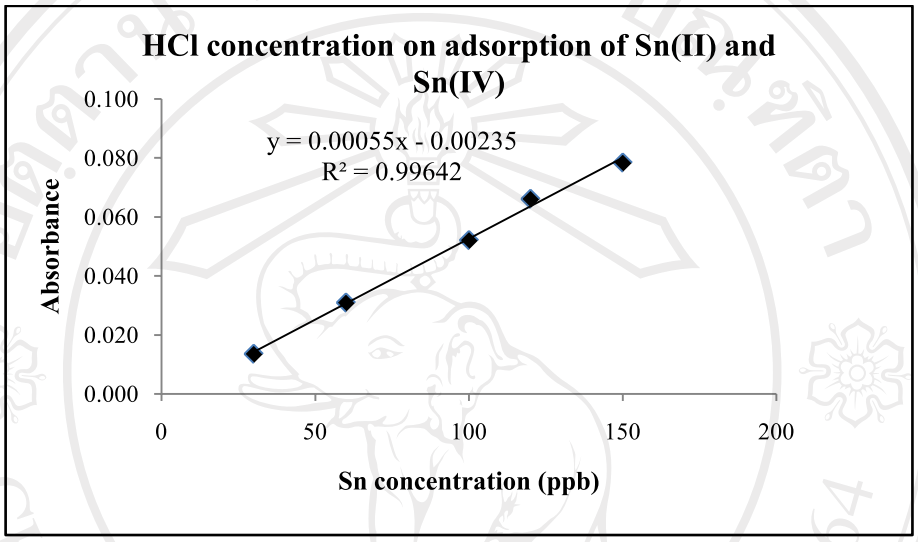
APPENDICES

APPENDIX A

CALIBRATION CURVE BY GFAAS

A-1 Calibration curve for determination of tin by GFAAS



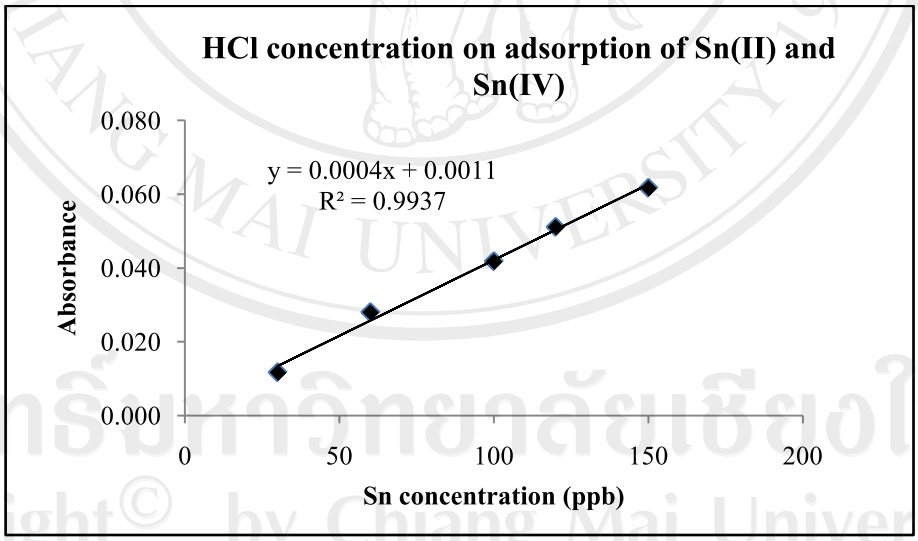


Figure A-1 Calibration curve for the study on effect of HCl concentration on adsorption of Sn(II) and Sn(IV)

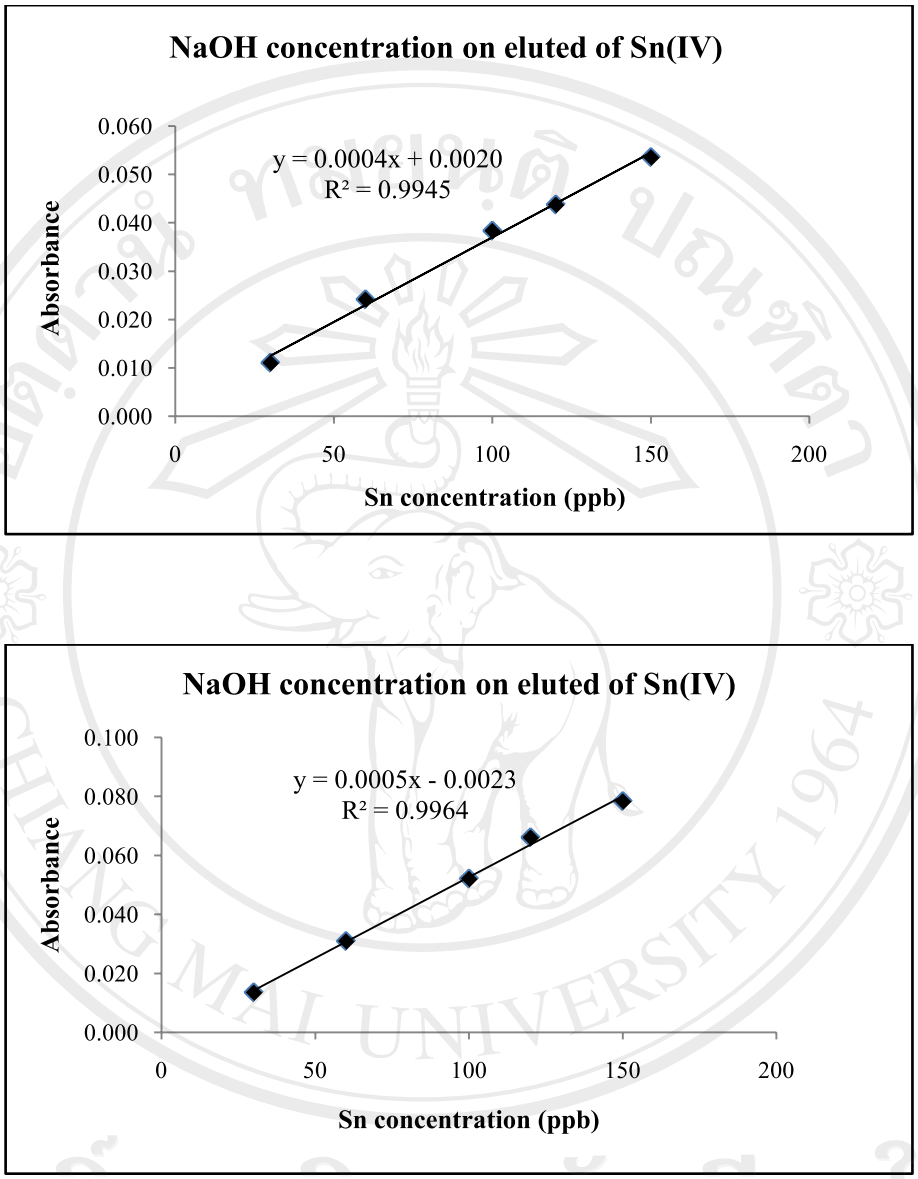


Figure A-2 Calibration curve of NaOH concentration on recovery of Sn(IV)

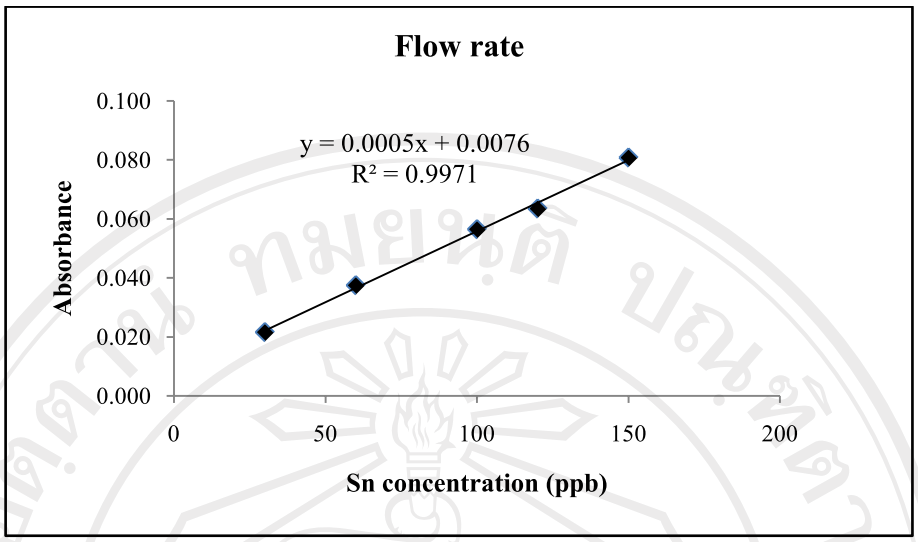


Figure A-3 Calibration curve of flow rate on recovery of Sn(IV)

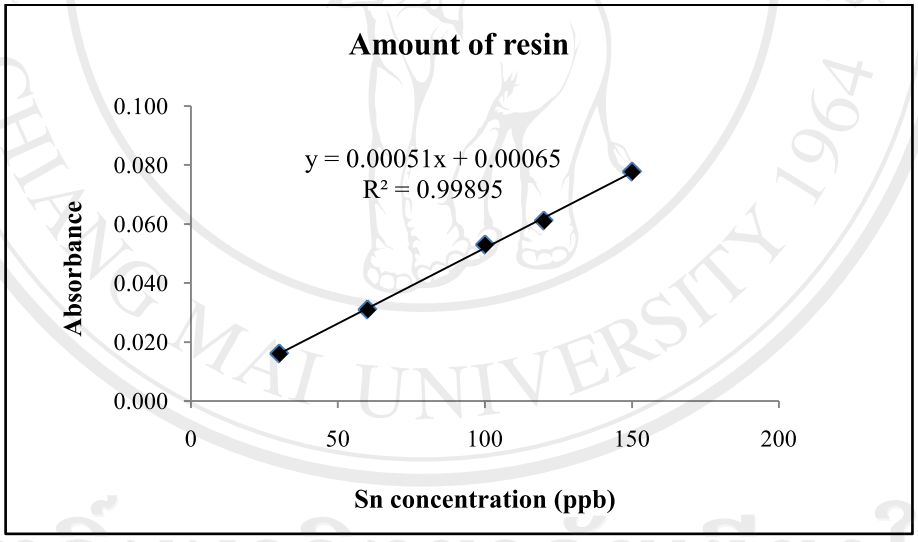


Figure A-4 Calibration curve of resin amount on recovery of Sn(IV)

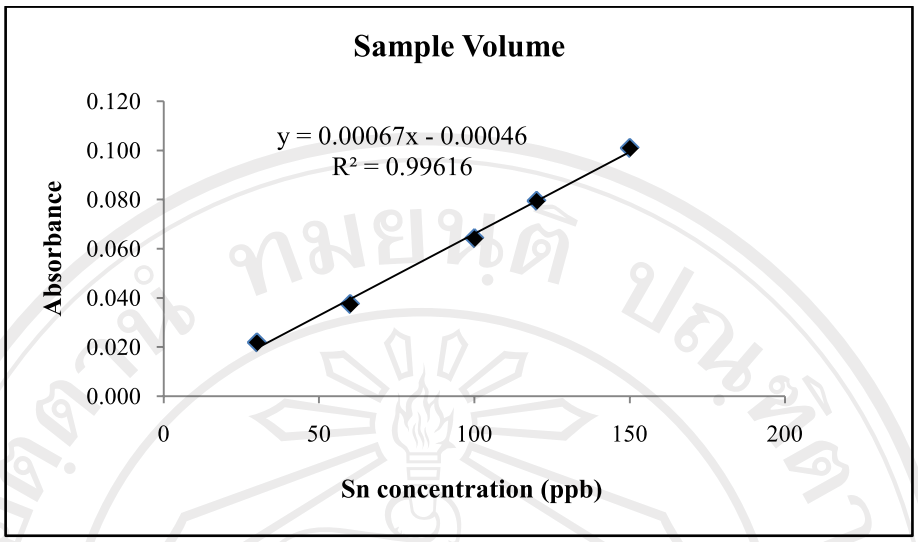


Figure A-5 Calibration curve of sample volume on recovery of Sn(IV)

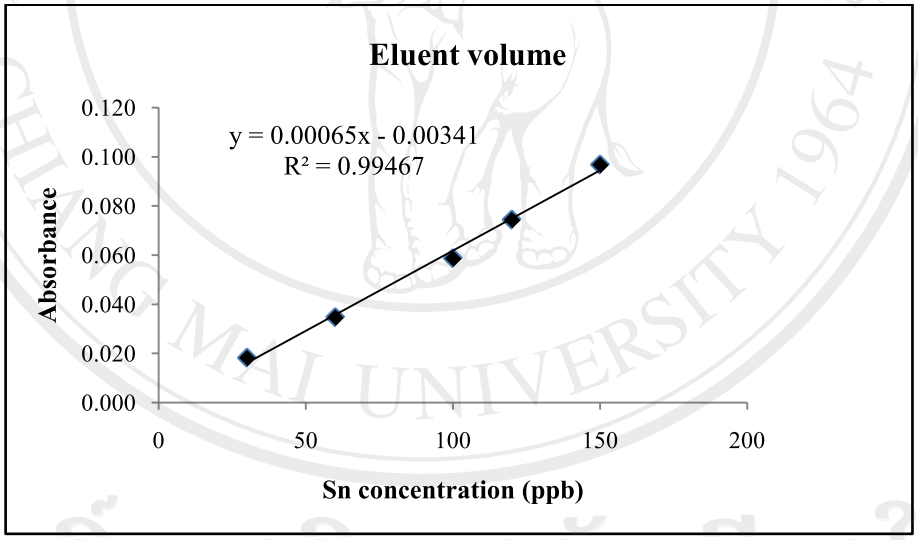


Figure A-6 Calibration curve of eluent volume on recovery of Sn(IV)

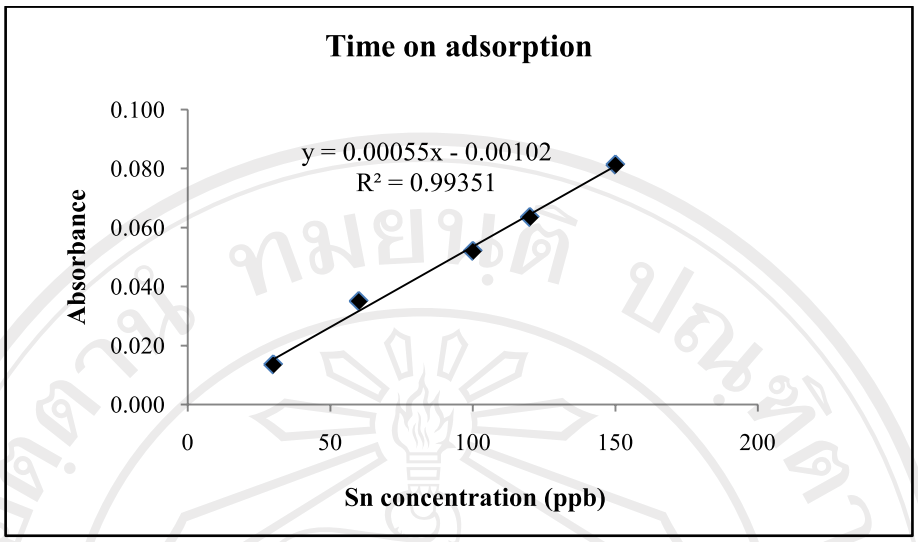


Figure A-7 Calibration curve of time on adsorption of Sn(IV)

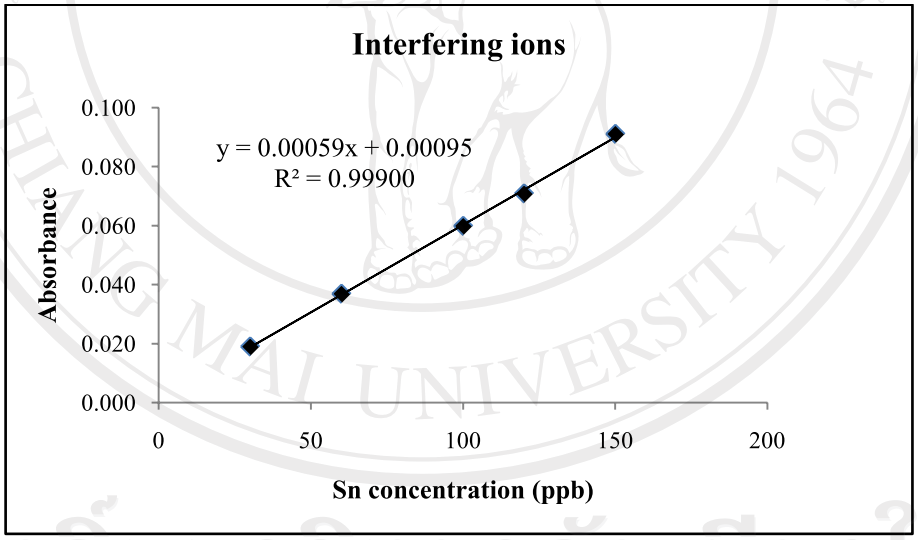
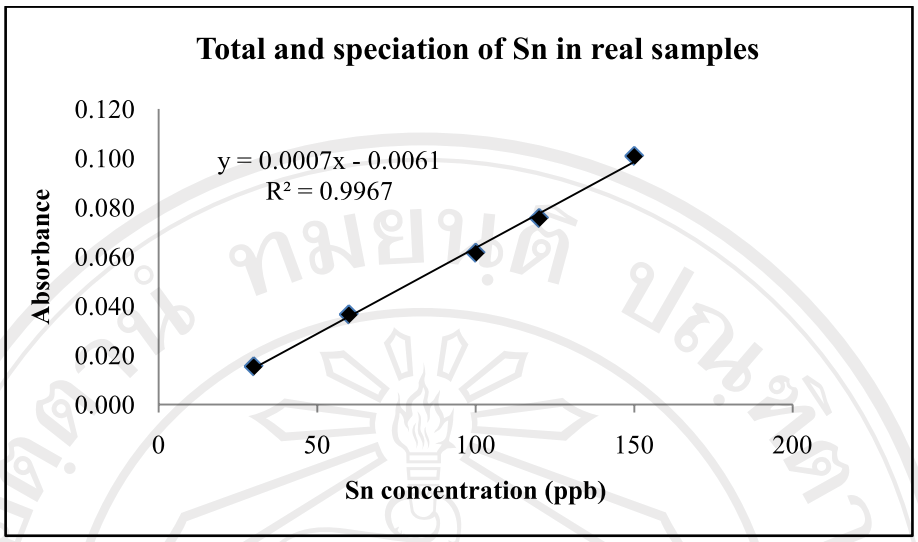
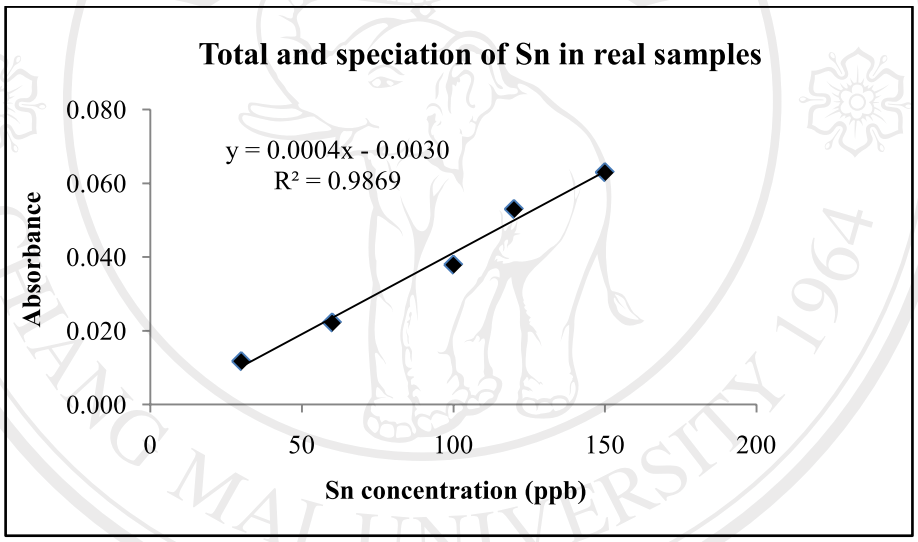


Figure A-8 Calibration curve of interfering ions on recovery of Sn(IV)





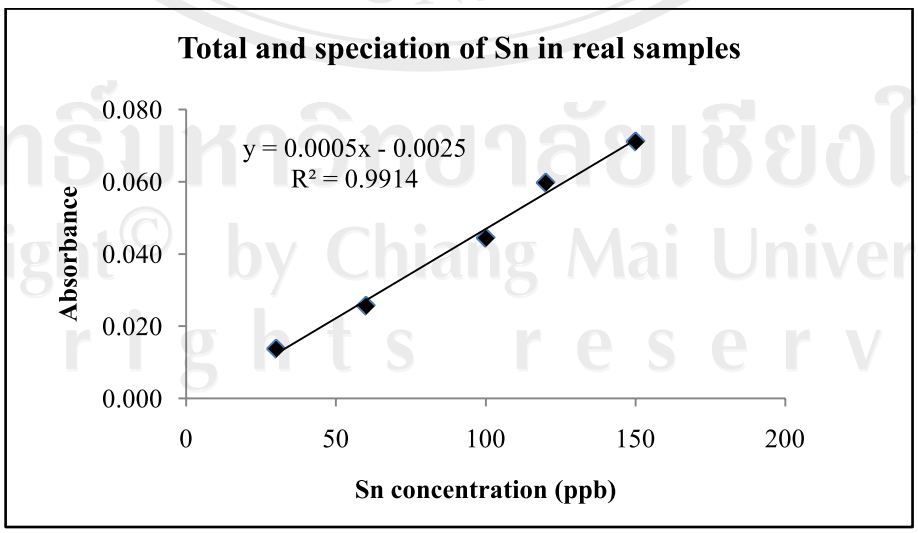


Figure A-9 Calibration curve of total and speciation of Sn in real samples

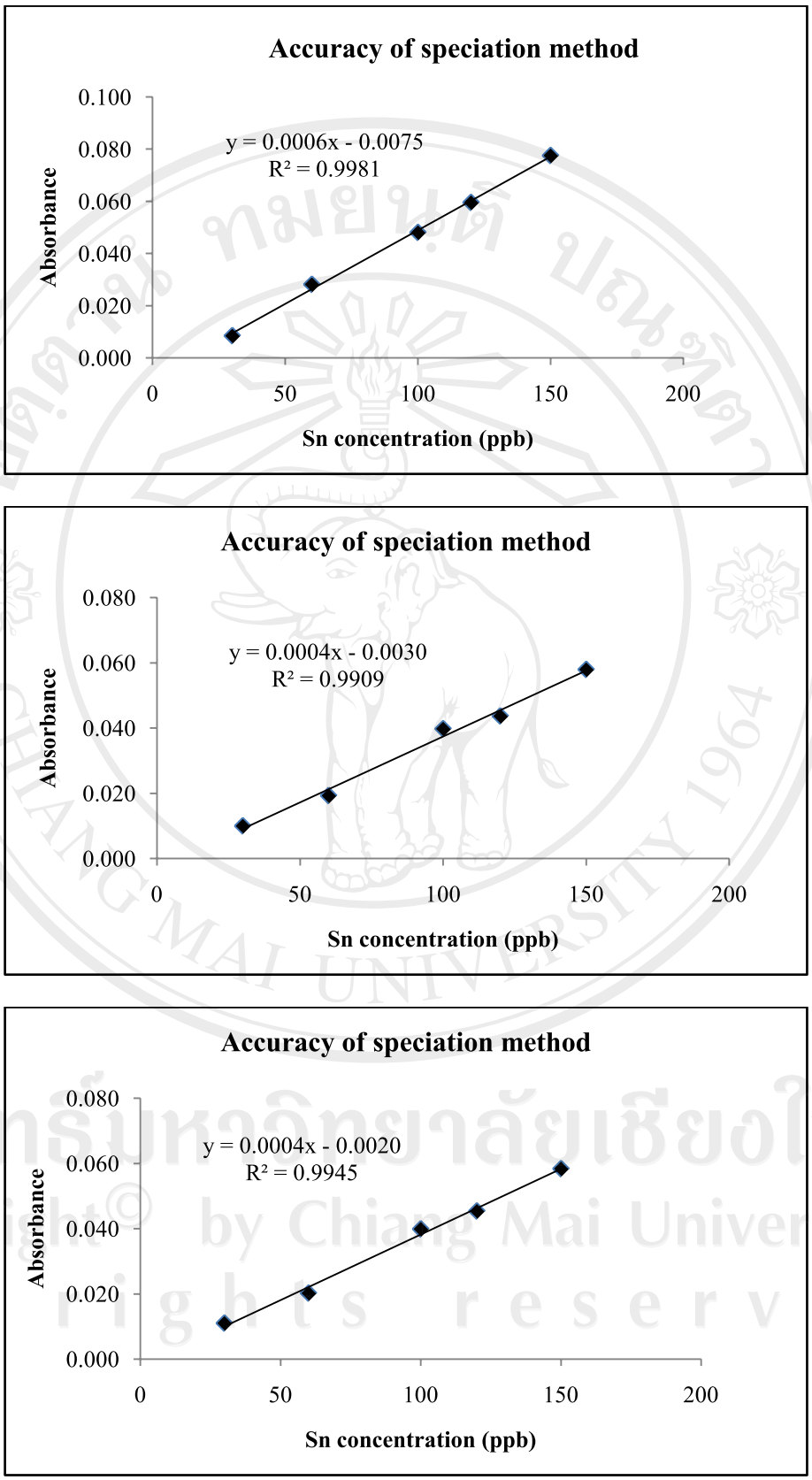


Figure A-10 Calibration curve of accuracy of speciation method

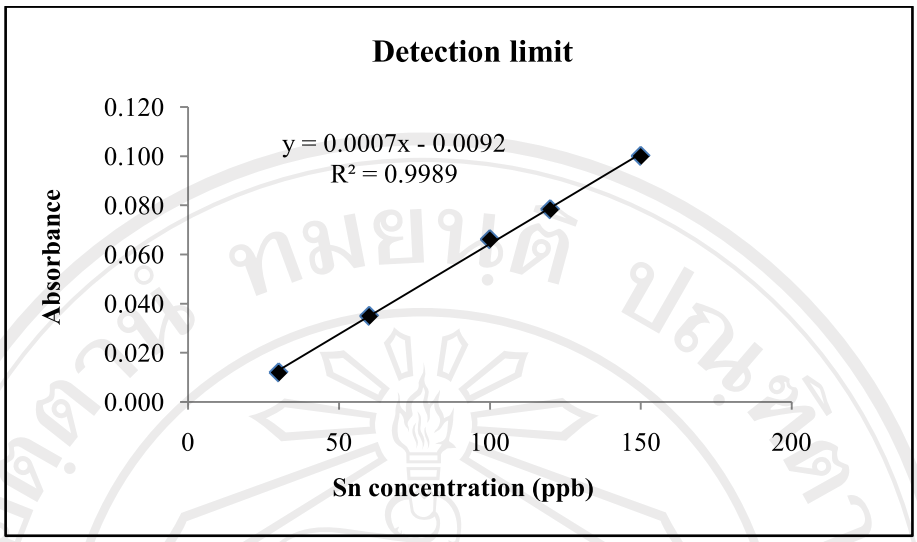


Figure A-11 Calibration curve of detection limit

APPENDIX B

STATISTIC FORMULAE

B-1 Standard deviation [49-51]

The most common measure of the error or a statistical measure of precision in an experimental quantity is standard deviation (SD) of a set of data. SD defines a series of n measurements of the same measure and, the quantity is characterizing the distribution of the results and given by the formula:

$$\mathrm{SD} = \left[\sum (X_i - \overline{X})^2 / (n-1)\right]^{1/2}$$

Where

X_i is the result of the i measurement

$\overline{X}$ is the arithmetic mean of the n results considered

n is the number of measurement

The definition is estimated the standard deviation for n values of a sample of a population and is always calculated using n-1. If the analysis was repeated several times to produce several sample sets of data, it would be expected that each set of measurements would have a different mean and a different estimate of the standard deviation.

B-2 Relative standard deviation [49-50]

The most useful test parameter is the precision of replicate injections of the analytical reference solution, prepared as directed under the individual reagent. The precision of replicate injections is expressed in term of relative standard deviation as follows:

$$\%RSD = (SD / \overline{X}) \times 100$$

Where

SD is standard deviation

$\overline{X}$ is the mean of data

B-3 The detection limit [51]

The detection limit is the minimum concentration of analyte that can be detected and its signals significantly differenced from blank and can be calculated from following equation.

$$\text{Detection limit} = (3 \times SD)/\text{slope}$$

Where

3 is Z-value at 99% confidence level

SD is the standard deviation of blank

Slope is slope of calibration curve

APPENDIX C

PRECISION AND DETECTION LIMIT OF TIN BY GFAAS

C-1 The detection limit

The detection limit of the method for determination of tin was investigated by analyzing blank (0.2% HNO_3) ten times. The detection limit was calculated by statistical formula in Appendix B and given in **Table C-1**.

Table C-1 Absorbance obtained for blank solution

No.	Abs. of 0.2% HNO_3
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

Detection limit = (3 x SD)/slope

Detection limit = (3 x 0.0006)/0.0007 = 2.57

C-2 Precision

The precision of the GFAAS instrument was studied by repeating the measurement of 60 µg/l standard solutions ten times. The results obtained are shown in **Table C-2**.

Table C-2 The precision of the 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

%RSD = $(SD / \overline{X})$ x 100

%RSD = (0.00179/0.0783) x 100 = 2.28

C-3 Accuracy

The method was examined by determining the recovery of the added 80 µg/l of Sn(IV) in sample solution. The results are shown in **Table C-3**.

Table C-3 The determination of tin(IV) in real and spiked samples

Sample	Measured* (µg/l)	Spiked (µg/l)	Found* (µg/l)	Recovery (%)*
No. 1	150.90	80	230.06	98.95
No. 2	129.90	80	200.17	100.95
No. 3	125.76	80	199.06	91.62
No. 4	140.36	80	205.56	81.50
No. 5	200.00	80	267.78	84.72
No. 6	159.29	80	230.22	88.67
No. 7	205.00	80	270.00	81.25
No. 8	133.33	80	203.33	89.58

* Mean ± SD (N=3)

No. 1 sample,

$$\% \text{ Recovery} = \frac{spike\ sample\ result - sample\ result}{spike\ amount\ added} \times 100$$

$$\% \text{ Recovery} = \frac{230.06 - 150.90}{80.00} \times 100$$

$$\% \text{ Recovery} = 98.95$$

The concentration of % recovery in the other wastewater samples can be calculated similar to this way.

C-4 Adsorption efficiency [52]

The adsorption efficiency was present in percent adsorption using the following equation:

$$\% \text{ Adsorption} = \frac{(X - Y)}{X} \times 100$$

Where

X is the concentration of the metal ion in added solution (µg/l)

Y is the concentration of the metal ion in eluant (µg/l)

Table C-4 The percentage of adsorption efficiency in the HCl concentration

HCl (M)	Abs.	Conc. (µg/l)	Conc.(µg/l)[d]	% Adsorption of Sn(IV)
1.0	0.0100	22.45	56.14	69.47
2.0	0.0080	18.82	47.05	74.41
3.0	0.0064	15.91	39.77	78.37
4.0	0.0052	13.73	34.32	81.33
5.0	0.0038	11.18	27.95	84.80
6.0	0.0047	12.82	32.05	82.57
7.0	0.0038	11.18	27.95	84.80
8.0	0.0062	15.55	38.86	78.86
9.0	0.0038	11.18	27.95	84.80

[d] Dilution factor = 2.5

Calibration curve: y = 0.00055x - 0.00235

$R^2 = 0.9964$

The absorbance of model solution after passed through the column was 0.0012 or 16.04 µg/l

The concentration of Sn(IV) ion in initial model solution was 200 µg/l

1.0 M HCl, X = 200 -16.14 = 183.86 µg/l, Y= 56.14 µg/l

The concentration of Sn(IV) ion on adsorption was 183.86 µg/l

$$\% \text{ Adsorption of Sn(IV)} = \frac{(X - Y)}{X} \times 100$$

$$\% \text{ Adsorption of Sn(IV)} = \frac{(183.86 - 56.14)}{183.86} \times 100$$

$$\% \text{ Adsorption of Sn(IV)} = 69.46$$

The percentage of adsorption efficiency in the other HCl concentration can be calculated similar to this way.

C-5 The percent recovery of Sn(IV) from optimization method

The percent recovery of Sn(IV) from optimization method was calculated by the equation below:

$$\% \text{ Recovery} = \frac{Conc.of\ Sn(IV)ion\ after\ eluted\ (ppb)}{Conc.\ of\ Sn(IV)ion\ initial\ solution\ (ppb)} \times 100$$

Table C-5 The percentage recovery of Sn(IV) from optimization of NaOH

NaOH (M)	Abs.	Conc. (µg/l)	Conc. (µg/l)[d]	% Recovery
1.0	0.0173	38.25	95.63	46.38
2.0	0.0289	67.25	168.13	82.63
3.0	0.0280	65.00	162.50	79.82
4.0	0.0300	70.00	175.00	86.07
5.0	0.0292	68.00	170.00	83.57
6.0	0.0279	64.75	161.88	79.51
7.0	0.0221	50.25	125.63	61.38

[d] Dilution factor = 2.5

Calibration curve: y = 0.0004x + 0.0020

$R^2 = 0.9945$

The absorbance of blank was 0.0008 or 2.87 µg/l

The concentration of Sn(IV) ion initial model solution was 200 µg/l

1.0 M NaOH, Conc. = 95.63 – 2.87 = 92.76

$$\% \text{ Recovery} = \frac{Conc.of\ Sn(IV)ion\ after\ eluted\ (ppb)}{Conc.\ of\ Sn(IV)ion\ initial\ solution\ (ppb)} \text{ x } 100$$

% Recovery = (92.76/200) x 100

= 46.38

The percentage recovery in the other NaOH concentration can be calculated similar to this way.

APPENDIX D

RESULTS OF DETERMINATION IN WASTEWATER SAMPLES

Table D-1 Sn(IV) in wastewater samples by GFAAS

Sample	Sn(IV)				SD
	Replications	Abs.	Conc. (µg/l)	Average	
No. 1	1	0.0041	145.71		
	2	0.0036	165.00	150.90	12.35
	3	0.0041	142.00		
No. 2	1	0.0034	135.71		
	2	0.0018	120.00	129.90	8.62
	3	0.0037	134.00		
No. 3	1	0.0033	134.29		
	2	0.0016	115.00	125.76	9.84
	3	0.0034	128.00		
No 4	1	0.0043	148.57		
	2	0.0030	142.50	140.36	9.47
	3	0.0035	130.00		
No 5	1	0.0065	180.00		
	2	0.0062	230.00	200.00	26.46
	3	0.0065	190.00		
No. 6	1	0.0053	162.86		
	2	0.0031	175.00	159.29	17.77
	3	0.0040	140.00		
No. 7	1	0.0054	210.00		
	2	0.0051	202.50	205.00	4.33
	3	0.0051	202.50		
No. 8	1	0.0020	125.00		
	2	0.0020	125.00	133.33	14.43
	3	0.0030	150.00		

Table D-2 Sn(IV) in spiked samples

Sample	Added (µg/l)	Concentration of Sn(IV)				SD
		Replications	Abs.	Conc. (µg/l)	Average	
No. 1	80	1	0.0055	216.67	230.06	14.83
		2	0.0086	246.00		
		3	0.0071	227.50		
No. 2	80	1	0.0054	215.00	200.17	13.88
		2	0.0062	198.00		
		3	0.0055	187.50		
No. 3	80	1	0.0052	211.67	199.06	11.91
		2	0.0057	188.00		
		3	0.0059	197.50		
No. 4	80	1	0.0052	211.67	205.56	9.18
		2	0.0068	210.00		
		3	0.0058	195.00		
No. 5	80	1	0.0080	258.33	267.78	19.32
		2	0.0108	290.00		
		3	0.0082	255.00		
No. 6	80	1	0.0067	236.67	230.22	17.89
		2	0.0085	244.00		
		3	0.0064	210.00		
No. 7	80	1	0.0080	275.00	270.00	8.66
		2	0.0074	260.00		
		3	0.0080	275.00		
No. 8	80	1	0.0050	200.00	203.33	12.83
		2	0.0047	192.50		
		3	0.0057	217.50		

Table D-3 The percent recovery of Sn(IV) in wastewater samples

Sample	(%)Recovery of Sn(IV)				SD
	Replications			Average	
	1	2	3		
No. 1	88.69	101.25	106.88	98.94	9.31
No. 2	99.11	97.50	106.25	100.95	4.66
No. 3	96.73	91.25	86.88	91.62	4.94
No. 4	78.87	84.38	81.25	81.50	2.76
No. 5	97.92	75.00	81.25	84.72	11.85
No. 6	92.26	86.25	87.50	88.67	3.17
No. 7	81.25	71.88	90.63	81.25	7.65
No. 8	100.00	84.38	84.38	89.58	7.37

Table D-4 Total Sn in wastewater samples

Sample	Total Sn				SD
	Replications	Abs.	Conc.(µl/l)	Average	
No. 1	1	0.0309	1057.14		
	2	0.0234	1320.00	1261.71	182.55
	3	0.0327	1408.00		
No. 2	1	0.0479	1542.86		
	2	0.0304	1670.00	1641.62	88.07
	3	0.0403	1712.00		
No. 3	1	0.0436	1420.00		
	2	0.0304	1420.00	1524.67	129.87
	3	0.0346	1484.00		
No. 4	1	0.0394	1300.00		
	2	0.0253	1415.00	1331.67	72.86
	3	0.0295	1280.00		
No. 5	1	0.0401	1320.00		
	2	0.0249	1395.00	1411.67	101.04
	3	0.0355	1520.00		
No. 6	1	0.0444	1442.86		
	2	0.0285	1575.00	1549.95	97.03
	3	0.0383	1632.00		
No. 7	1	0.0210	3240.00		
	2	0.0192	3024.00	3068.00	126.36
	3	0.0185	2940.00		
No. 8	1	0.0168	2280.00		
	2	0.0173	2330.00	2340.00	53.54
	3	0.0181	2410.00		

Table D-5 Concentration of Sn(II) by subtracting the content of Sn(IV) from total tin content

Sample	Concentration of Sn(II) (µg/l)				SD
	Replications			Average	
	1	2	3		
No. 1	911.43	1155.00	1266.00	1110.81	181.37
No. 2	1407.14	1550.00	1578.00	1511.71	91.64
No. 3	1285.71	1555.00	1356.00	1398.90	139.68
No. 4	1151.43	1272.50	1150.00	1191.31	70.32
No. 5	1140.00	1165.00	1330.00	1211.67	103.24
No. 6	1280.00	1400.00	1492.00	1390.67	106.31
No. 7	3030.00	2821.50	2737.50	2863.00	150.60
No. 8	2155.00	2205.00	2260.00	2206.67	52.52

APPENDIX E

MATRIX MODIFICATION

E-1 Matrix modifier [6, 29]

The matrix modifier can either stabilize the analyte element in order to permit a higher pyrolysis temperature or make the matrix more volatile for more effective pyrolysis.

In GFAAS, the possibility of tin to form volatile compounds during the ashing and drying steps and its interaction with the carbon of the graphite tube wall causes erratic results easily. The modifiers stabilize the analyte of interest to a higher temperature so that the interfering matrix can be removed during the drying stage. In this work, palladium with magnesium nitrate was employed as the matrix modifier. For the study on detection limit, the results have shown that the detection limit for determination of tin by GFAAS was 2.57µg/l. For the other methods [5-6], ascorbic acid (VC) was employed as the matrix modifier. The detection limit for determination of tin by GFAAS was 0.4 µg/l. The different value of detection limit obtained from the different type of matrix modifiers.

APPENDIX F

THE RELEVANCY OF THE RESEARCH WORK TO THAILAND

Nowadays, tin is used in most electronic industrial that leads to the contamination of tin metal in environment. This contamination could be harmful to human and environmental. Tin is a toxic metal which could gather in a human's body and the tissue of animals and high concentration of tin brings serious interference to the metabolism of zinc. In general, there are mainly two chemical species of inorganic tin in environmental samples, Sn(II) and Sn(IV), respectively. Due to the toxicity of tin depends on the chemical forms of the species, which are related to their characteristics and concentrations. Differential toxicities of the different forms of an element have dictated an increasing development and use of analytical determination of the chemical species. Thus, speciation analysis of tin in wastewater from electronic industry has progressively become important. Moreover, the northern of Thailand has been many electronic industrial, especially Lamphun and Chiang Mai. The information from study speciation of tin will be useful for evaluation hazardous level of tin in wastewater from industry.

In this work, the tin species in wastewater samples were studied using ion-exchange resins for speciation of tin species. For the determination of total tin, it was determined after oxidizing of Sn(II) to Sn(IV) by the addition concentrated HNO_3 and H_2O_2. The concentration of Sn(II) was calculated as the difference between the total Sn content and the Sn(IV) content. The determination of tin concentration was detected by graphite furnace atomic absorption spectrometry. The results of this work

will be useful for evaluation hazardous level of tin in wastewater from industry and treatment the wastewater from industry before released to the rivers and environment.

CURRICULUM VITAE

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Phetcharat Siriwi and Sukjit Kungwankunakorn, Study on Speciation of Tin (Sn) in Wastewater from Electronic Industrial, poster presentation, The International congress for Innovation in Chemistry (PERCH-CIC Congress VI), 3-6 May 2009, Chonburi, Thailand.