

## CHAPTER 3

### RESULTS AND DISCUSSION

#### 3.1 Analytical characteristics of the method

##### 3.1.1 Precision

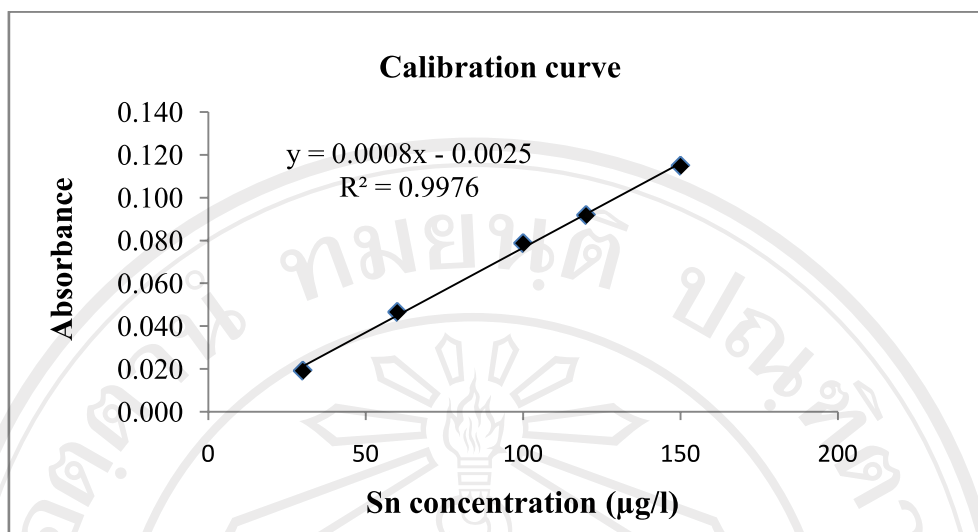
The precision of the GFAAS instrument was studied by repeating the measurement of 100 ppb standard solutions ten times. The results obtained are shown in **Table 3.1**. The results exhibited that the precision with replicate injections, expressed as the relative standard deviation (%RSD), was found to be 2.28 %. This indicated that the GFAAS instrument provided good repeatability (less than 5% RSD) for tin under the optimum conditions. The calculation of detection limit value and relative standard deviation (%RSD) value are shown in Appendix C. The calibration curve was programmatic generated by graphite furnace atomic absorption spectrometry (GFAAS) system. The calibration curve was plotted between the absorbance and the concentrations of tin(IV). The linear range of calibration curve was in the range of 30-150  $\mu\text{g/l}$ . As shown in **Table 3.2** and **Figure 3.1**, the obtained calibration equation was  $y = 0.0008x - 0.0025$  and  $R^2$  was 0.9976. The sensitivity defined as the slope of regression line was  $0.0008 \text{ ppb}^{-1}$ . The calibration curves for determination of tin by GFAAS are shown in Appendix A.

**Table 3.1** The precision of GFAAS instrument for Sn analysis

No.	Abs. of Sn 100 µg/l
1	0.0770
2	0.0762
3	0.0750
4	0.0787
5	0.0787
6	0.0807
7	0.0787
8	0.0780
9	0.0805
10	0.0791
Mean	0.0783
SD	0.00179
%RSD	2.28

**Table 3.2** The absorbance of tin concentration by GFAAS

Sn concentration (µg/l)	Absorbance
0.2% HNO <sub>3</sub>	0.0013
30	0.0192
60	0.0466
100	0.0787
120	0.0918
150	0.1148



**Figure 3.1** The calibration curve of tin determination

### 3.1.2 Limit of detection

The limit of detection (LOD) of the proposed method for the determination of Sn was studied under optimal experimental conditions after application of the preconcentration procedure to blank solution of 0.2% HNO<sub>3</sub> ten times. The results are shown in **Table 3.3**. The detection limit of Sn based on ten times the standard deviations of the blank was 2.57 µg/l. The calculation of detection limit value is shown in Appendix C.

**Table 3.3** Absorbance obtained from blank solution

No.	Abs. of 0.2% HNO <sub>3</sub>
1	-0.0012
2	0.0008
3	-0.0011
4	-0.0004
5	-0.0007
6	-0.0005
7	-0.0017
8	-0.0005
9	-0.0007
10	-0.0010
Mean	-0.0007
SD	0.0006
Slope	0.0007
Detection limit (µg/l)	2.57

### 3.1.3 Accuracy

The method was applied to analysis of wastewater samples. To estimate the accuracy of the procedure, different amounts of the investigated Sn(IV) was spiked with a 80 µg/l of standard solution to 100 ml wastewater sample. The resulting solutions were submitted to preconcentration procedure. Sn(IV) was determined by GFAAS. The recoveries of spiked analyte are given in **Table 3.4**. A good agreement

was obtained between the added and measured analyte amounts in wastewater samples. The results confirm the validity of the proposed method. The calculation of accuracy is shown in Appendix C.

**Table 3.4** The average recoveries of Sn(IV) analysis

Sample	Concentration of Sn(IV)		%Recovery*
	Added (µg/l)	Found (µg/l)*	
No. 1	-	150.90 ± 12.35	98.94 ± 9.31
	80	230.06 ± 14.83	
No. 2	-	129.90 ± 8.62	100.95 ± 4.66
	80	200.17 ± 13.88	
No. 3	-	125.76 ± 9.84	91.62 ± 4.94
	80	199.06 ± 11.91	
No. 4	-	140.36 ± 9.47	81.50 ± 2.76
	80	205.56 ± 9.18	
No. 5	-	200.00 ± 26.46	84.72 ± 11.85
	80	267.78 ± 19.32	
No. 6	-	159.29 ± 17.77	88.67 ± 3.17
	80	230.22 ± 17.89	
No. 7	-	205.00 ± 4.33	81.25 ± 7.65
	80	270.00 ± 8.66	
No. 8	-	133.33 ± 14.43	89.58 ± 7.37
	80	203.33 ± 12.83	

\*Mean ± SD (N=3)

### 3.2 Optimization of speciation method

The method for speciation of Sn (II) and Sn(IV) ions was developed using solid phase extraction and determined by GFAAS. The solid phase extraction for speciation of tin was used Amberlite IRA-400 resin. Amberlite IRA-400 resin was packed into a short glass column. The performance of column method was tested with model solution before its application to the real samples. Sn(IV) was eluted by NaOH solution. The analyte in eluted solution was detected by GFAAS.

The solid phase extraction is also found very important place in the speciation studies of tin species. The ion exchange was widely employed in chemical separation procedure, because of its advantage of relative simplicity in the operation and high pre-concentration factor [6].

In order to perform the speciation of Sn from separated solution efficiently, several parameters that influence the separation efficiency should be studied and optimized. The analytical parameters including eluent concentration, flow rate, amount of resin, sample volume, eluent volume, time on adsorption of Sn(IV) and interfering ions were investigated for the quantitative recovery of Sn(IV).

#### 3.2.1 Effect of the HCl concentration on adsorption of Sn(II) and Sn(IV)

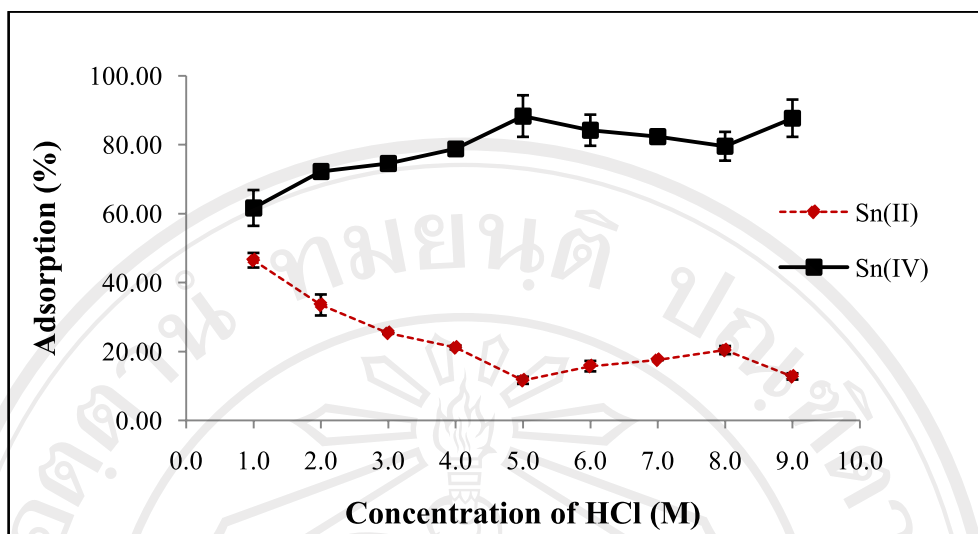
The acidity of the aqueous solution is one of the important factors affecting the adsorption of Sn(II) and Sn(IV) [11]. The effects of acidity on the adsorption efficiency of Sn(II) and Sn(IV) on the Amberlite IRA-400 resin were investigated between 1.0 and 9.0 mol/l HCl. From the results in **Table 3.5** and **Figure 3.2**, the maximum adsorption of Sn(IV) is at about 4.0-9.0 mol/l HCl and the adsorption of Sn(II) decreased gradually with the increasing of HCl concentration. As a result, the separation of Sn(II) and Sn(IV) has given the good result at 5.0 mol/L

HCl. In high concentration of HCl solution, not only the inorganic tin exists as Sn(II) and Sn(IV) but also organo-tin has the tendency to cleavage the C-Sn bond and form Sn(II) or Sn(IV) [40]. Sn(II) exists as  $\text{SnCl}_4^{2-}$  which has a regular tetrahedral configuration, whereas Sn(IV) exists as  $\text{SnCl}_6^{2-}$  and has an octahedral configuration. From the calculation methods of B3LYP/Lan12DZ, the bond length of  $\text{SnCl}_4^{2-}$  and  $\text{SnCl}_6^{2-}$  were 2.82 Å and 2.54 Å, respectively [41-43]. The bond length of  $\text{SnCl}_4^{2-}$  was longer than that of  $\text{SnCl}_6^{2-}$  [44]. Consequently,  $\text{SnCl}_6^{2-}$  has smaller size and higher charge density and the adsorption on the resin was easier. Thus, the separation of Sn(II) and Sn(IV) was achieved. The concentration of HCl at 5.0 mol/l was employed. The calculation of the percent adsorption is shown in Appendix C.

**Table 3.5** Effect of the HCl concentration on percent adsorption of Sn(II) and Sn(IV)

HCl concentration (mol/l)	%Adsorption*	%Adsorption*
	Sn(II)	Sn(IV)
1.0	46.50 ± 2.1	61.68 ± 2.8
2.0	33.52 ± 3.0	72.27 ± 0.3
3.0	25.40 ± 0.2	74.60 ± 0.2
4.0	21.18 ± 0.5	78.82 ± 0.5
5.0	11.66 ± 1.0	88.34 ± 6.0
6.0	15.77 ± 1.5	84.23 ± 4.5
7.0	17.60 ± 0.1	82.40 ± 0.1
8.0	20.43 ± 1.2	79.57 ± 4.2
9.0	12.79 ± 0.9	87.71 ± 5.4

\*Mean ± SD (N=3)



**Figure 3.2** Effect of the HCl concentration on percent adsorption of Sn(II) and Sn(IV)

### 3.2.2 Effect of the NaOH concentration on the recovery of Sn(IV)

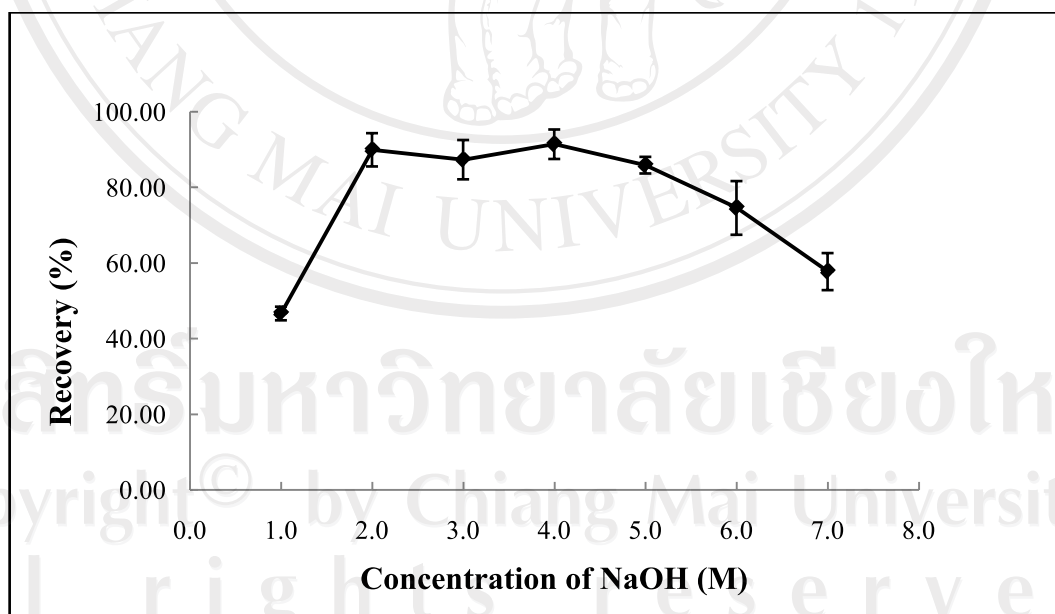
Using NaOH as the eluent, the effects of eluent concentration on the recovery of Sn(IV) were investigated in the range of 1.0-7.0 mol/l. From the results in **Table 3.6** and **Figure 3.3**, the recovery of Sn(IV) started to increase when the concentration of NaOH at 2.0 mol/l before starting to decrease when the concentration of NaOH at 5.0 mol/l. Thus, Sn(IV) could be eluted efficiently from the resin when the concentration of NaOH was between 2.0-5.0 mol/l. When the concentration of NaOH is higher than 5.0 M, the adsorption of Sn(IV) cannot be eluted completely with 3.0 ml of NaOH solution. The NaOH solution with the high concentration could be effected on the amount of detectable Sn(IV). It may be assumed that the matrix of NaOH solution has interfered the signal of Sn(IV) atom. Thus, the amount of detectable Sn(IV) has been decreased. Consequently, the percent recovery of Sn(IV) has been decreased when using high concentration NaOH solution. The calculation of recovery is shown in Appendix C.



**Table 3.6** Effect of the NaOH concentration on the percent recovery of Sn(IV)

NaOH concentration (mol/l)	%Recovery* Sn(IV)
1.0	46.67 ± 1.85
2.0	89.97 ± 4.48
3.0	87.36 ± 5.22
4.0	91.44 ± 3.93
5.0	85.90 ± 2.26
6.0	74.59 ± 7.16
7.0	57.75 ± 4.94

\*Mean ± SD (N=3)

**Figure 3.3** Effect of NaOH concentration on the percent recovery of Sn(IV)

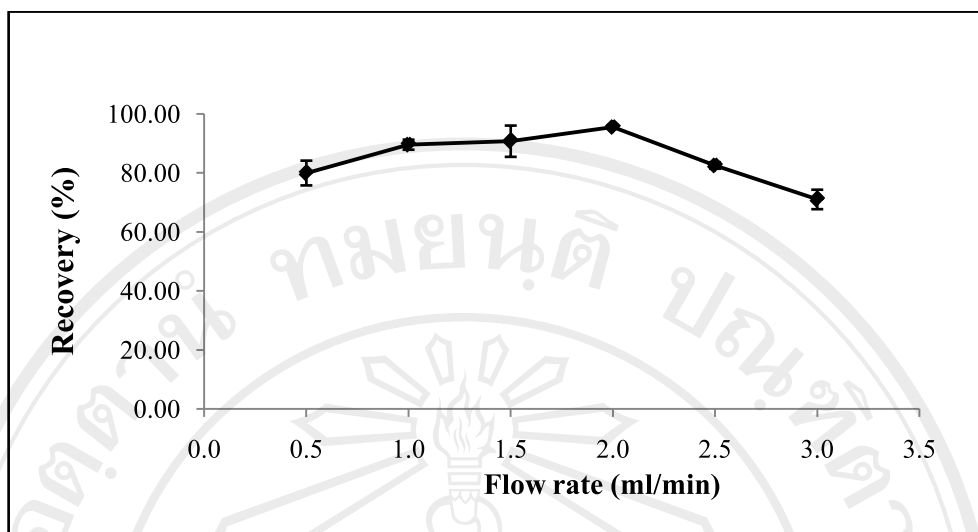
### 3.2.3 Effect of flow rate on the recovery of Sn(IV)

The flow rate of solution and eluent solution through the column is one of the factors affecting the duration of the determination. The flow rate through the column is directly related to the contact of the solution with the resin [45]. In this work, the effects of the flow rate of the sample and eluent solutions were studied. The flow rate of the sample and eluent solutions on the recovery of Sn(IV) were investigated in the range of 0.5-3.0 ml/min. From the results in **Table 3.7** and **Figure 3.4**, the flow rate of sample and eluent solutions had no obvious effect on the quantitative recovery of Sn(IV) in the range of 1.0-2.0 ml/min. A 2.0 ml/min was chosen as the flow rate of sample and eluent solutions in this study.

**Table 3.7** Effect of flow rate on the percent recovery of Sn(IV)

Flow rate (ml/min)	%Recovery* Sn(IV)
0.5	79.94 ± 4.23
1.0	89.54 ± 1.69
1.5	90.73 ± 5.33
2.0	95.57 ± 0.57
2.5	82.50 ± 1.07
3.0	70.99 ± 3.30

\*Mean ± SD (N=3)



**Figure 3.4** Effect of flow rate on the percent recovery of Sn(IV)

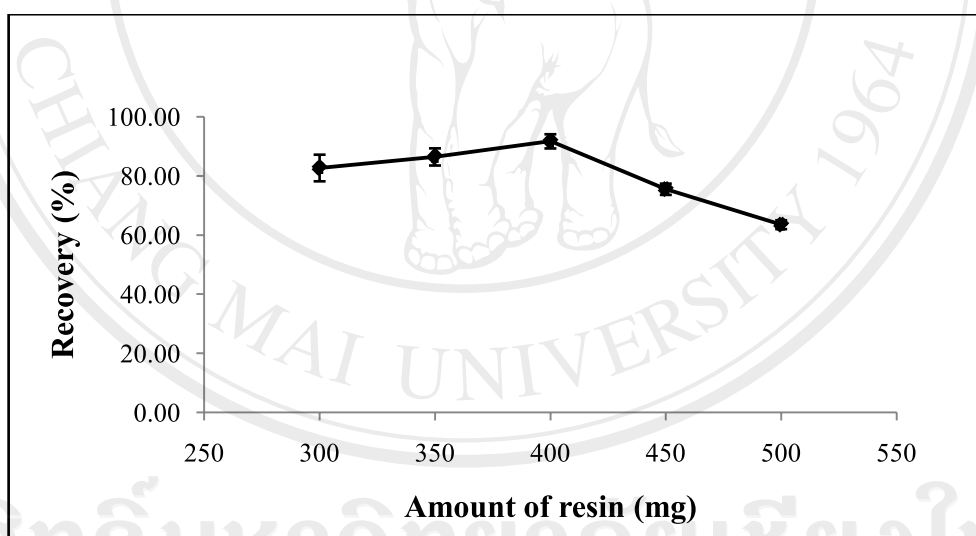
### 3.2.4 Effect of resin amount on the recovery of Sn(IV)

In the solid phase extraction studies, amount of resin is an important factor for the quantitative recoveries of the analytes [46]. The amount of resin is related to the capacity of resin. The total capacity of an ion exchange resin is defined as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin. The capacity may be expressed in terms of milliequivalents per dry gram of resin or in terms of millequivalents per milliliter of wet resin [47]. In this work, the effects of the amount of Amberlite IRA-400 resin on adsorption of Sn(IV) were studied from 300 to 500 mg. The results are shown in **Table 3.8** and **Figure 3.5**. The recovery values for Sn(IV) were found quantitatively in the resin amount of 400 mg. In all further studies, the short glass column was packed with 400 mg of Amberlite IRA-400 resin. If the amount of resin is more than 500 mg the adsorption analyte cannot be eluted completely with 3.0 ml of 2.0 mol/l NaOH.

**Table 3.8** Effect of resin amount on the percent recovery of Sn(IV)

Amount of resin (mg)	%Recovery* Sn(IV)
300	84.02 ± 3.25
350	87.10 ± 1.97
400	91.84 ± 1.31
450	78.44 ± 1.42
500	65.74 ± 0.91

\*Mean ± SD (N=3)

**Figure 3.5** Effect of resin amount on the percent recovery of Sn(IV)**3.2.5 Effect of sample volume on the recovery of Sn(IV)**

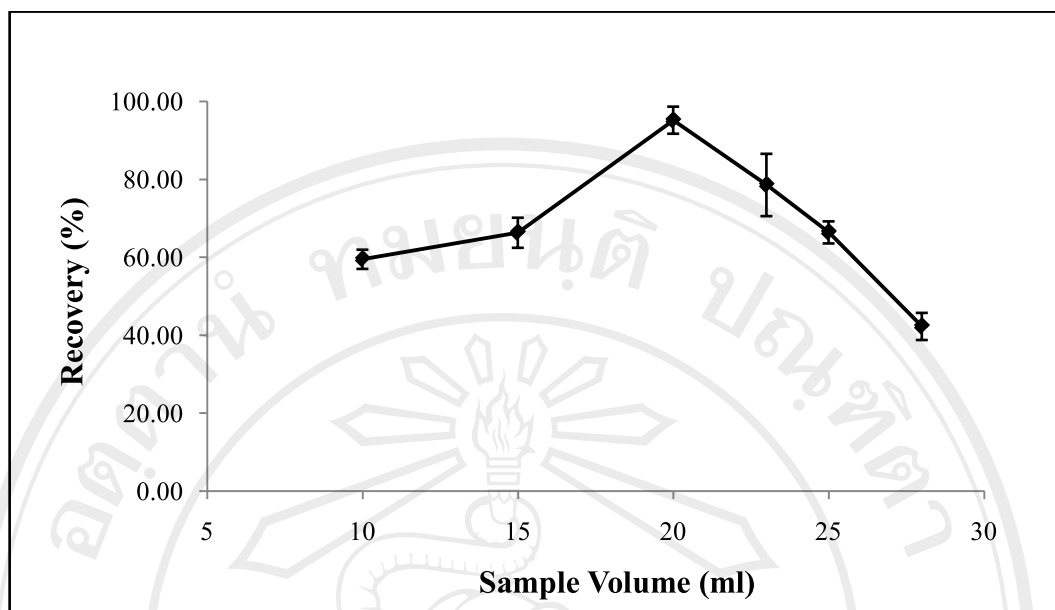
In order to study with high sample volumes, the effect of sample volumes on the recovery of Sn(IV) was also investigated with the sample volume from 10 ml to 30 ml by model solutions containing 0.2 µg/ml of Sn(IV). The results are shown in **Table 3.9** and **Figure 3.6**. Sn(IV) was recovered quantitatively in the range of 15-25

ml. The highest sample volume was 20 ml for analyte ion when the final volume was 3.0 ml. A 400 mg is a suitable amount of resin for 20 ml sample volume. In case of the sample volume is higher than 20 ml, the resin capacity is not sufficient for the analyte loading. Therefore, the obtained recovery is tended to decrease.

**Table 3.9** Effect of sample volume on the percent recovery of Sn(IV)

Sample volume (ml)	%Recovery* Sn(IV)
10	59.59 ± 2.47
15	66.31 ± 3.86
20	95.20 ± 3.47
23	78.57 ± 7.99
25	66.41 ± 2.83
28	42.27 ± 3.48

\*Mean ± SD (N=3)



**Figure 3.6** Effect of sample volume on the percent recovery of Sn(IV)

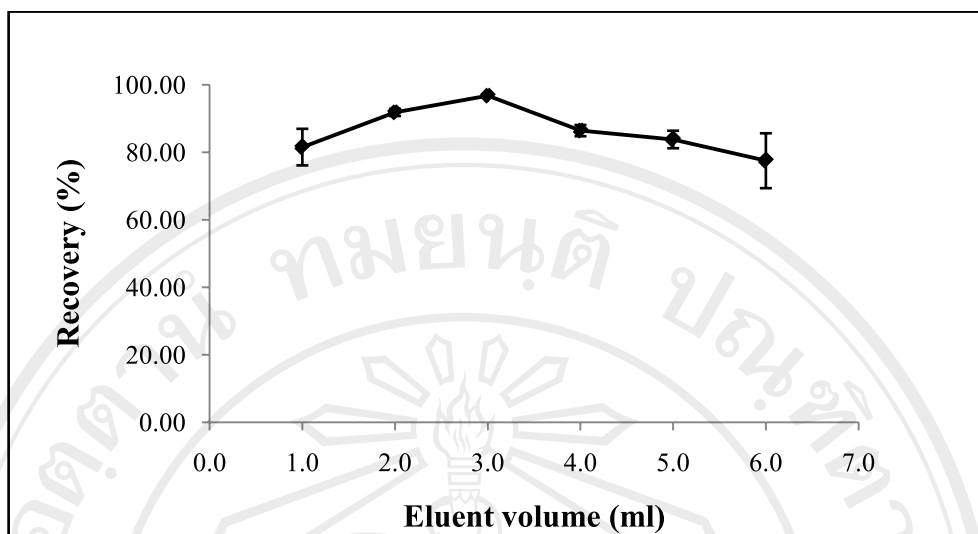
### 3.2.6 Effect of eluent volume on the recovery of Sn(IV)

The volume of the NaOH as eluent was also tested. The effects of eluent volume on recovery of Sn(IV) were varied from 1.0-6.0 ml. The results obtained are shown in **Table 3.10** and **Figure 3.7**. Sn(IV) was recovered quantitatively in the range of 2.0-5.0 ml. In this work, a 3.0 ml of 2.0 mol/l NaOH was used.

**Table 3.10** Effect of eluent volume on the percent recovery of Sn(IV)

Eluent volume (ml)	%Recovery* Sn(IV)
1.0	81.51 ± 5.42
2.0	91.79 ± 7.07
3.0	96.75 ± 0.16
4.0	86.41 ± 1.66
5.0	83.77 ± 2.59
6.0	77.49 ± 8.14

\*Mean ± SD (N=3)



**Figure 3.7** Effect of eluent volume on the percent recovery of Sn(IV)

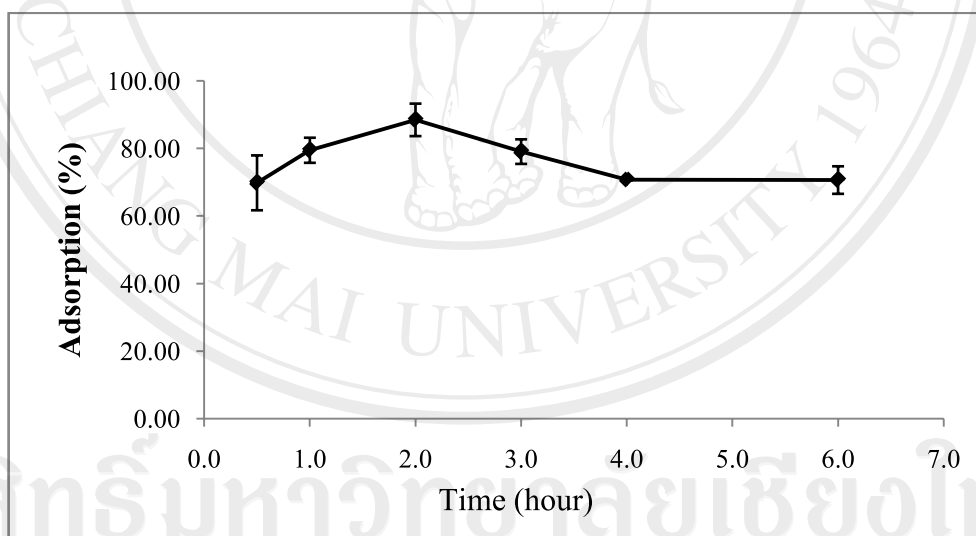
### 3.2.7 Effect of time on the adsorption of Sn(IV)

The adsorption time of Sn(IV) on Amberlite IRA-400 resin is necessary for the separation of Sn(IV). In order to ensure the reaction is complete and the separation of tin species is efficient, the effect of equilibration time was examined. The effect of time on the adsorption of Sn(IV) was investigated in the range of 0.5-6.0 hours. From the results in **Table 3.11** and **Figure 3.8**, it could be seen that the adsorption of Sn(IV) after 0.5 hour was increased gradually and the maximum adsorption of Sn(IV) was at 2.0 hours. Lengthened time, the adsorption of Sn(IV) was no longer increased. Thus, a 2.0 hours was chosen as the adsorption time in this work.

**Table 3.11** Effect of time on the percent adsorption of Sn(IV)

Time (hour)	%Absorption* Sn(IV)
0.5	69.85 ± 8.13
1.0	79.50 ± 3.71
2.0	88.50 ± 4.81
3.0	79.10 ± 3.64
4.0	70.78 ± 0.23
6.0	70.68 ± 4.08

\*Mean ± SD (N=3)

**Figure 3.8** Effect of time on the percent adsorption of Sn(IV)**3.2.8 Effect of interfering ions on the recovery of Sn(IV)**

In order to assess the possible analytical application of the recommended speciation preconcentration procedure on Amberlite IRA-400 resin, the effects of possible matrix ions in the wastewater samples on the determination of Sn(IV) were



investigated by adding known concentration of  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Cr}^{3+}$  ions into a model solution. The concentration of each interfering ion was investigated in the range of 1.0-1000 mg/l. The tolerance limits of the various interfering ions are shown in **Table 3.12** and **Table 3.13**. From the results, the recoveries of Sn(IV) and interfering ions were in the range of 83-93% and 84-104%, respectively. The acceptable recovery of the 1000  $\mu\text{g/l}$  analyte was in the range of 75-120% [48]. In this work, the concentration of Sn(IV) at 200  $\mu\text{g/l}$  was used for the studied of percent recovery. The percent recoveries have shown in the range of 83-93%. Thus, it could conclude that the determination of Sn(IV) was not interfered by interfering ions with the acceptable recovery value.

**Table 3.12** The recoveries of interfering ions

Interfering ion	Concentration (mg/l)	%Recovery
$\text{Cd}^{2+}$	1000	94
$\text{Cu}^{2+}$	1000	104
$\text{Ni}^{2+}$	1000	94
$\text{Pb}^{2+}$	1000	84
$\text{Cr}^{3+}$	1000	86
$\text{Fe}^{2+}$	1000	91

**Table 3.13** The concentration of interfering ions on the recovery of Sn(IV)

Concentration of interfering ion (mg/l)	%Recovery* Sn(IV)
0.1	83.35 ± 2.06
0.2	91.10 ± 7.03
1.0	84.71 ± 1.83
2.0	87.51 ± 4.86
3.0	87.28 ± 3.52
50	93.63 ± 2.59
250	86.98 ± 1.71
500	90.17 ± 2.31
1000	88.15 ± 7.83

\*Mean ± SD (N=3)

Summary of optimum conditions of speciation method for the determination of Sn(IV) are shown in **Table 3.14**.

**Table 3.14** Optimum conditions of speciation method

Parameter	Studied value	Optimum value
HCl concentration (mol/l)	1.0-9.0	5.0
NaOH concentration (mol/l)	1.0 -7.0	2.0
Flow rate (ml/min)	0.5- 3.0	2.0
Amount of resin (mg)	300-500	400
Sample volume (ml)	10- 30	20.0
Eluent volume (ml)	1.0- 6.0	3.0
Time on the adsorption (hour)	0.5- 6	2.0

### 3.3 Determination of Sn(II) and Sn(IV) ions in wastewater samples

The optimized method was applied to the determination of tin species in the wastewater samples. The wastewater samples were collected from various industrial sites in Chiang Mai and Lamphun, Thailand. A 20 ml of each wastewater sample was preconcentrated following the proposed method and the procedure explained in **Section 2.4.2**. Then, the analyte in solution samples was detected by graphite furnace atomic absorption spectrometry (GFAAS). The results are shown in **Table 3.15** and **Figure 3.9**. The determination of Sn(IV) in wastewater samples can be ordered as following: No. 7 > No. 5 > No. 6 > No. 1 > No. 4 > No. 8 > No. 2 > No. 3, respectively.

The concentrations of Sn(IV) in No. 7 and No. 5 wastewater samples are higher than those in the other samples. Because the No. 7 and No. 5 wastewater samples were collected from the electronic industries which used tin for manufacturing process. Thus, the concentrations of Sn(IV) in No. 7 and No. 5 samples were higher than those in the other samples.

The No. 8 sample was obtained from the same site with the No. 7 sample, but the No. 8 sample has passed the treatment step from treatment plant. Therefore, the result has shown that the concentration of Sn(IV) in No. 8 sample was lower than No. 7 sample. The No. 1, No. 2, No. 3, No. 4 and No. 6 samples were not collected from the electronic industries. So, the concentrations of Sn(IV) in No. 1, No. 2, No. 3, No. 4 and No. 6 samples were lower than that in No. 7 and No. 5 samples. The concentration of Sn(IV) in wastewater samples is different according to by the source of wastewater sample.

The concentration of Sn(II) was calculated by subtracting the content of Sn(IV) from total tin content. The concentration of Sn(II) was calculated by the equation below:

$$\text{Sn (II)} = \text{Total tin} - \text{Sn(IV)}$$

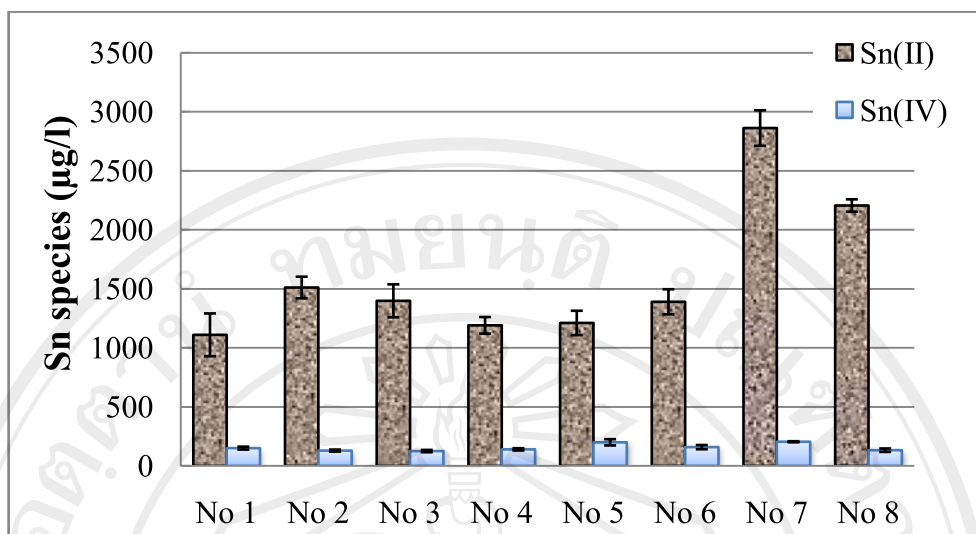
From the results, the concentrations of Sn(II) in studied wastewater samples were in the range of 1191.31-2863.00 µg/l.

**Table 3.15** Sn(II) and Sn(IV) in studied wastewater samples

Sample	Sn(II)* <sup>a</sup> (µg/l)	Sn(IV)* (µg/l)
No. 1	1110.81 ± 181.37	150.90 ± 12.35
No. 2	1511.71 ± 91.64	129.90 ± 8.62
No. 3	1398.90 ± 139.68	125.76 ± 9.84
No. 4	1191.31 ± 70.32	140.36 ± 9.47
No. 5	1211.67 ± 103.24	200.00 ± 26.46
No. 6	1390.67 ± 106.31	159.29 ± 17.77
No. 7	2863.00 ± 150.60	205.00 ± 4.33
No. 8	2206.67 ± 52.52	133.33 ± 14.43

\* Mean ± SD (N=3)

<sup>a</sup> Calculated by subtracting Sn(IV) from total Sn



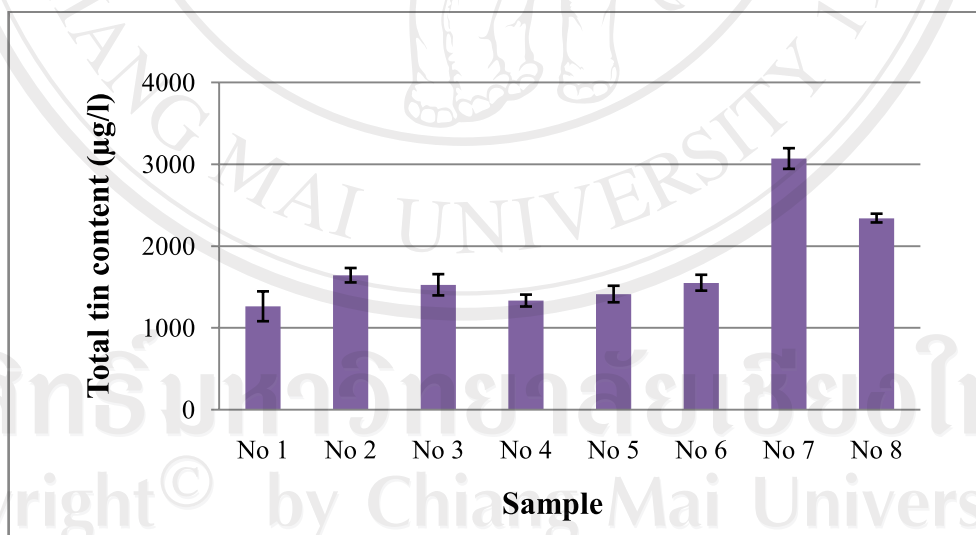
**Figure 3.9** The concentration of tin species in wastewater samples

### 3.4 Determination of total tin in wastewater samples

Total tin was determined after digestion and oxidizing Sn by the addition of concentrated nitric acid and  $H_2O_2$ . The oxidation procedure was performed by the procedure given by Yuan *et al.* [26] and the procedure explained in **Section 2.4.1**. The wastewater samples were collected from various industrial sites in the northern of Thailand. The No. 1, No. 2, No. 3 No. 4, No. 5 and No. 6 wastewater samples were collected from the industries in Chiang Mai and the No. 7 and No. 8 wastewater were collected from the Lamphun industrial estate. The results are given in **Table 3.16** and **Figure 3.10**, which indicated that the amounts of total tin in No. 7 wastewater samples were higher than those in No. 8, No. 2, No. 6, No. 3, No. 5, No. 4 and No. 1 wastewater samples, respectively. From the results, the concentrations of total tin in wastewater samples were between 1261.71 and 3068.00 µg/l.

**Table 3.16** The total Sn content in wastewater samples

Sample	Sn content* ( $\mu\text{g/l}$ )
No. 1	1261.71 $\pm$ 182.55
No. 2	1641.62 $\pm$ 88.07
No. 3	1524.67 $\pm$ 129.87
No. 4	1331.67 $\pm$ 72.86
No. 5	1411.67 $\pm$ 101.04
No. 6	1549.95 $\pm$ 97.03
No. 7	3068.00 $\pm$ 126.36
No. 8	2340.00 $\pm$ 53.54

\*Mean  $\pm$  SD (N=3)**Figure 3.10** The total content of Sn in wastewater samples.

### 3.5 Comparison of Sn(II) and Sn(IV) in wastewater samples

Naturally, tin can form a variety of both inorganic and organic compounds. Both Sn(II) and Sn(IV) could translate reciprocally. In the atmosphere, Sn(II) was oxidized to Sn(IV) and the oxidation gradually increased along with the time. In general, Sn(IV) is still the more stable oxidation state than Sn(II) [6]. As shown in **Table 3.17**, the concentrations of Sn(II) and Sn(IV) in studied wastewater samples are varied. Because the studied samples were collected from the different industrial sites and tin is applied for manufacturing in the various forms depending on the type of industry.

The ratio of Sn(II) and Sn(IV) in wastewater samples are shown in **Table 3.17**. From the results, the ratio of Sn(II) and Sn(IV) in wastewater samples were in the range of 6.0-16.6. The amount of Sn(II) was higher than that of Sn(IV). Comparison to other reports for the determination of Sn(IV), the amount of Sn(IV) in this proposed method is different from other results [5-6]. Because the samples in this method were collected from wastewater, while the samples of the other reports were collected from natural water. The amount of oxygen in wastewater sample was lower than those in the natural water samples. Oxygen which dissolves in water is performed as oxidizing agent. Generally, Sn(II) is oxidized to Sn(IV) when the amount of oxygen in water is high. Thus, the amount of Sn(IV) in natural water is higher than that of Sn(II). Sn(IV) is still the more stable oxidation state than Sn(II). Consequently, the amount of Sn(IV) in wastewater sample was lower than Sn(II), whereas the amount of Sn(IV) in natural water sample is higher than Sn(II).



**Table 3.17** The determination of tin species in wastewater samples

Sample	Sn(II)* <sup>a</sup>	Sn(IV)*	Total*	Ratio
	µg/l	µg/l	µg/l	Sn(II)/Sn(IV)
No. 1	1110.81 ± 181.37	150.90 ± 12.35	1261.71 ± 182.55	7.3
No. 2	1511.71 ± 91.64	129.90 ± 8.62	1641.62 ± 88.07	11.3
No. 3	1398.90 ± 139.68	125.76 ± 9.84	1524.67 ± 129.87	11.1
No. 4	1191.31 ± 70.32	140.36 ± 9.47	1331.67 ± 72.86	8.5
No. 5	1211.67 ± 103.24	200.00 ± 26.46	1411.67 ± 101.04	6.0
No. 6	1390.67 ± 106.31	159.29 ± 17.77	1549.95 ± 97.03	8.7
No. 7	2863.00 ± 150.60	205.00 ± 4.33	3068.00 ± 126.36	13.9
No. 8	2206.67 ± 52.52	133.33 ± 14.43	2340.00 ± 53.54	16.6

\* Mean ± SD (N=3)

<sup>a</sup> Calculated by subtracting Sn(IV) from total Sn

### 3.6 Comparison with other methods

Direct determinations of tin species in the real samples are difficult and limited.

The solid phase extraction is also found very important place in the speciation studies of tin species. Graphite furnace atomic absorption spectrometry (GFAAS) is a favorable method for the determination of tin at very low concentration, which has high sensitivity, selectivity and much less interference [6].

Comparison to other reports [19-20] for the preconcentration of tin, especially the conventional liquid-liquid extraction method, the proposed method (solid phase extraction) is characterized with simplicity, rapidity, selectivity, safety, low cost and high preconcentration factor. It is safe because of no additional dangerous solvents. In



addition, it uses very small amount of sample volume and solution during the preconcentration procedure.

In order to examine the reliability of the proposed method, the 80  $\mu\text{g/l}$  of Sn(IV) standard solution was spiked to wastewater sample. The results are shown in **Table 3.4**. A good agreement was obtained from the acceptable percent recovery which similar to the other reports. These results confirmed the validity of this proposed method.