CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 The study of Visible Spectra of Ag-PAR, Cd-PAR, Cu-PAR, Ni-PAR, and Pb-PAR Complexes at Various pH.

The visible spectra of PAR alone at various pH is shown in Figure 4.1. From the results of these spectra, maximum absorbance of PAR occur in the pH range 5.94-9.98. In the strong basic solutions (pH value more than 10.92), the absorbance decreases and wavelenght shifts from the maximal value. The results of the study of Ag-PAR, Cd-PAR, Cu-PAR, Ni-PAR and Pb-PAR complexes at various pH value obtained from the procedure in the experimental section 3.5 are shown in Figures 4.2 to 4.6, respectively. Figure 4.2 shows that Ag-PAR complex can be formed not only in the slight acid solution but also in the basic solution (pH 5.94-12.04). Figure 4.3 indicates that Cd-PAR complex can be formed in the pH range 6.30-11.99. The tendency of the formed Cd-PAR complex has been increased directly with the pH value. Figures 4.4 to 4.6 illustrate the visible spectra of Cu-PAR, Ni-PAR, and Pb-PAR complexes. The inclination of formed complexes of these metals can be occurred as same as Cd-PAR complex. The maxima absorbance of Cu-PAR, Ni-PAR, and Pb-PAR complexes are shown at 11.96, 11.98, and 10.40 of pH value, respectively. By using these spectra, the pH for determination these metals are chosen at the pH range between 7-8. The reason for these selected pH value is that the interferences can occurred at higher pH value (in basic solution).

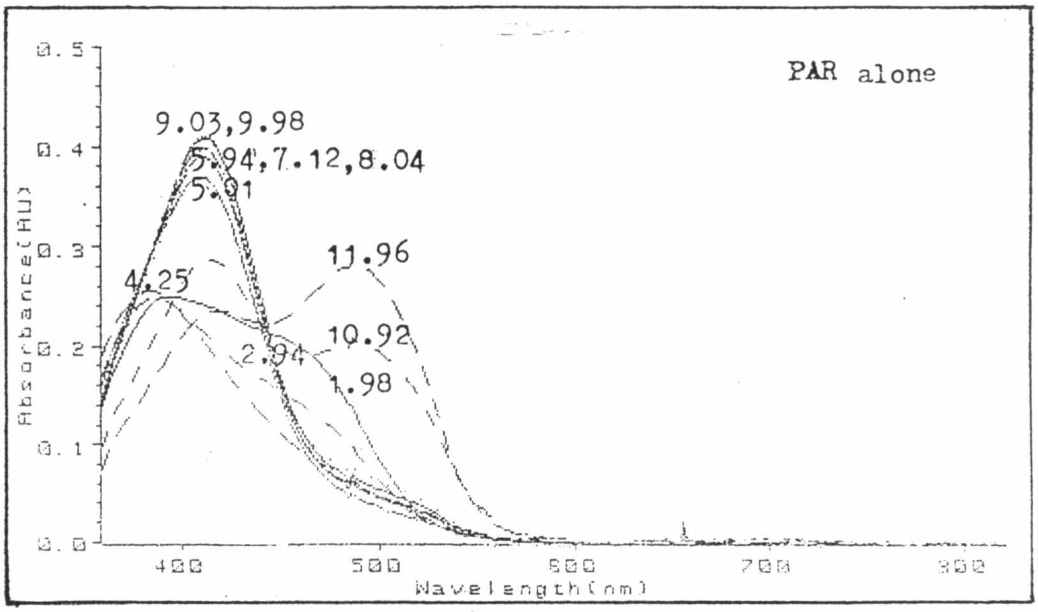

Figure 4.1 The visible spectra of PAR alone at various pH.

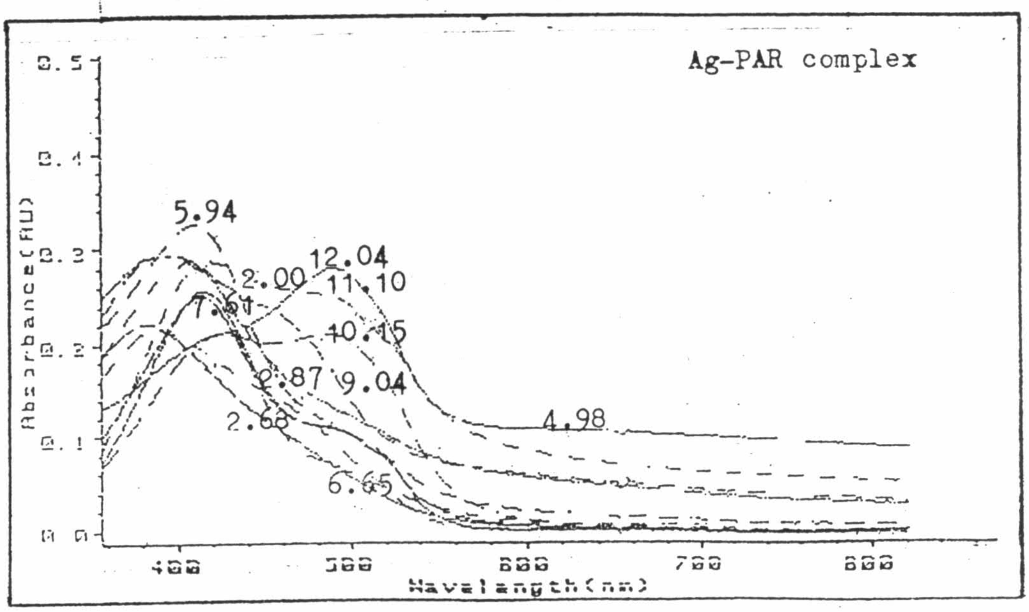

Figure 4.2 The Ag-PAR complex spectra at various pH

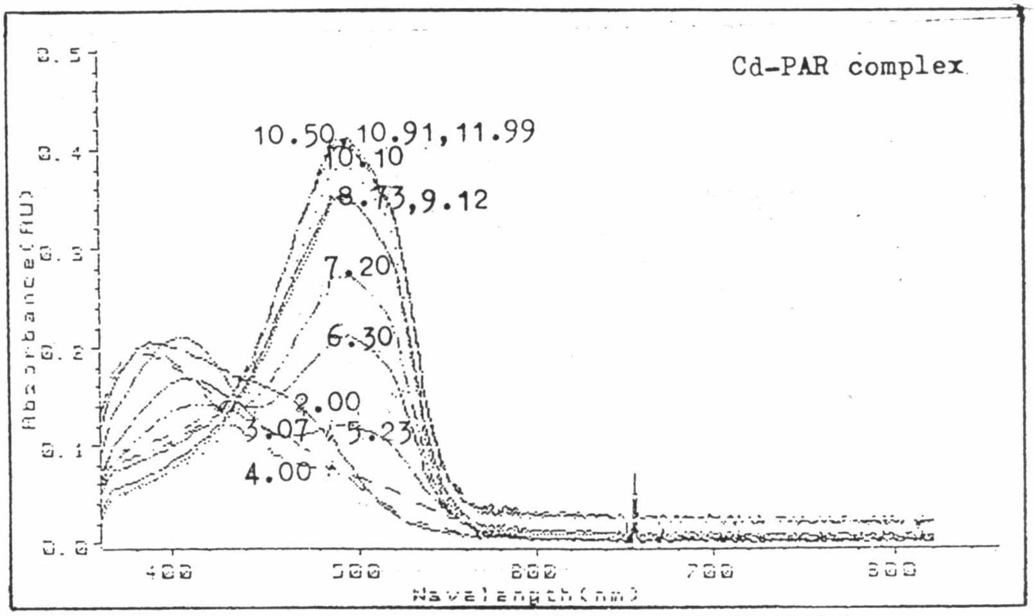

Figure 4.3 The Cd-PAR complex spectra at various pH

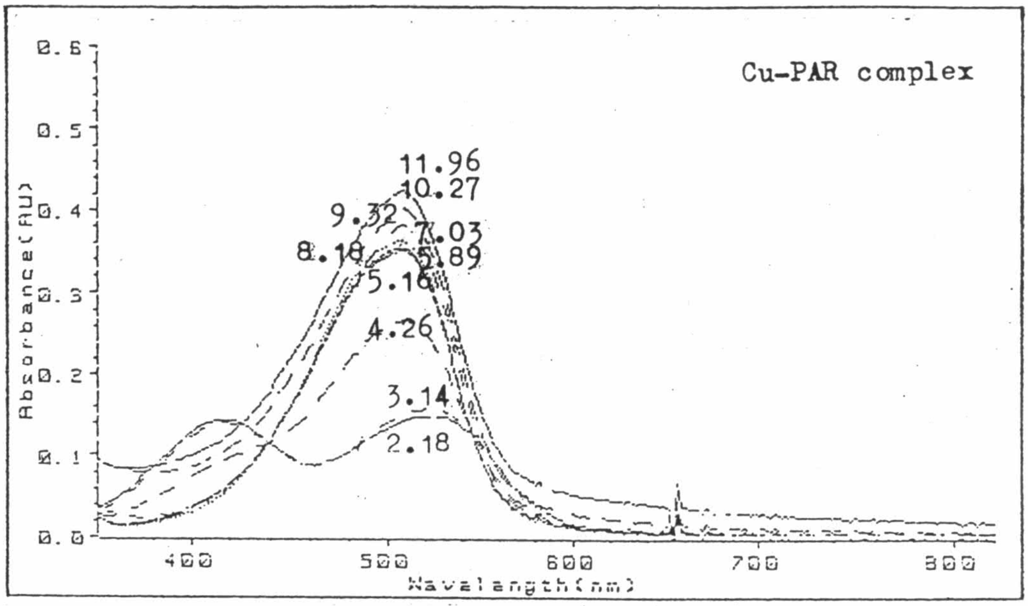

Figure 4.4 The Cu-PAR complex spectra at various pH

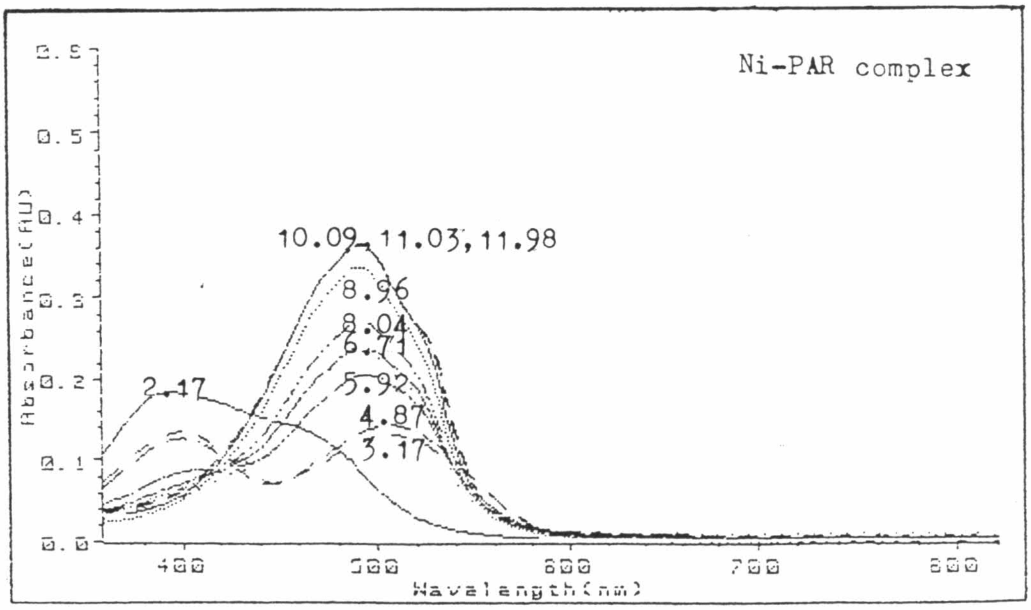

Figure 4.5 The Ni-PAR complex spectra at various pH

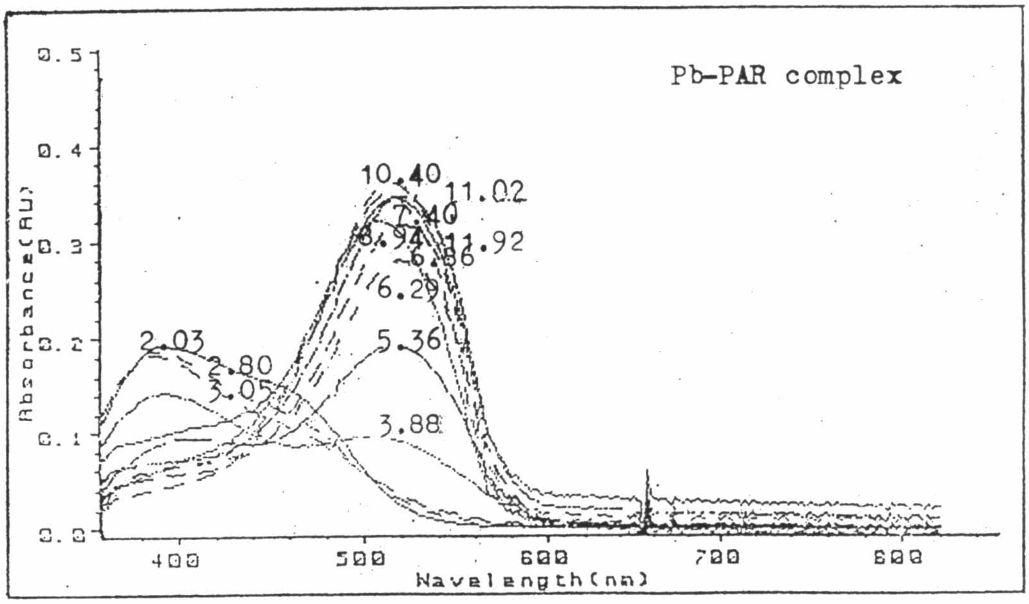

Figure 4.6 The Pb-PAR complex spectra at various pH

4.2 The Study of Sensitivity of Ag, Cd, Cu, Ni, and Pb on Shimadzu AA-670 Atomic Absorption Spectrometer.

The results of the study of sensitivity of Ag, Cd, Cu, Ni and Pb obtained from the procedure in the experimental section 3.6 are given in Tables 4.1 to 4.5, respectively. The graph plotted the concentration of each metal against absorbance are shown in Figures 4.7 to 4.11. The calculated value of sensitivity for Ag, Cd, Cu, Ni and Pb are 0.02, 0.03, 0.03, 0.10 and 0.12 ppm, respectively. Table 4.6 are summarized the working range of each metal and the sensitivity of each metal from the manual and from the experiment by using Shimadzu AA-670 atomic absorption spectrometer.

Table 4.1 The relationships between absorbance and concentration of Ag element for the study of sensitivity on Shimadzu AA-670 Atomic Absorption Spectrometer.

Concentration (ppm)	Absorbance
0.10	0.010
0.50	0.053
1.00	0.106
1.50	0.162
2.00	0.207
4.00	0.410

Regression Output

Constant	0.0029
Std Err of Y Est	0.0035
R Squared	0.9995
No. of Observations	6
Degree of Freedom	4
X Coefficient (s)	0.1023
Std Err of Coef.	0.0011
Sensitivity	0.02

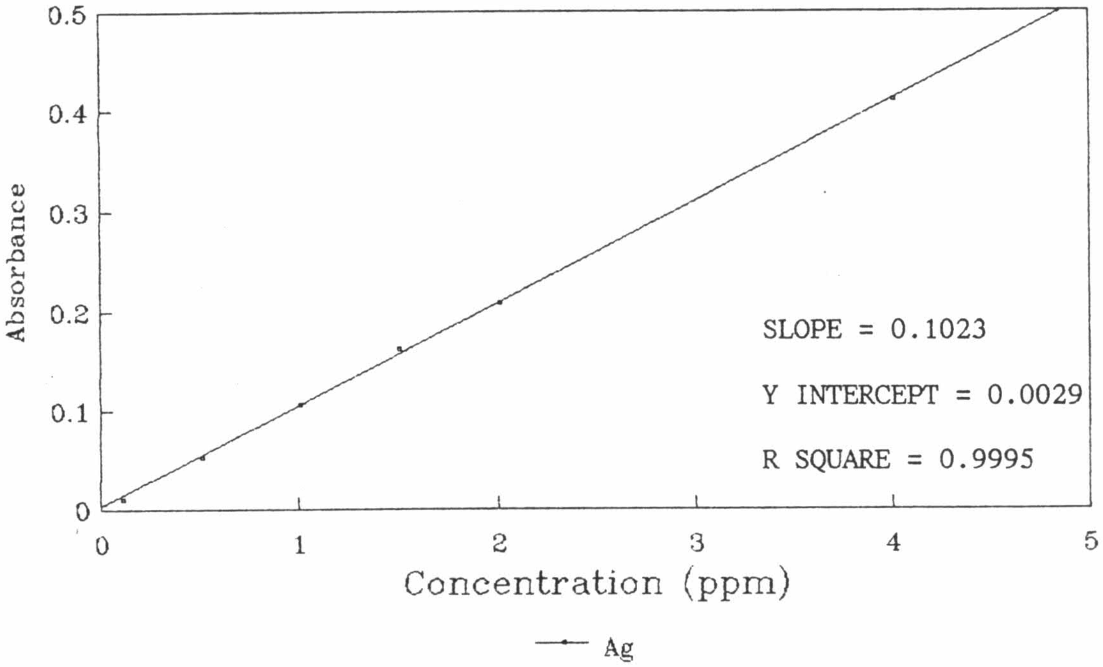

Figure 4.7 The calibration curve for the study of Ag

Table 4.2 The relationships between absorbance and concentration of Cd element for the study of sensitivity on Shimadzu AA-670 Atomic Absorption Spectrometer.

Concentration (ppm)	Absorbance
0.05	0.007
0.10	0.015
0.20	0.033
0.40	0.063
0.80	0.126
1.00	0.164

Regression Output

Constant	-0.0011
Std Err of Y Est	0.0022
R Squared	0.9991
No. of Observations	6
Degree of Freedom	4
X Coefficient (s)	0.1627
Std Err of Coef.	0.0025
Sensitivity	0.03

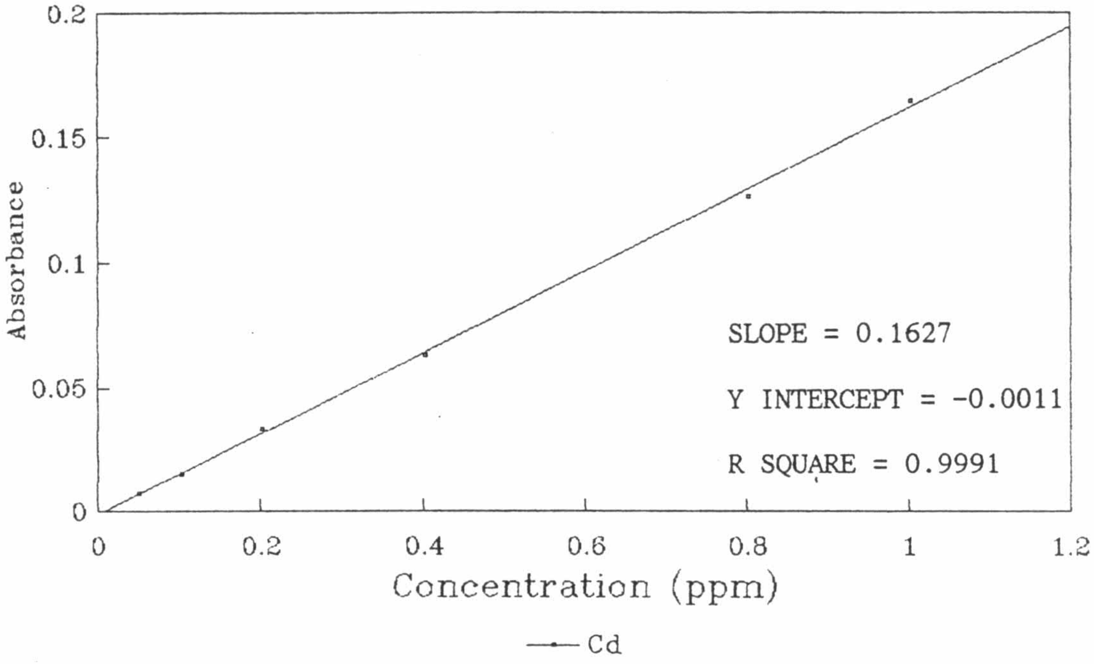

Figure 4.8 The calibration curve for the study of Cd

Table 4.3 The relationships between absorbance and concentration of Cu element for the study of sensitivity on Shimadzu AA-670 Atomic Absorption Spectrometer.

Concentration (ppm)	Absorbance
0.10	0.004
0.50	0.034
1.00	0.069
1.50	0.102
2.00	0.133
4.00	0.255

Regression Output

Constant	0.0026
Std Err of Y Est	0.0039
R Squared	0.9985
No. of Observations	6
Degree of Freedom	4
X Coefficient (s)	0.0639
Std Err of Coef.	0.0013
Sensitivity	0.03

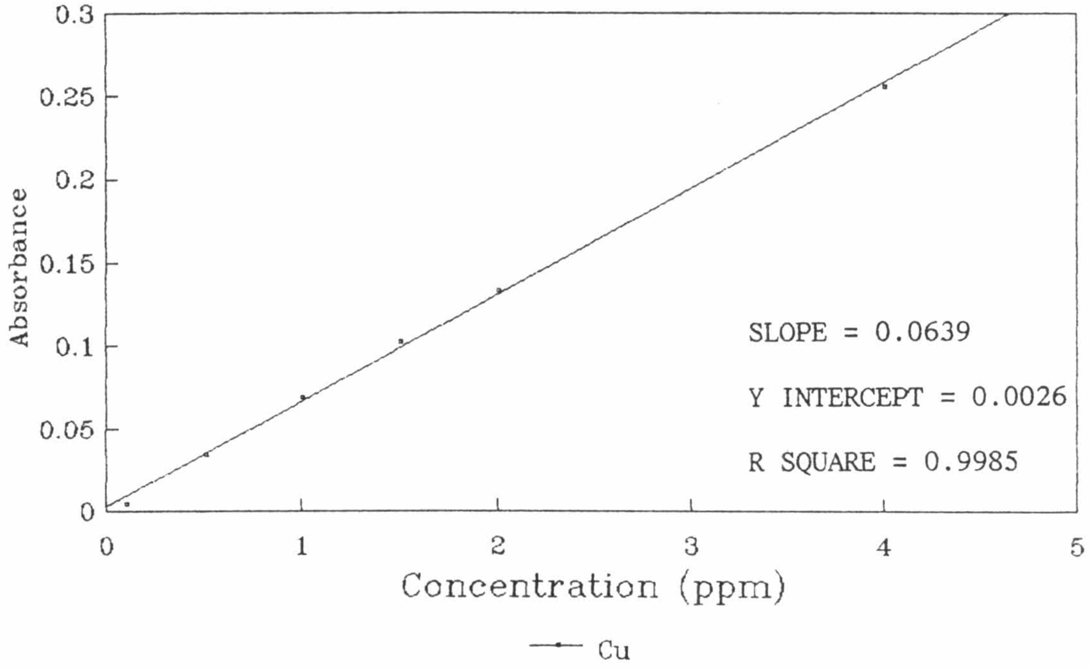

Figure 4.9 The calibration curve for the study of Cu.

Table 4.4 The relationships between absorbance and concentration of Ni element for the study of sensitivity on Shimadzu AA-670 Atomic Absorption Spectrometer.

Concentration (ppm)	Absorbance
0.10	0.006
0.50	0.031
1.00	0.064
1.50	0.090
2.00	0.118
4.00	0.227

Regression Output

Constant	0.0076
Std Err of Y Est	0.0035
R Squared	0.9992
No. of Observations	6
Degree of Freedom	4
X Coefficient (s)	0.0325
Std Err of Coef.	0.0004
Sensitivity	0.10

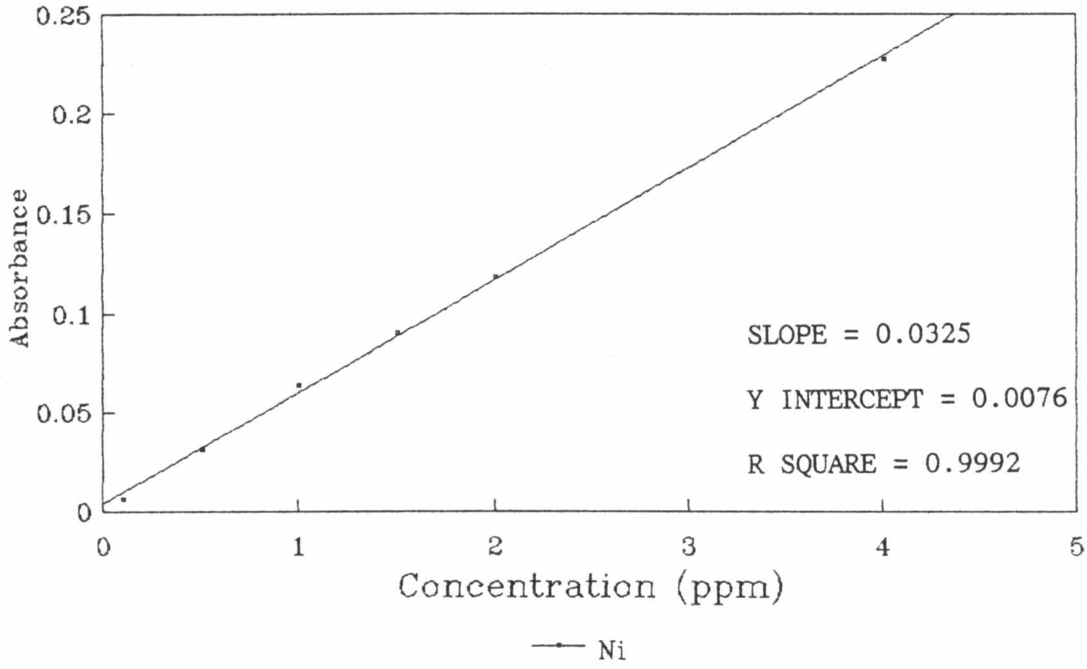

Figure 4.10 The calibration curve for the study of Ni

Table 4.5 The relationships between absorbance and concentration of Pb element for the study of sensitivity on Shimadzu AA-670 Atomic Absorption Spectrometer.

Concentration (ppm)	Absorbance
0.50	0.013
1.00	0.024
2.00	0.051
4.00	0.101
8.00	0.185
10.00	0.246

Regression Output

Constant	0.0015
Std Err of Y Est	0.0052
R Squared	0.9975
No. of Observations	6
Degree of Freedom	4
X Coefficient (s)	0.0240
Std Err of Coef.	0.0006
Sensitivity	0.12

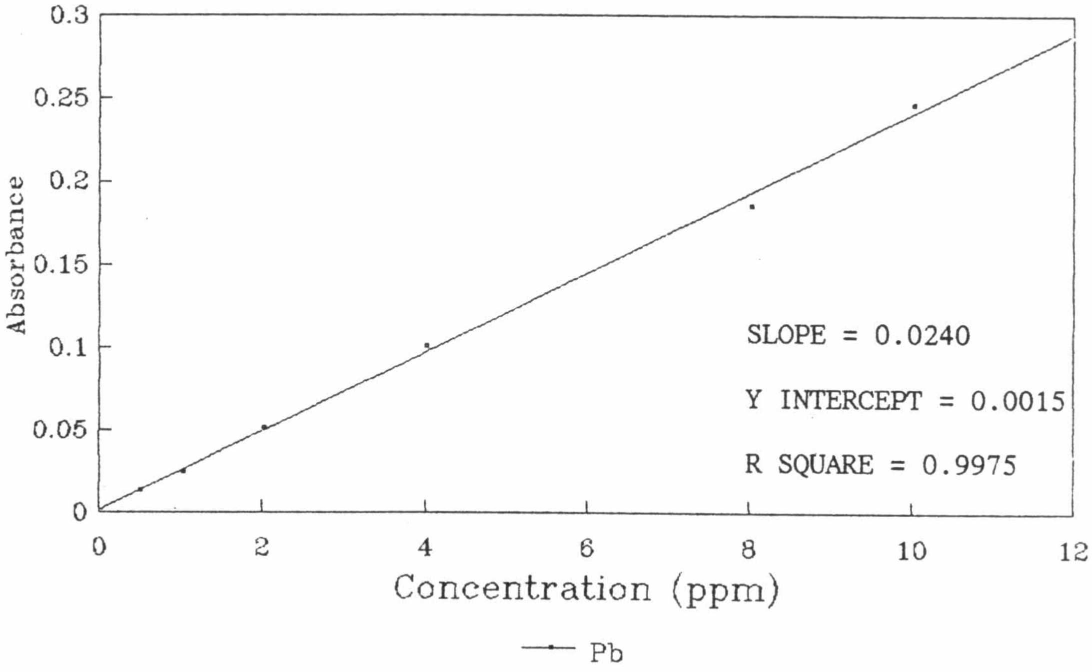

Figure 4.11 The calibration curve for the study of Pb

Table 4.6 The working range for each metal and the sensitivity from the instrumental manual and from the experiment.

Metal	working range from instrumental manual (ppm)	sensitivity from instrumental manual (ppm)	working range from experiment (ppm)	sensitivity from experiment (ppm)
Ag	0.10 - 10.00	0.06	0.10 - 4.00	0.02
Cd	0.10 - 3.00	0.02	0.05 - 1.00	0.03
Cu	0.10 - 15.00	0.09	0.10 - 4.00	0.03
Ni	0.20 - 20.00	0.10	0.10 - 4.00	0.10
Pb	0.30 - 25.00	0.20	0.50 - 10.00	0.12

4.3 The Study of Detection Limit of Ag, Cd, Cu, Ni, and Pb on Shimadzu AA-670 Atomic Absorption Spectrometer.

The results of the study of detection limit for Ag, Cd, Cu, Ni, and Pb in the experimental section 3.7 are summarized in Table 4.7. The detection limit for Ag, Cd, Cu, Ni, and Pb are 0.06, 0.03, 0.09, 0.05, and 0.03 ppm, respectively. Table 4.8 is shown the detection limit of these metals from the manual and from the experiment.
The sensitivity and the detection limit from the manual and from the experiment are summarized in Table 4.9.

Table 4.7 The results of the study of detection limit for Ag, Cd, Cu, Ni, and Pb

Metal	Concentration (ppm)	Absorbance	Signal
Ag	0.06	0.003	
Cd	0.03	0.003	
Cu	0.09	0.006	
Ni	0.05	0.003	
Pb	0.30	0.006	

Table 4.8 The detection limit from the manual and the experiment.

Metal	Detection Limit from manual (ppm)	Detection Limit from experiment (ppm)
Ag	0.10	0.06
Cd	0.03	0.03
Cu	0.10	0.09
Ni	0.20	0.05
Pb	0.30	0.30

Table 4.9 The sensitivity and the detection limit from the manual and from the experiment.

Metal	Sensitivity (ppm)		Detection Limit (ppm)	
	from manual	from experiment	from manual	from experiment
Ag	0.06	0.02	0.10	0.06
Cd	0.02	0.03	0.03	0.03
Cu	0.09	0.03	0.10	0.09
Ni	0.10	0.10	0.20	0.05
Pb	0.20	0.12	0.30	0.30

4.4 The Study of the Effect of Variables on Percentage of Recovery of C_{18} SPE Cartridge by Using Cd-PAR Complex and Cu-PAR Complex as the Models of the Study.

4.4.1 The study of nitric acid concentration effect

The results of the study of nitric acid concentration effect on percentage of recovery according to experimental section 3.10.1 are presented in Tables 4.10 to 4.11 for Cd and Cu, respectively. The graph plotted the recovery for Cd and Cu against concentration of nitric acid are shown in Figure 4.12. It is found that the suitable concentration of nitric acid obtained from this study is 1.0 M for both metals. Therefore, the concentration of nitric acid at 1.0 M is chosen as the optimal concentration for the study of each metal.

Table 4.10 The results of the study of the effect of nitric acid concentration on percentage of recovery by using Cd-PAR complex as a model

Conc.of HNO_3 (M)	Conc.of Cd before extraction* (ppm)	Conc.of Cd after extraction (ppm)	Recovery (%)
0.1	0.05	0.638	63.80
0.5	0.05	0.735	73.50
1.0	0.05	0.753	75.80
2.0	0.05	0.622	62.20
4.0	0.05	0.603	60.30

* **Remark:** The detection limit of Cd is 0.03 ppm.

Table 4.11 The results of the study of the effect of nitric acid concentration on percentage of recovery by using Cu-PAR complex as a model

Conc.of HNO_3 (M)	Conc.of Cu before extraction* (ppm)	Conc. of Cu after extraction (ppm)	Recovery (%)
0.1	0.02	0.378	94.50
0.5	0.02	0.406	101.50
1.0	0.02	0.411	102.75
2.0	0.02	0.410	102.50
4.0	0.02	0.404	101.10

* **Remark:** The detection limit of Cu is 0.09 ppm.

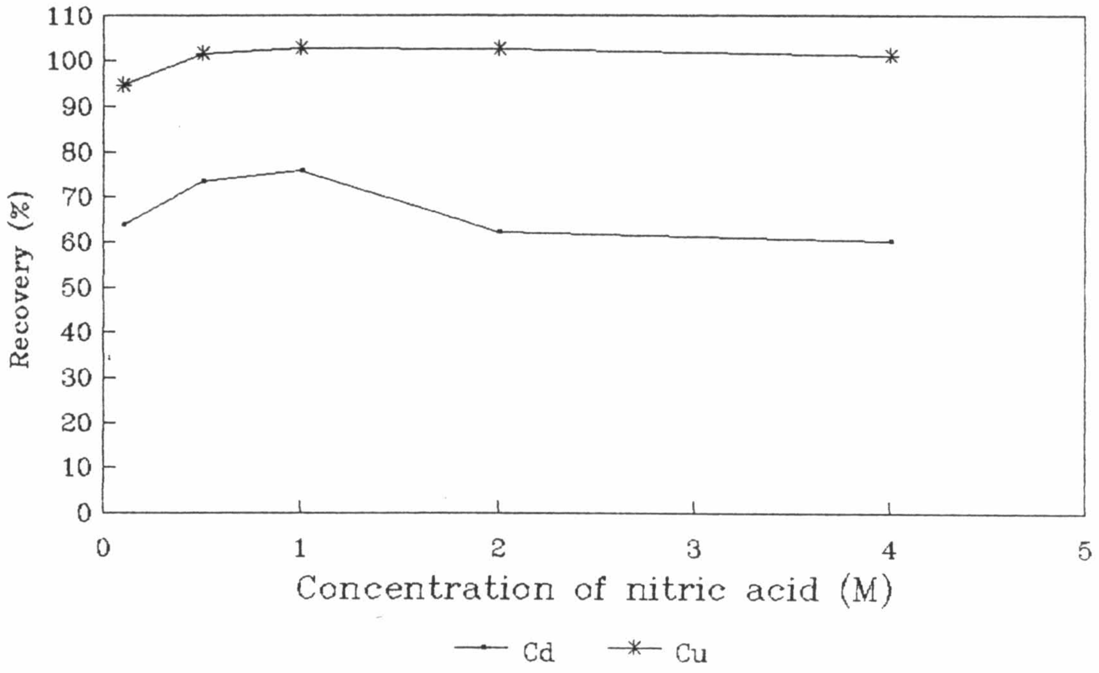

Figure 4.12 The effect of concentration of nitric acid on percentage of recovery by using Cd-PAR complex and Cu-PAR complex as the models

4.4.2 The study of nitric acid volume effect

The results of the nitric acid volume effect on percentage of recovery according to experimental section 3.10.2 are presented in Tables 4.12 to 4.13 for Cd and Cu, respectively. The graph plotted the recovery for Cd and Cu against volume of 1.0 M nitric acid are shown in Figure 4.13. It is found that the minimal volume of 1.0 M nitric acid employed in this study to obtain the maximal value of recovery is 4.0 mL for Cd and 3.0 mL for Cu. Hence, the volume of 1.0 M nitric acid at 4.0 mL is chosen as the optimal volume for the study of each metal.

Table 4.12 The results of the effect of volume of nitric acid solution on percentage of recovery by using Cd-PAR complex as a model

Volume of 1.0 M HNO_3 (mL)	Conc.of Cd before extraction* (ppm)	Conc. of Cd after extraction (ppm)	Recovery (%)
1.0	0.05	0.681	68.10
2.0	0.05	0.703	70.30
3.0	0.05	0.716	71.60
4.0	0.05	0.742	74.20
5.0	0.05	0.738	73.80

* **Remark:** The detection limit of Cd is 0.03 ppm.

Table 4.13 The results of the effect of volume of nitric acid solution on percentage of recovery by using Cu-PAR complex as a model

Volume of 1.0 M HNO_3 (mL)	Conc.of Cu before extraction* (ppm)	Conc. of Cu after extraction (ppm)	Recovery (%)
1.0	0.02	0.349	87.25
2.0	0.02	0.387	96.75
3.0	0.02	0.399	99.75
4.0	0.02	0.399	99.75
5.0	0.02	0.399	99.75

* **Remark:** The detection limit of Cu is 0.09 ppm.

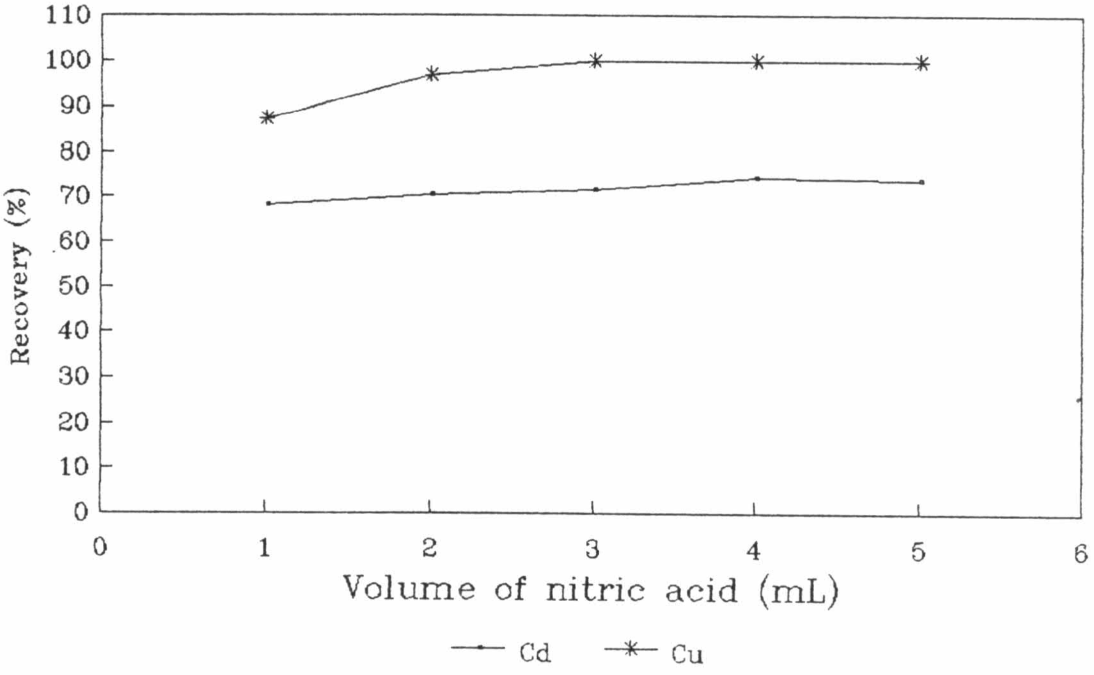

Figure 4.13 The effect of volume of 1.0 M nitric acid on percentage of recovery by using Cd-PAR complex and Cu-PAR complex as the models.

4.4.3 The study of pH effect

The results of the study of pH effect on percentage of recovery according to experimental section 3.10.3 are presented in Tables 4.14 to 4.15 for Cd and Cu, respectively. The gragh plotted the recovery for Cd and Cu against pH of the extracted solution are shown in Figure 4.14. It is found that the percentage of recovery of Cd increases in the basic solution (above pH 8.05) while the percentage of Cu decreases in the basic solution. The extracted solution should be controlled the pH value about 7-8.

Table 4.14 The results of the study of the effect of the pH value of the extracted solution on percentage of recovery by using Cd-PAR complex as a model

pH of complex	Conc.of Cd before extraction* (ppm)	Conc. of Cd after extraction (ppm)	Recovery (%)
5.02	0.05	0.698	69.80
6.07	0.05	0.747	74.70
7.03	0.05	0.739	73.90
8.05	0.05	0.812	81.20
9.07	0.05	0.852	85.20
10.01	0.05	0.877	87.70

* **Remark:** The detection limit of Cd is 0.03 ppm.

Table 4.15 The results of the study of the effect of the pH value of the extracted solution on percentage of recovery by using Cu-PAR complex as a model

pH of complex	Conc.of Cu before extraction* (ppm)	Conc. of Cu after extraction (ppm)	Recovery (%)
5.02	0.02	0.404	101.00
6.07	0.02	0.411	102.75
7.03	0.02	0.402	100.51
8.05	0.02	0.404	101.00
9.07	0.02	0.379	94.75
10.01	0.02	0.204	51.00

* **Remark:** The detection limit of Cu is 0.09 ppm.

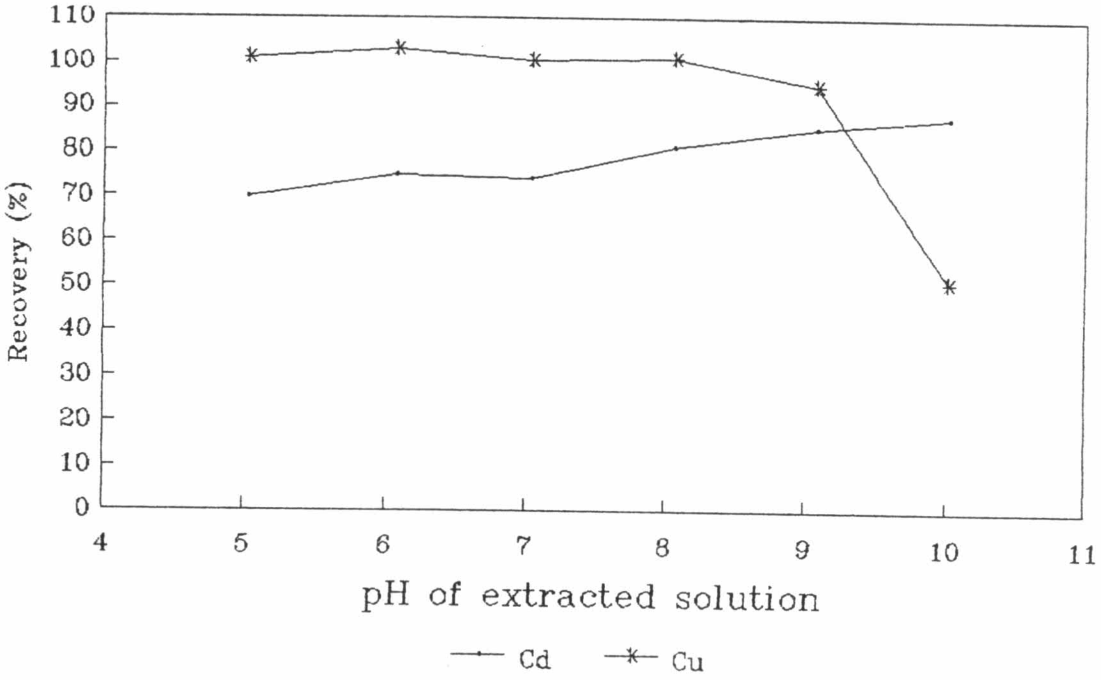

Figure 4.14 The effect of the pH value of extracted solution on percentage of recovery by using Cd-PAR complex and Cu-PAR complex as the models.

4.4.4 The study of the flow rate effect in the retention step

The results of the study of the flow rate effect in the retention step on percentage of recovery according to experimental section 3.10.4 are presented in Tables 4.16 to 4.17 for Cd and Cu, respectively. The gragh plotted the recovery for Cd and Cu against flow rate in the retention step are shown in Figure 4.15. It is found that the maximal flow rate obtained from this study is 3.0 mL/min for

Cd and 6.0 mL/min for Cu. To reduce the analysis times, the fastest flow rate is the best choice to select. By using the instrument in this laboratory, suitable flow rate at 6.0 mL/min is chosen as the optimal flow for the study of each metal because the usage of vacuum pump at higher flow rate is overload the motor.

Table 4.16 The results of the effect of flow rate in the retention step on percentage of recovery by using Cd-PAR complex as a model

flow rate on retention step (mL/min)	Conc.of Cd before extraction* (ppm)	Conc. of Cd after extraction (ppm)	Recovery (%)
2.0	0.05	0.786	78.60
3.0	0.05	0.804	80.40
4.0	0.05	0.762	76.20
6.0	0.05	0.787	78.70
8.0	0.05	0.786	78.60
10.0	0.05	0.780	78.00

* **Remark:** The detection limit of Cd is 0.03 ppm.

Table 4.17 The results of the effect of flow rate in the retention step on percentage of recovery by using Cu-PAR complex as a model

flow rate on retention step (mL/min)	Conc.of Cu before extraction* (ppm)	Conc. of Cu after extraction (ppm)	Recovery (%)
2.0	0.02	0.391	97.75
3.0	0.02	0.393	98.25
4.0	0.02	0.396	99.00
6.0	0.02	0.402	100.50
8.0	0.02	0.396	99.00
10.0	0.02	0.397	99.25

* **Remark:** The detection limit of Cu is 0.09 ppm.

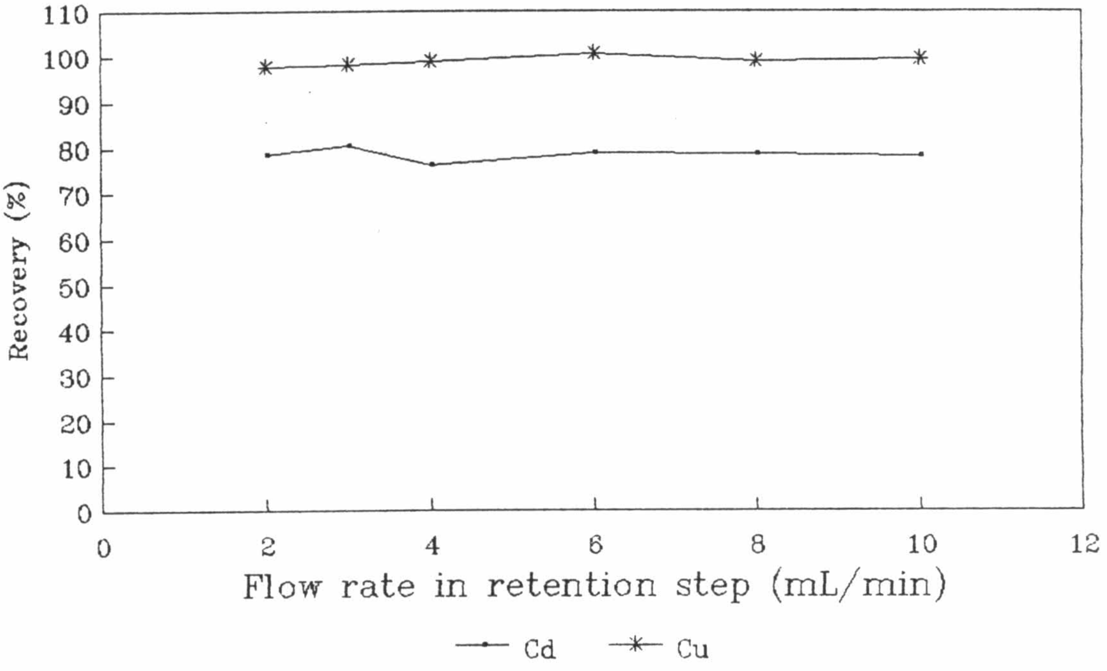

Figure 4.15 The effect of flow rate in the retention step on percentage of recovery by using Cd-PAR complex and Cu-PAR complex as the models.

4.4.5 <u>The study of the flow rate effect in the elution step</u>

The results of the study of the flow rate effect in the elution step on percentage of recovery according to experimental section 3.10.5 are presented in Tables 4.18 to 4.19 for Cd and Cu, respectively. The graph plotted the recovery for Cd and Cu against flow rate in the elution step are shown in Figure 4.16. It is found that the maximal flow in this study is 0.1 mL/min for Cd and 0.5

mL/min for Cu. To reduce the analysis times, the suitable flow rate at 6.0 mL/min is chosen as the optimal flow for the study of each metal.

Table 4.18 The results of the effect of flow rate in the elution step on percentage of recovery by using Cd-PAR complex as a model

flow rate on elution step (mL/min)	Conc.of Cd before extraction* (ppm)	Conc. of Cd after extraction (ppm)	Recovery (%)
0.1	0.05	0.809	80.90
0.5	0.05	0.780	78.00
1.5	0.05	0.805	80.50
3.0	0.05	0.760	76.00
6.0	0.05	0.745	74.50
9.0	0.05	0.731	73.10

* **Remark:** The detection limit of Cd is 0.03 ppm.

Table 4.19 The results of the effect of flow rate in the elution step on percentage of recovery by using Cu-PAR complex as a model

flow rate on elution step (mL/min)	Conc.of Cu before extraction* (ppm)	Conc. of Cu after extraction (ppm)	Recovery (%)
0.1	0.02	0.377	94.25
0.5	0.02	0.386	96.50
1.5	0.02	0.365	91.25
3.0	0.02	0.372	93.00
6.0	0.02	0.369	92.25
9.0	0.02	0.361	90.25

* **Remark:** The detection limit of Cu is 0.09 ppm.

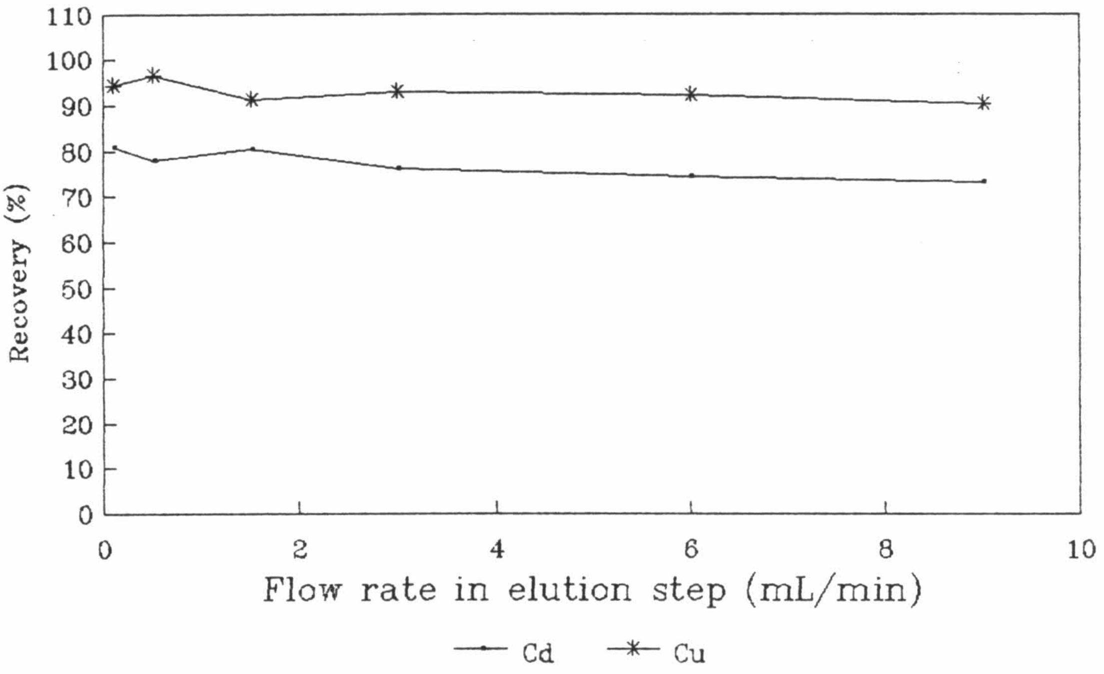

Figure 4.16 The effect of flow rate in the elution step on percentage of recovery by using Cd-PAR complex and Cu-PAR complex as the models.

4.4.6 The study of PAR concentration effect

The results of the study of PAR concentration effect on percentage of recovery according to experimental section 3.10.6 are presented in Tables 4.20 to 4.21 for Cd and Cu, respectively. The graph plotted the recovery for Cd and Cu against PAR concentration are shown in Figure 4.17. It is found that 10-fold PAR concentration than each metal (Cd and Cu) obtained from this study is sufficient.

For analysis of these metals as the mixture metals in water, the large excess of PAR concentration for these metals (over 10-fold) are recommended. In these research work, the concentration of PAR is chosen at 10-fold of metal as the optimal PAR concentration for the study of each metal.

Table 4.20 The results of the effect of concentration of PAR on percentage of recovery by using Cd-PAR complex as a model

Conc. of PAR $x10^5$ M	Conc.of Cd before extraction* (ppm)	Conc. of Cd after extraction (ppm)	Recovery (%)
2.0	0.05	0.763	76.30
4.0	0.05	0.779	77.90
8.0	0.05	0.771	77.10
20.0	0.05	0.828	82.80
40.0	0.05	0.812	81.20

* **Remark:** The detection limit of Cd is 0.03 ppm.

Table 4.21 The results of the effect of concentration of PAR on percentage of recovery by using Cu-PAR complex as a model

Conc. of PAR $\times 10^5$ M	Conc. of Cu before extraction (ppm)	Conc. of Cu after extraction (ppm)	Recovery (%)
0.8	0.02	0.398	99.50
1.6	0.02	0.395	98.75
3.2	0.02	0.416	104.00
8.0	0.02	0.401	100.25
16.0	0.02	0.399	99.75

* **Remark:** The detection limit of Cu is 0.09 ppm.

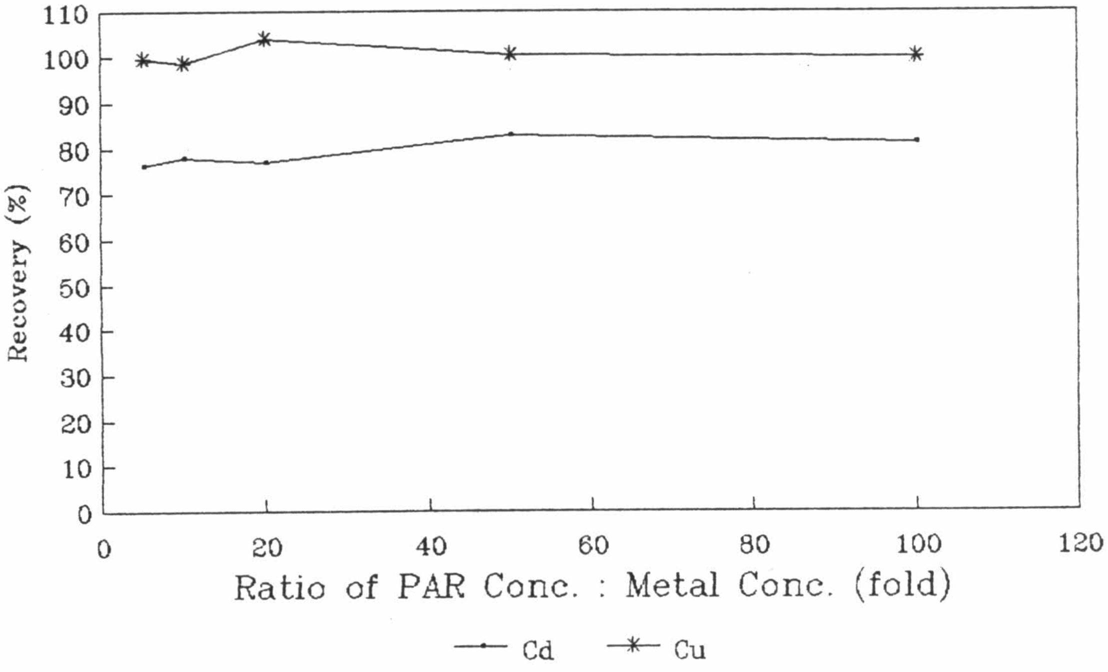

Figure 4.17 The effect of PAR concentration on percentage of recovery by using Cd-PAR complex and Cu-PAR complex as the models.

4.4.7 The study of sorbent mass

The results of the study of sorbent mass on percentage of recovery according to the experimental section 3.10.7 are presented in Tables 4.22 to 4.23 for Cd and Cu, respectively. The graph plotted the recovery for Cd and Cu against sorbent mass are shown in Figure 4.18. It is found that the minimal sorbent mass obtained from this study is 500 mg for Cd and 400 mg for Cu. Hence, the sorbent mass at 500 mg is chosen as the optimal mass for the study of each metal.

Table 4.22 The results of the effect of the sorbent mass on percentage of recovery by using Cd-PAR complex as a model

C_{18} SPE mass (mg)	Conc.of Cd before extraction* (ppm)	Conc. of Cd after extraction (ppm)	Recovery (%)
100	0.05	0.337	33.70
200	0.05	0.485	48.50
300	0.05	0.673	67.30
400	0.05	0.804	80.40
500	0.05	0.828	82.80

* **Remark:** The detection limit of Cd is 0.03 ppm.

Table 4.23 The results of the effect of the sorbent mass on percentage of recovery by using Cu-PAR complex as a model

C_{18} SPE mass (mg)	Conc. of Cu before extraction* (ppm)	Conc. of Cu after extraction (ppm)	Recovery (%)
100	0.02	0.304	76.00
200	0.02	0.386	96.50
300	0.02	0.391	97.75
400	0.02	0.408	102.00
500	0.02	0.395	98.75

* **Remark:** The detection limit of Cu is 0.09 ppm.

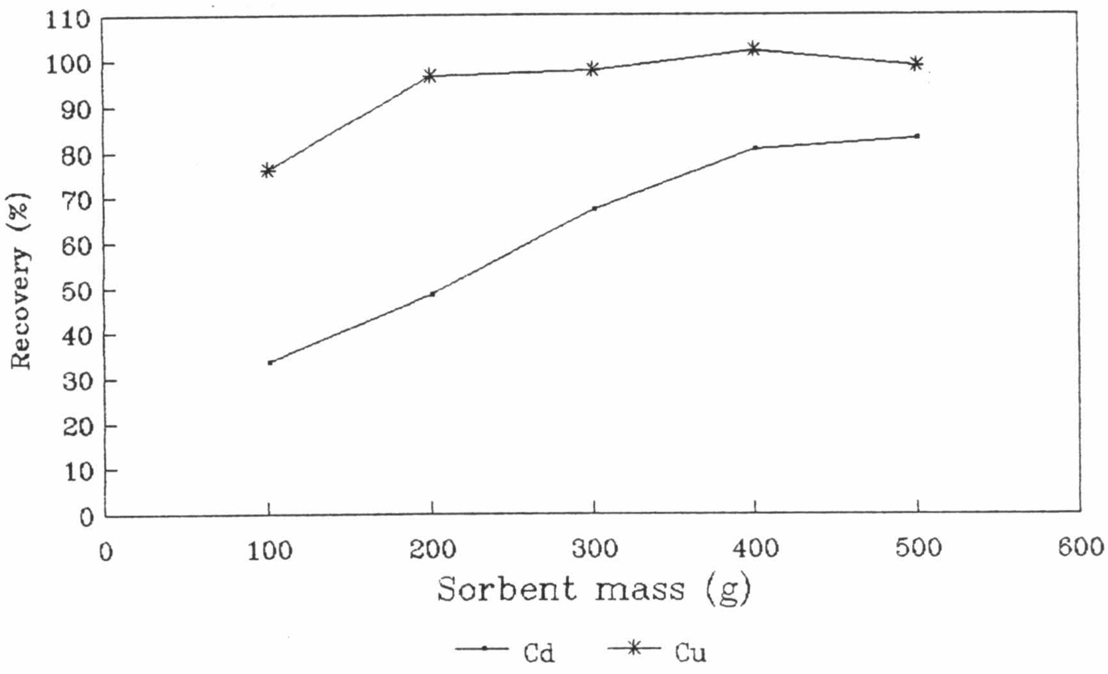

Figure 4.18 The effect of sorbent mass on percentage of recovery by using Cd-PAR complex and Cu-PAR complex as the models.

The suitable conditions for determination each metal can be performed by using the selected conditions that are summarized in Table 4.24.

Table 4.24 The suitable conditions for determination Cd and Cu by using Cd-PAR complex and Cu-PAR complex as the models and the selected conditions for each metal

Conditions	Determination of Cd by using Cd-PAR complex	Determination of Cu by using Cu-PAR complex	Selected Conditions for each metal
HNO_3 conc.	1.0 M	1.0 M	1.0 M
HNO_3 volume	3.0 mL	4.0 mL	4.0 mL
pH of extrated Solution	increases in the basic solution	decreases in the basic solution	7-8
flow rate in retention step	3.0 mL/min	6.0 mL/min	6.0 mL/min
flow rate in elution step	0.1 mL/min	0.5 mL/min	6.0 mL/min
PAR conc. per metal conc.	10 fold	10 fold	10 fold
Sorbent mass	500 mg	400 mg	500 mg

4.5 The Study of Precision on C_{18} SPE cartridges for Determination Ag, Cd, Cu, Ni, and Pb as a Single Component and as the Mixture Components.

The results of the study of precision on C_{18} SPE cartridges for determination each metal as a single component in water are shown in Tables 4.25 to 4.29. The precision data of these metals on C_{18} SPE cartridges are summarized in Table 4.30. The average recoveries of Ag, Cd, Cu, Ni, and Pb are 81.82, 84.81, 96.08, 95.36, and 81.64, respectively. The percentage of relative standard deviation of Ag, Cd, Cu, Ni, and Pb are 3.11, 3.47, 1.53, 1.48, and 1.01, respectively.

The results of the study of precision on C_{18} SPE cartridges for determination each metal as the mixture components in water are shown in Table 4.31. The average recoveries of Ag, Cd, Cu, Ni, and Pb are 81.05, 89.41, 100.86, 98.62, and 83.57, respectively. The percent RSD of Ag, Cd, Cu, Ni, and Pb are 4.97, 3.88, 1.15, 1.93, and 4.35, respectively.

Table 4.25 The results of Cd precision on C_{18} SPE cartridge for determination as a single component in water

Cartridges No.	Conc. of Cd before extraction (ppm)	Conc. of Cd after extraction (ppm)	Recovery (%)
1	0.05	0.871	87.10
2	0.05	0.841	84.10
3	0.05	0.874	87.40
4	0.05	0.875	87.50
5	0.05	0.818	81.80
6	0.05	0.810	81.00

average ($\bar{x}$) 84.81

% RSD 3.47

Table 4.26 The results of Cu precision on C_{18} SPE cartridge for determination as a single component in water

Cartridges No.	Conc. of Cu before extraction (ppm)	Conc. of Cu after extraction (ppm)	Recovery (%)
1	0.02	0.389	97.25
2	0.02	0.383	95.75
3	0.02	0.387	96.75
4	0.02	0.381	95.25
5	0.02	0.375	93.75
6	0.02	0.391	97.75

average ($\bar{x}$) 96.08

% RSD 1.53

Table 4.27 The results of Ag precision on C_{18} SPE cartridge for determination as a single component in water

Cartridges No.	Conc. of Ag before extraction (ppm)	Conc. of Ag after extraction (ppm)	Recovery (%)
1	0.10	1.571	78.55
2	0.10	1.656	82.80
3	0.10	1.695	84.75
4	0.10	1.686	84.30
5	0.10	1.590	79.50
6	0.10	1.621	81.05

average ($\bar{X}$) 81.82

% RSD 3.11

Table 4.28 The results of Ni precision on C_{18} SPE cartridge for determination as a single component in water

Cartridges No.	Conc. of Ni before extraction (ppm)	Conc. of Ni after extraction (ppm)	Recovery (%)
1	0.20	3.856	96.40
2	0.20	3.879	96.98
3	0.20	3.788	94.70
4	0.20	3.811	95.28
5	0.20	3.719	92.98
6	0.20	3.833	95.82

average ($\bar{x}$) 95.36

% RSD 1.48

Table 4.29 The results of Pb precision on C_{18} SPE cartridge for determination as a single component in water

Cartridges No.	Conc. of Pb before extraction (ppm)	Conc. of Pb after extraction (ppm)	Recovery (%)
1	0.50	8.156	81.56
2	0.50	8.269	82.69
3	0.50	8.129	81.29
4	0.50	8.191	81.91
5	0.50	8.028	80.28
6	0.50	8.211	82.11

average ($\bar{x}$) 81.64

% RSD 1.01

Table 4.30 The study of precision of each metal on C_{18} SPE cartidge for determination as a single component in water.

Metal	Study Conc. (ppm)	Detection limit (ppm)	Average recovery (%)	RSD (%)
Ag	0.05	0.06	81.82	3.11
Cd	0.05	0.03	84.81	3.47
Cu	0.02	0.09	96.08	1.53
Ni	0.20	0.05	95.36	1.48
Pb	0.50	0.30	81.64	1.01

Table 4.31 The results of precision of each metal on C_{18} SPE cartridge for determination as the mixture components in water

Metal		1	2	3	4	5	6	7	8	9	10	average %recovery	RSD (%)
Ag	Abs.	0.163	0.174	0.183	0.172	0.168	0.175	0.161	0.157	0.161	0.163		
	Conc.	1.572	1.683	1.770	1.666	1.626	1.695	1.552	1.516	1.552	1.578		
	%recovery	78.60	84.15	88.50	83.30	81.30	84.75	77.60	75.80	77.60	78.90	81.05	4.97
Cd	Abs.	0.142	0.144	0.149	0.140	0.146	0.138	0.132	0.142	0.143	0.137		
	Conc.	0.897	0.912	0.949	0.884	0.929	0.868	0.827	0.899	0.909	0.867		
	%recovery	89.70	91.20	94.90	88.40	92.90	86.80	82.70	89.90	90.90	86.70	89.41	3.88
Cu	Abs.	0.235	0.235	0.232	0.233	0.232	0.229	0.237	0.236	0.232	0.232		
	Conc.	4.061	4.075	4.006	4.027	4.014	3.945	4.103	4.083	4.019	4.012		
	%recovery	101.52	101.88	100.15	100.68	100.35	98.62	102.58	102.08	100.48	100.30	100.86	1.15
Ni	Abs.	0.212	0.223	0.215	0.211	0.215	0.209	0.211	0.213	0.215	0.211		
	Conc.	3.914	4.126	3.978	3.892	3.985	3.859	3.897	3.930	3.973	3.896		
	%recovery	97.85	103.15	99.45	97.30	99.62	96.48	97.42	98.25	99.32	97.40	98.62	1.93
Pb	Abs.	0.229	0.240	0.230	0.220	0.234	0.234	0.230	0.241	0.234	0.232		
	Conc.	8.041	8.514	8.078	7.666	8.250	8.848	8.362	8.821	8.548	8.441		
	%recovery	80.41	85.14	80.78	76.66	82.50	88.48	83.62	88.21	85.48	84.41	83.57	4.35

4.6 The Study of the Accuracy for Solid-Phase Extraction Technique.

The results of checking the accuracy for this technique are shown in Table 4.32. In this table, the percentage of error for directed aspiration to AAS and the usage of SPE technique prior to analysis by AAS have been compared. The percentage of error for directed aspiration for determination of Ag, Cd, Cu, Ni, and Pb are -18.18, -16.98, -5.88, -35.71, and -4.60, respectively. Whereas the percentage of error by using SPE technique for determination of Ag, Cd, Cu, Ni, and Pb are -15.98, -4.34, 0.29, -5.00, and -13.40, respectively (These values are directly calculated). The percentage of error can be calculated by concerning with the percent recovery of each metal (For Ag 81.05, Cd 89.41, Cu 100.86, Ni 98.62, Pb 83.57 %). The percentage of error for these metals by correcting with the percent recovery are 3.64, 6.98, 0.59, 3.69, and 3.63 for Ag, Cd, Cu, Ni, and Pb, respectively. By comparison of the percent error, the SPE technique is an excellent technique for determining trace amounts of these metals in water.

Table 4.32 The results of the checked accuracy for SPE technique

Metal		True value	Directed aspiration	SPE technique	
				Direct Calculation	Cal. concern with % recovery
Ag	Abs. from AAS		0.012	0.183	
	Conc. (ppm)	0.132	0.108	0.1109 ± 0.0007	0.1368
	Error (%)		-18.18	-15.98	3.64
Cd	Abs. from AAS		0.007	0.125	
	Conc. (ppm)	0.053	0.044	0.0507 ± 0.0007	0.0567
	Error (%)		-16.98	-4.34	6.98
Cu	Abs. from AAS		0.012	0.169	
	Conc. (ppm)	0.170	0.160	0.1705 ± 0.0013	0.1690
	Error (%)		-5.88	0.29	-0.59
Ni	Abs. from AAS		0.006	0.127	
	Conc. (ppm)	0.168	0.108	0.1596 ± 0.0007	0.1618
	Error (%)		-35.71	-5.00	-3.69
Pb	Abs. from AAS		0.012	0.154	
	Conc. (ppm)	0.435	0.415	0.3767 ± 0.0007	0.4508
	Error (%)		-4.60	-13.40	3.63

4.7 The Determination of Heavy Metals in Real Water Samples.

Six collected water samples are analyzed by SPE technique that is developed in this study. The results of the unknown water samples are shown in Table 4.33. For determination these collected water samples, Ag, Cd and Pb are not detectable whereas Cu and Ni can be detected by using SPE technique.

Table 4.33 The results of determination of Ag, Cd, Cu, Ni and Pb in real water samples

Sample	Ag		Cd		Cu		Ni		Pb	
	Conc.AAS (ppm)	Conc.SPE (ppm)	Conc.AAS (ppm)	Conc.SPE (ppm)	Conc.AAS (ppm)	Conc.SPE (ppm)	Conc.AAS (ppm)	Conc.SPE (ppm)	Conc.AAS (ppm)	Conc.SPE (ppm)
A	nd	nd	nd	nd	nd	0.0128	nd	0.0033	nd	nd
B	nd	nd	nd	nd	nd	0.0358	nd	0.0111	nd	nd
C	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
D	nd	nd	nd	nd	nd	nd	nd	0.0027	nd	nd
E	nd	nd	nd	nd	nd	0.0058	nd	0.0057	nd	nd
F	nd	nd	nd	nd	nd	0.0087	nd	0.0034	nd	nd

Remark : **A** represents Purist-drinking water

B represents British Portacel-drinking water

C represents Tap water

D represents Rain water

E represents Chao Phya River water

F represents Chulalongkorn University Pool water

nd represents not detectable