DPSV mode.



Mode: DPSV
Supporting electrolyte: KCl (0.1 M)
Drop size: 13

General Parameters:	i) Initial E:	-1300 mV
	ii) Final E:	-400 mV
	iii) Rotation rate:	100 rpm
	iv) Sensitivity:	1 μA/V
	v) Deposition time:	300 s
Specific Parameters:	i) Scan rate:	5 mV/s
	ii) Pulse amplitude:	50 mV
	iii) Sample width:	17 ms
	iv) Pulse width:	50 ms
	v) Pulse period:	200 ms
	vi) Quiet time:	30 s

Figure 5.24: Determination of detection limit for zinc using DPSV mode.

The following table (Table 5.20) shows the detection limits of lead, cadmium, and zinc for the DPSV mode in 0.1 M potassium chloride solution.

Table 5.20: The detection limits of lead, cadmium, and zinc in 0.1 M KCl by DPSV mode.

Metal	Detection limits (ppb)
Lead	0.4975
Cadmium	1.9900
Zinc	0.4975

By comparing the Table 5.9 (detection limits in DPP mode) and the Table 5.20 (detection limit in DPSV mode), it is found that the DPSV mode can provide the lower detection limit than the DPP mode. The detection limits for the metals in the DPSV mode are in the ppb level.

The DPSV mode can preconcentrate the metals on the working electrode before the stripping step. So, this preconcentration step allows the DPSV mode to generate the high signal-to-noise ratio, until provide the very low detection limits for the metals.

Since, the DPSV mode is more sensitive technique and has lower detection limit than the DPP mode. So, the DPSV mode has used to determine the concentration of the metals in river water.

5.6Determination the concentrations of the metals (lead, cadmium, and zinc) in river water by using the DPSV mode.

The water samples are taken from the Sungai Penchala. There are three stations have chosen for this project, such as:

(a) Station 1 – mosque;

(b) Station 2 – behind the Nanking Vegetation;

(c) Station 3 – Damansara Intan SS2.

The station 1 is situated at the industrial area, whereas the station 2 is the squatter housing area. On the other hand, station 3 is in the housing area and beside the highway. The Figure 5.25, 5.26, and 5.27 show the voltammogram for the station 1, 2, and 3 in Appendix IV, V, VI. The Table 5.21 shows the concentrations of the lead, cadmium, zinc and the peak currents from the voltammograms of the station 1, 2, and 3.

The following table (Table 5.22) shows the concentration of the metals (lead, cadmium, and zinc) obtains from the calibration graphs (Graph 5.6, and 5.7). All these calibration graphs are showed in Appendix VII, VIII, and IX. After that, the concentrations from the calibration graphs will convert into the concentrations of the metals in the river by using the calculation, which is showed in Appendix X. The Table 5.23 shows the concentration of the metals (lead, cadmium, and zinc) in three stations.

Table 5.21: The concentrations of the lead, cadmium, zinc and the peak currents from the voltammograms of the station 1, 2, and 3.

Station	Peak current for lead, X 10^{-7} (ppm)	Peak current for cadmium, X 10^{-7} (ppm)	Peak current for zinc, X 10^{-6} (ppm)
1	-5.256	-2.037	-1.231
2	-3.835	-1.749	-1.146
3	-3.382	-1.742	-1.130

Table 5.22: The concentrations of the lead, cadmium, and zinc from the calibration graphs.

Station	Concentration of lead (ppm)	Concentration of cadmium (ppm)	Concentration of zinc (ppm)
1	0.073	0.0051	0.0125
2	0.047	0.0040	0.0110
3	0.039	0.0039	0.0105

Table 5.23: The concentrations of the lead, cadmium, and zinc in the river water (Sungai Penchala).

Station	Concentration of lead (ppm)	Concentration of cadmium (ppm)	Concentration of zinc (ppm)
1	0.122	0.0085	0.0208
2	0.078	0.0067	0.0183
3	0.065	0.0065	0.0175

In this project, the water samples are not filtered. So, the objective in this study is to determine the total concentrations of the metals in the water samples, including the suspended and dissolved metals.

From the Table 5.23, it can find that the concentrations of the three types of metals (lead, cadmium, and zinc) in the three stations are quite low. The DOE Interim National Water Quality Standards for Malaysia (Appendix V) show the natural level for the metals are liked the following:

(a) Lead - < 0.05 ppm;

(b) Cadmium - < 0.01 ppm;

(c) Zinc - < 5 ppm.

However, the procedure which has used to determine the metals in the river water is not so accurate, because the real concentration can only be obtained with the proper water monitoring program continuously. Furthermore, the monitoring program requires more stations to be experimented.

Finally, the DPSV technique has successfully determined the concentration of the metals (lead, cadmium, and zinc) in Sungai Penchala. So, it is a useful technique for the trace metal analysis.