

REFERENCES

- [1] Jain, A. and Verma, K.K. Recent advances in applications of single-drop microextraction: A review. *Analytica Chimica Acta* 706 (2011): 37-65.
- [2] Yangcheng, L., Quan, L., Guangsheng, L., and Youyuan, D. Directly suspended droplet microextraction. *Analytica Chimica Acta* 566 (2006): 259-264.
- [3] Liu, W. and Lee, H.K. Continuous-flow microextraction exceeding 1000-fold concentration of dilute analytes. *Analytical Chemistry* 72 (2000): 4462-4467.
- [4] Sarafraz-Yazdi, A. and Amiri, A. Liquid-phase microextraction. *TrAC Trends in Analytical Chemistry* 29 (2010): 1-14.
- [5] Pedersen-Bjergaard, S. and Rasmussen, K.E. Electrokinetic migration across artificial liquid membranes: New concept for rapid sample preparation of biological fluids. *Journal of Chromatography A* 1109 (2006): 183-190.
- [6] Gjelstad, A., Andersen, T.M., Rasmussen, K.E., and Pedersen-Bjergaard, S. Microextraction across supported liquid membranes forced by pH gradients and electrical fields. *Journal of Chromatography A* 1157 (2007): 38-45.
- [7] Gjelstad, A., Rasmussen, K.E., and Pedersen-Bjergaard, S. Electrokinetic migration across artificial liquid membranes: Tuning the membrane chemistry to different types of drug substances. *Journal of Chromatography A* 1124 (2006): 29-34.
- [8] Balchen, M., Gjelstad, A., Rasmussen, K.E., and Pedersen-Bjergaard, S. Electrokinetic migration of acidic drugs across a supported liquid membrane. *Journal of Chromatography A* 1152 (2007): 220-225.
- [9] Balchen, M., Reubsaet, L., and Pedersen-Bjergaard, S. Electromembrane extraction of peptides. *Journal of Chromatography A* 1194 (2008): 143-149.
- [10] Lee, J., Khalilian, F., Bagheri, H., and Lee, H.K. Optimization of some experimental parameters in the electro membrane extraction of chlorophenols from seawater. *Journal of Chromatography A* 1216 (2009): 7687-7693.
- [11] Basheer, C., Tan, S.H., and Lee, H.K. Extraction of lead ions by electromembrane isolation. *Journal of Chromatography A* 1213 (2008): 14-18.
- [12] Kubáň, P., Strieglerová, L., Gebauer, P., and Boček, P. Electromembrane extraction of heavy metal cations followed by capillary electrophoresis with capacitively coupled contactless conductivity detection. *ELECTROPHORESIS* 32 (2011): 1025-1032.

- [13] Kjelsen, I.J.Å.s., Gjelstad, A., Rasmussen, K.E., and Pedersen-Bjergaard, S. Low-voltage electromembrane extraction of basic drugs from biological samples. Journal of Chromatography A 1180 (2008): 1-9.
- [14] Gjelstad, A., Rasmussen, K., and Pedersen-Bjergaard, S. Electromembrane extraction of basic drugs from untreated human plasma and whole blood under physiological pH conditions. Analytical and Bioanalytical Chemistry 393 (2009): 921-928.
- [15] Gjelstad, A., Rasmussen, K.E., and Pedersen-Bjergaard, S. Simulation of flux during electro-membrane extraction based on the Nernst-Planck equation. Journal of Chromatography A 1174 (2007): 104-111.
- [16] Gjelstad, A. Electromembrane extraction - an alternative sample preparation technique. The Column 2010. Available from: <http://www.chromatographyonline.com/lcgc/Sample+Preparation+Techniques/ArticleStandard/Article/detail/674163>
- [17] Balchen, M., Halvorsen, T.G., Reubsaet, L., and Pedersen-Bjergaard, S. Rapid isolation of angiotensin peptides from plasma by electromembrane extraction. Journal of Chromatography A 1216 (2009): 6900-6905.
- [18] Eibak, L.E.E., Gjelstad, A., Rasmussen, K.E., and Pedersen-Bjergaard, S. Kinetic electro membrane extraction under stagnant conditions-Fast isolation of drugs from untreated human plasma. Journal of Chromatography A 1217 (2010): 5050-5056.
- [19] Nojavan, S. and Fakhari, A.R. Electro membrane extraction combined with capillary electrophoresis for the determination of amlodipine enantiomers in biological samples. Journal of Separation Science 33 (2010): 3231-3238.
- [20] Payán, M.R., López, M.Á.B., Torres, R.F., Navarro, M.V., and Mochón, M.C. Electromembrane extraction (EME) and HPLC determination of non-steroidal anti-inflammatory drugs (NSAIDs) in wastewater samples. Talanta 85 (2011): 394-399.
- [21] Seidi, S., Yamini, Y., Heydari, A., Moradi, M., Esrafil, A., and Rezazadeh, M. Determination of thebaine in water samples, biological fluids, poppy capsule, and narcotic drugs, using electromembrane extraction followed by high-performance liquid chromatography analysis. Analytica Chimica Acta 701 (2011): 181-188.
- [22] Alhooshani, K., et al. Electromembrane extraction and HPLC analysis of haloacetic acids and aromatic acetic acids in wastewater. Talanta 86 (2011): 109-113.

- [23] Petersen, N.J., et al. On-chip electro membrane extraction with online ultraviolet and mass spectrometric detection. *Analytical Chemistry* 83 (2011): 44-51.
- [24] Jamt, R.E.G., et al. Electromembrane extraction of stimulating drugs from undiluted whole blood. *Journal of Chromatography A* 1232 (2012): 27-36.
- [25] Davarani, S.S.H., Najarian, A.M., Nojavan, S., and Tabatabaei, M.-A. Electromembrane extraction combined with gas chromatography for quantification of tricyclic antidepressants in human body fluids. *Analytica Chimica Acta* (2012).
- [26] Šlampová, A., Kubáň, P., and Boček, P. Electromembrane extraction using stabilized constant d.c. electric current-A simple tool for improvement of extraction performance. *Journal of Chromatography A* 1234 (2012): 32-37.
- [27] Tan, T.Y., Basheer, C., Ng, K.P., and Lee, H.K. Electro membrane extraction of biological anions with ion chromatographic analysis. *Analytica Chimica Acta* 739 (2012): 31-36.
- [28] Rezazadeh, M., Yamini, Y., Seidi, S., and Esrafilı, A. Pulsed electromembrane extraction: A new concept of electrically enhanced extraction. *Journal of Chromatography A* 1262 (2012): 214-218.
- [29] Rezazadeh, M., Yamini, Y., Seidi, S., and Ebrahimpour, B. Electromembrane surrounded solid phase microextraction: A novel approach for efficient extraction from complicated matrices. *Journal of Chromatography A* 1280 (2013): 16-22.
- [30] Davarani, S.S.H., Moazami, H.R., Keshtkar, A.R., Banitaba, M.H., and Nojavan, S. A selective electromembrane extraction of uranium (VI) prior to its fluorometric determination in water. *Analytica Chimica Acta* 783 (2013): 74-79.
- [31] Safari, M., Nojavan, S., Davarani, S.S.H., and Morteza-Najarian, A. Speciation of chromium in environmental samples by dual electromembrane extraction system followed by high performance liquid chromatography. *Analytica Chimica Acta* 789 (2013): 58-64.
- [32] Dadfarnia, S. and Haji Shabani, A.M. Recent development in liquid phase microextraction for determination of trace level concentration of metals—A review. *Analytica Chimica Acta* 658 (2010): 107-119.
- [33] Miró, M. and Frenzel, W. Automated membrane-based sampling and sample preparation exploiting flow-injection analysis. *TrAC Trends in Analytical Chemistry* 23 (2004): 624-636.

- [34] Hylton, K. and Mitra, S. Automated, on-line membrane extraction. *Journal of Chromatography A* 1152 (2007): 199-214.
- [35] GmbH, D.E. Hollow fiber membrane module. 2009. Available from: <http://www.dice.de/products/separel/index.html>
- [36] Rasmussen, K.E. and Pedersen-Bjergaard, S. Developments in hollow fibre-based, liquid-phase microextraction. *TrAC Trends in Analytical Chemistry* 23 (2004): 1-10.
- [37] Lee, J., Lee, H.K., Rasmussen, K.E., and Pedersen-Bjergaard, S. Environmental and bioanalytical applications of hollow fiber membrane liquid-phase microextraction: A review. *Analytica Chimica Acta* 624 (2008): 253-268.
- [38] Pedersen-Bjergaard, S. and Rasmussen, K.E. Liquid-phase microextraction with porous hollow fibers, a miniaturized and highly flexible format for liquid-liquid extraction. *Journal of Chromatography A* 1184 (2008): 132-142.
- [39] Ghambarian, M., Yamini, Y., and Esrafil, A. Developments in hollow fiber based liquid-phase microextraction: principles and applications. *Microchimica Acta* 177 (2012): 271-294.
- [40] Petersen, N.J., Rasmussen, K.E., Pedersen-Bjergaard, S., and Gjelstad, A. Electromembrane extraction from biological fluids. *Analytical Sciences* 27 (2011): 965-965.
- [41] Yamini, Y., Seidi, S., and Rezazadeh, M. Electrical field-induced extraction and separation techniques: Promising trends in analytical chemistry – A review. *Analytica Chimica Acta* (2014).
- [42] Parthasarathy, N., Pelletier, M., and Buffle, J. Hollow fiber based supported liquid membrane: a novel analytical system for trace metal analysis. *Analytica Chimica Acta* 350 (1997): 183-195.
- [43] Pattillo, C. Liquid membrane transport phenomenon. 1995. Available from: <http://www.rpi.edu/dept/chem-eng/Biotech-Environ/patillo/membrane.biochem/mem.transport.html>
- [44] W.H.O. Guidelines for drinking-water quality fourth edition. Water Sanitation and Health (WSH) 2011. Available from: http://www.who.int/water_sanitation_health/publications/2011/dwq_chapters/en/
- [45] Choppala, G., Bolan, N., and Park, J.H. Chapter two - Chromium contamination and its risk management in complex environmental settings. in Donald, L.S. (ed.) *Advances in Agronomy*, pp. 129-172: Academic Press, 2013.

- [46] EPA, U.S. Toxicological review of hexavalent chromium. 1998. Available from: <http://www.epa.gov/iris/toxreviews/0144tr.pdf>
- [47] Gherasim, C.-V., Bourceanu, G., Olariu, R.-I., and Arsene, C. A novel polymer inclusion membrane applied in chromium (VI) separation from aqueous solutions. Journal of Hazardous Materials 197 (2011): 244-253.
- [48] EPA, U.S. Chromium in drinking water. 2012. Available from: <http://water.epa.gov/drink/info/chromium/index.cfm>
- [49] EPA, U.S. METHOD 7196A chromium, hexavalent (colorimetric). 1992. Available from: <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/7196a.pdf>
- [50] G. Svehla PhD, D., FRSC. VOGEL's qualitative inorganic. 7th ed. Edinburgh Gate, Harlow Essex CM20 2JE, England: Addison Wesley Longman Ltd., 1997.
- [51] Miller, J.C. and Miller, J.N. Statistics for analytical chemistry. 3rd ed. Market Cross House, Cooper street, Chichester, West Sussex, P019 1EB, England: Ellis Horwood Limited, 1993.
- [52] Guo, L. and Lee, H.K. Electro membrane extraction followed by low-density solvent based ultrasound-assisted emulsification microextraction combined with derivatization for determining chlorophenols and analysis by gas chromatography-mass spectrometry. Journal of Chromatography A 1243 (2012): 14-22.
- [53] Davarani, S.S.H., Pourahadi, A., Nojavan, S., Banitaba, M.H., and Nasiri-Aghdam, M. Electro membrane extraction of sodium diclofenac as an acidic compound from wastewater, urine, bovine milk, and plasma samples and quantification by high-performance liquid chromatography. Analytica Chimica Acta 722 (2012): 55-62.
- [54] Lide, D.R. CRC Handbook of chemistry and physics : A Ready-Reference Book of Chemical and Physical Data. 88 ed. 6000 Broken Sound Parkway NW, suit 300: CRC Press (Taylor & Francis Group), 2007-2008.
- [55] Lide, D.R. CRC Handbook of chemistry and physics. 85 ed.: CRC Press (Taylor & Francis Group), 2004.
- [56] ChemicalBook. 2-nitrophenyl octyl ether (37682-29-4). 2008. Available from: http://www.chemicalbook.com/ProductChemicalPropertiesCB4378118_EN.htm
- [57] Liu, X., Bouchard, G., Girault, H.H., Testa, B., and Carrupt, P.-A. Partition coefficients of ionizable compounds in o-nitrophenyl octyl ether/water measured by the potentiometric method. Analytical Chemistry 75 (2003): 7036-7039.
- [58] Mohr, G.J. Materials and polymers in optical sensing. (2002).

- [59] Jorge, M., Gulaboski, R., Pereira, C.M., and Cordeiro, M.N.D.S. Molecular dynamics study of 2-nitrophenyl octyl ether and nitrobenzene. The Journal of Physical Chemistry B 110 (2006): 12530-12538.
- [60] ChemicalBook. Aliquat 336 (5137-55-3). 2008. Available from: http://www.chemicalbook.com/ProductMSDSDetailCB4412612_EN.htm
- [61] Organics, A. material safety data sheet Aliquat 336. 2009. Available from: <https://www.fishersci.ca/viewmsds.do?catNo=AC194970025>
- [62] ChemAxon. Aliquat336. Available from: <http://www.chemicalize.org/structure/#!mol=Aliquat+336>
- [63] Ho, T.S., Halvorsen, T.G., Pedersen-Bjergaard, S., and Rasmussen, K.E. Liquid-phase microextraction of hydrophilic drugs by carrier-mediated transport. Journal of Chromatography A 998 (2003): 61-72.
- [64] G.Y.Jung, Kim, Y.S., and Lim, H.B. Simultaneous determination of chromium(III) and chromium(VI) in aqueous solution by capillary electrophoresis with on-column uv-vis detection. Analytical Sciences 13 (1997): 463-467.
- [65] Seip, K.F., Jensen, H., Sønsteby, M.H., Gjelstad, A., and Pedersen-Bjergaard, S. Electromembrane extraction: Distribution or electrophoresis? ELECTROPHORESIS 34 (2013): 792-799.
- [66] Taverniers, I., De Loose, M., and Van Bockstaele, E. Trends in quality in the analytical laboratory. II. Analytical method validation and quality assurance. TrAC Trends in Analytical Chemistry 23 (2004): 535-552.

APPENDIX

Table A.1 t-Test : Comparison between the proposed method and the standard method (ICP-OES) (drinking water A, n=3, confidential level 95%)

<i>F-Test Two-Sample for Variances</i>		
	<i>ICP-OES</i>	<i>proposed method</i>
Mean	58.50476151	53.97515955
Variance	0.007144382	36.60173228
Observations	3	3
df	2	2
F	0.000195192	
P(F<=f) one-tail	0.000195154	
F Critical one-tail	0.052631579	
<i>t-Test: Two-Sample Assuming Equal Variances</i>		
	<i>ICP-OES</i>	<i>proposed method</i>
Mean	58.50476151	53.97515955
Variance	0.007144382	36.60173228
Observations	3	3
Pooled Variance	18.30443833	
Hypothesized Mean Difference	0	
df	4	
t Stat	1.296664037	
P(T<=t) one-tail	0.132245135	
t Critical one-tail	2.131846786	
P(T<=t) two-tail	0.264490271	
t Critical two-tail	2.776445105	

Table A.2 t-Test : Comparison between the proposed method and the standard method (ICP-OES) (drinking water B, n=3, confidential level 95%)

<i>F-Test Two-Sample for Variances</i>		
	<i>ICP-OES</i>	<i>proposed method</i>
Mean	59.62019	56.45949926
Variance	2.009029	8.655765973
Observations	3	3
df	2	2
F	0.232103	
P(F<=f) one-tail	0.18838	
F Critical one-tail	0.052632	
<i>t-Test: Two-Sample Assuming Unequal Variances</i>		
	<i>ICP-OES</i>	<i>proposed method</i>
Mean	59.62019	56.45949926
Variance	2.009029	8.655765973
Observations	3	3
Hypothesized Mean Difference	0	
df	3	
t Stat	1.676359	
P(T<=t) one-tail	0.096131	
t Critical one-tail	2.353363	
P(T<=t) two-tail	0.192261	
t Critical two-tail	3.182446	

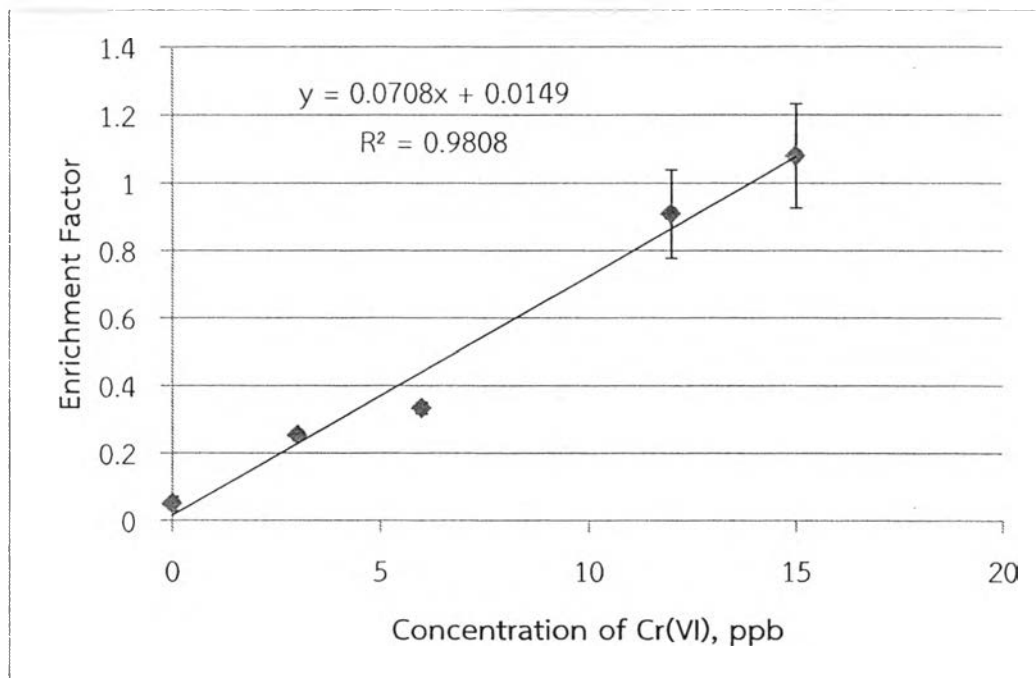


Figure A.1 Working range of Cr(VI) determined by electrical field assisted LPME in drinking water A

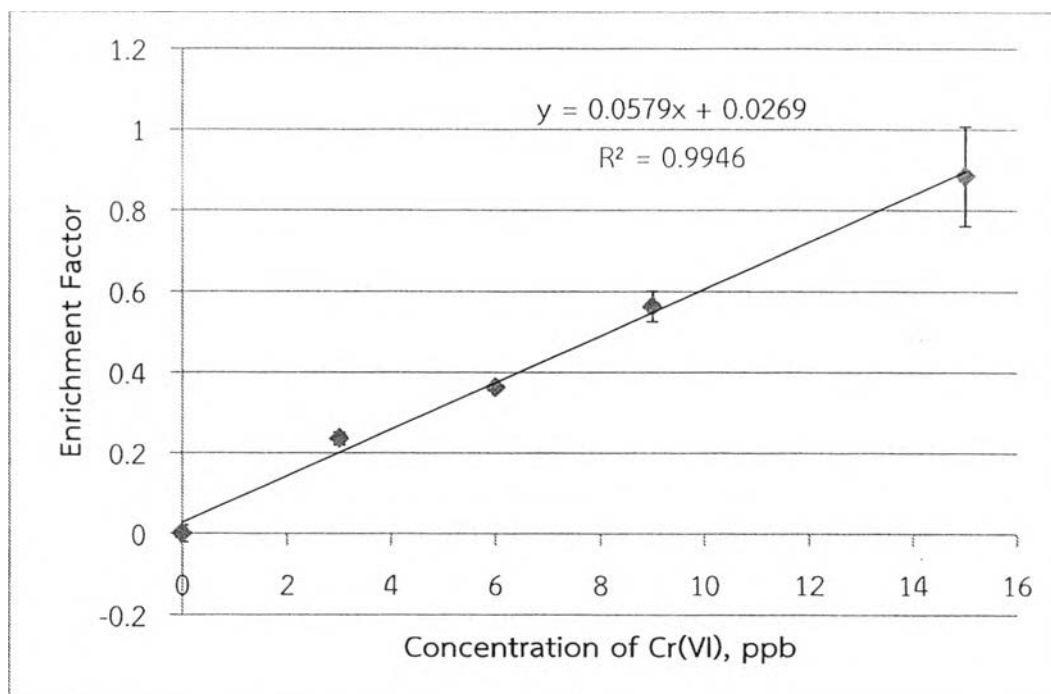


Figure A.2 Working range of Cr(VI) determined by electrical field assisted LPME in drinking water B

Table A.3 Calculation of standard deviation of slope of calibration curve.

	Formular	Milli Q water	Drinking water A	Drinking water B
	$S_{xx} = \sum (x_i - \bar{x})^2$	$S_{xx} = 472.5$	$S_{xx} = 464.4$	$S_{xx} = 399.6$
	$S_{yy} = \sum (y_i - \bar{y})^2$	$S_{yy} = 2.202$	$S_{yy} = 2.454$	$S_{yy} = 1.380$
Standard deviation about regression	$S_r = \sqrt{\frac{S_{yy}}{n-2}}$	$S_r = \sqrt{\frac{2.202}{18-2}} = 0.3710$	$S_r = \sqrt{\frac{2.454}{15-2}} = 0.4345$	$S_r = \sqrt{\frac{1.380}{15-2}} = 0.3258$
Standard deviation of slope	$S_m = \sqrt{\frac{S_r^2}{S_{xx}}}$	$S_m = \sqrt{\frac{0.3710^2}{472.5}} = 0.01707$	$S_m = \sqrt{\frac{0.4345^2}{464.4}} = 0.02016$	$S_m = \sqrt{\frac{0.3258^2}{399.6}} = 0.01630$



Table A.4 Analysis of Variance (ANOVA)

	Milli Q water	Drinking water A	Drinking water B
Slope	0.0671	0.0708	0.0579
Standard deviation of slope	0.01707	0.02016	0.01630
Grand average	$\bar{x} = \frac{(6 \times 0.0671) + (5 \times 0.0708) + (5 \times 0.0579)}{18} = 0.06538$		
Sum of square of factor (SSF)	$SSF = 6(0.0671 - 0.06538)^2 + 5(0.0708 - 0.06538)^2 + 5(0.0579 - 0.06538)^2 = 4.445 \times 10^{-4}$		
Sum of square of error (SSE)	$SSE = 5(0.01707)^2 + 4(0.02016)^2 + 4(0.01630)^2 = 4.150 \times 10^{-3}$		
Total sum of square (SST)	$SST = SSF + SSE = 4.594 \times 10^{-3}$		
Degree of freedom	$SST, df = N - 1 = 16 - 1 = 15$ $SSF, df = I - 1 = 3 - 1 = 2$		$SSE, df = N - I = 16 - 3 = 13$
Mean square	$MSE = \frac{SSE}{N - I} = \frac{4.150 \times 10^{-3}}{13} = 3.192 \times 10^{-4}$		$MSF = \frac{SSF}{I - 1} = \frac{4.445 \times 10^{-4}}{2} = 2.223 \times 10^{-4}$
F-value	$F = \frac{MSF}{MSE} = \frac{2.223 \times 10^{-4}}{3.192 \times 10^{-4}} = 0.6964$ $F_{critical, \alpha=0.05, df=2, 15} = 3.682$		



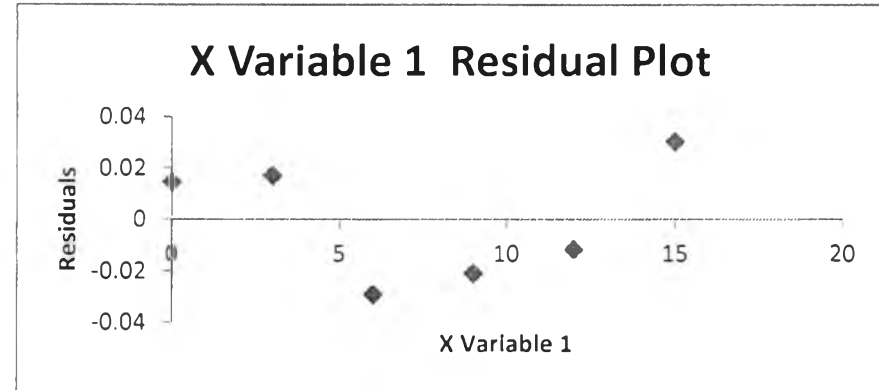
Table A.5 ANOVA (one-way)

<i>Source of variation</i>	<i>Sum of square (SS)</i>	<i>Degree of freedom (df)</i>	<i>Mean square (MS)</i>	<i>F</i>
Between Group	4.443×10^{-4}	2	2.222×10^{-4}	0.6961
Within Group	4.150×10^{-3}	13	3.192×10^{-4}	
Total	4.594×10^{-3}	15		



Table A.6 SUMMARY OUTPUT FOR MILLI Q WATER

<i>Regression Statistics</i>	
Multiple R	0.998006
R Square	0.996016
Adjusted R Square	0.99502
Standard Error	0.026629
Observations	6



ANOVA

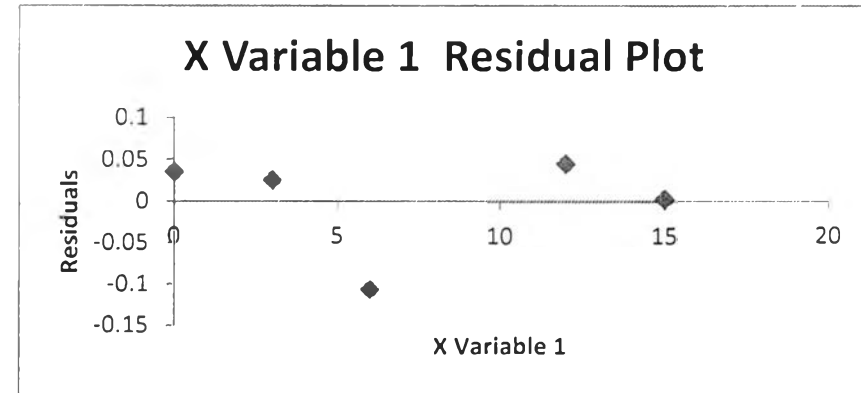
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	0.709095354	0.709095354	999.99525	5.96027E-06
Residual	4	0.002836395	0.000709099		
Total	5	0.711931749			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	-0.00071	0.019272588	-0.036797884	0.97240937	-0.054218474	0.052800093	-0.05422	0.0528
X Variable 1	0.067098	0.002121842	31.6227015	5.96027E-06	0.061207203	0.072989559	0.061207	0.07299



Table A.7 SUMMARY OUTPUT FOR DRINKING WATER A

<i>Regression Statistics</i>	
Multiple R	0.990356
R Square	0.980806
Adjusted R Square	0.974407
Standard Error	0.071113
Observations	5



ANOVA

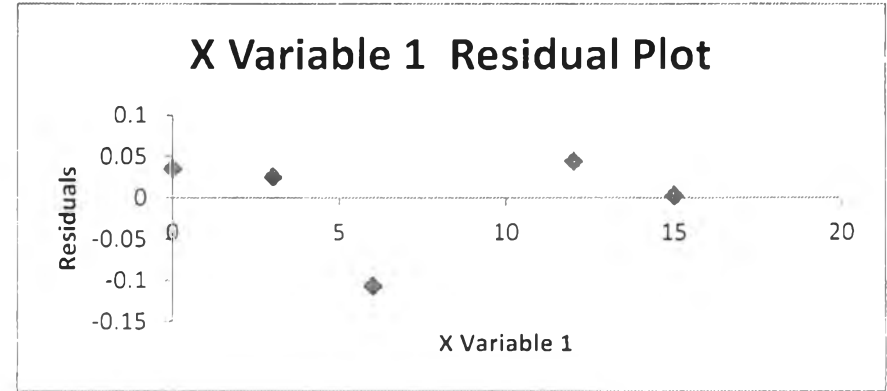
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	0.775213	0.775213	153.2948	0.001135
Residual	3	0.015171	0.005057		
Total	4	0.790384			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.014879	0.052009	0.286093	0.793425	-0.15064	0.180394	-0.15064	0.180394
X Variable 1	0.070766	0.005716	12.38123	0.001135	0.052577	0.088956	0.052577	0.088956



Table A.8 SUMMARY OUTPUT FOR DRINKING WATER B

<i>Regression Statistics</i>	
Multiple R	0.990356
R Square	0.980806
Adjusted R Square	
Square	0.974407
Standard Error	0.071113
Observations	5



ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	0.775213	0.775213366	153.2948405	0.001135202
Residual	3	0.015171	0.005057009		
Total	4	0.790384			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>	<i>Lower 95%</i>	<i>Upper 95%</i>	<i>Lower 95.0%</i>	<i>Upper 95.0%</i>
Intercept	0.014879	0.052009	0.28609313	0.793425149	-0.150635754	0.180394455	-0.15063575	0.180394
X Variable 1	0.070766	0.005716	12.38122936	0.001135202	0.05257651	0.088955653	0.05257651	0.088956

VITA

Miss Nattaporn Chanthasakda was born on the 11th of September 1988 in Bangkok, Thailand. She received her Bachelor's degree of Science from Chulalongkorn University in 2011 with second class honor. Then, she has continued the graduate study in the Department of Chemistry, Faculty of Science, Chulalongkorn University and her become a member of Chromaotgraphy and Separation Research Unit (ChSRU). She finished her Master's degree of Science in 2014.

Poster presentation and proceeding

"Electromembrane extraction for preconcentration of chromium(VI) ion" Nattaporn Chanthasakda, Pakorn Varanusupakul. Poster presentation and proceeding, 39th Congress on Science and Technology of Thailand (STT39), Bangkok International Trade & Exhibition Centre (BITEC), Bangkok, Thailand, 21-23 October, 2013.

"Electrical field assisted hollow fiber membrane liquid phase microextraction for determination of chromate ion" Nattaporn Chanthasakda, Pakorn Varanusupakul. Poster presentation, Ninth Mathematics and Physical Sciences Graduate Congress 2014 (9th MPSGC 2014), Faculty of Science, University of Malaya, Kuala Lumpur, Malaysia, 8-10 January, 2014.

"Electrical field assisted hollow fiber membrane liquid phase microextraction for determination of metal oxoanion" Nattaporn Chanthasakda, Pakorn Varanusupakul. Poster presentation, The Science Forum 2013, Faculty of Science, Chulalongkorn Unviersity, Bangkok, Thailand, 14-15 March, 2013.

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