REFERENCES

1. Y. Cai, Y. Cai, S. Mou and Y. Lu. Multi-walled carbon nanotubes as a solid-phase extraction adsorbent for the determination of chlorophenols in environmental water samples. *J. Chromatogr. A,* 2005, **1081**, 245-247.
2. Y. Alnouti, K. Srinivasan, D. Waddell, H. Bi, O. Kavetskaia and A. I. Gusev. Development and application of a new on-line SPE system combined with LC-MS/MS detection for high throughput direct analysis of pharmaceutical compounds in plasma. *J. Chromatogr. A,* 2005, **1080**, 99-106.
3. A. Zurutuza, S. Bayoudh, P. A. G. Cormack, L. Dambies, J. Deere, R. Bischoff and D. C. Sherrington. Molecularly imprinted solid-phase extraction of cocaine metabolites from aqueous samples. *Anal. Chim. Acta,* 2005, **542**, 14-19.
4. P. S. Roldan, I. L. Alcantara, C. C. F. Padilha and P. M. Padilha. Determination of copper, iron, nickel and zinc in gasoline by FAAS after sorption and preconcentration on silica modified with 2-aminotiazole groups. *Fuel,* 2005, **84**, 305-309.
5. G. Absalan and M. A. Mehrdjardi. Separation and preconcentration of silver ion using 2-mercaptobenzothiazole immobilized on surfactant-coated alumina. *Sep. Purif. Technol.,* 2003, **33**, 95-101.
6. Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng and M. Tian. Preconcentration of trace metals with 2-(methylthio)aniline-functionalized XAD-2 and their determination by flame atomic absorption spectrometry. *Anal. Chim. Acta,* 2004, **504**, 319-324.
7. A. M. Starvin, T. P. Rao. Solid phase extractive preconcentration of uranium (VI) onto diarylazobisphenol modified activated carbon. *Talanta,* 2004, **63**, 225-232.
8. O. Lev. Diagnostic application of organically doped sol-gel porous glass. *Analusis,* 1992, **20**, 543-553.
9. J.-Z. Xu, Y. Zhang, G.-X. Li and J.-J. Zhu. An electrochemical biosensor constructed by nanosized silver particles doped sol-gel film. *Mat. Sci. Eng. C.,* 2004, **24**, 833-836.
10. M. M. Ardakani, M. K. Kashani, M. S. Niasari and A. A. Ensafi. Lead ion-selective electrode prepared by sol-gel and PVC membrane techniques. *Sensor. Actuat. B-Chem.,* 2005, **107**, 438-445.

11. A. Khan, F. Mahmood, S. Ahmed and M. Y. Khokhar. Removal of Cd ions by sol-gel silica doped with 1-(2-pyridylazo)-2-naphthol. *J. Sol-gel Sci. Techn.*, 2003, **27**, 221-224.

12. S. Umethani and M. Matsui. Liquid-liquid distribution of 4-acyl-3-methyl-1-phenyl-5-pyrazolones and their zinc complexes. *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3426-3429.

13. B. Rusdiarso, A. Messaoudi and J.-P. Brunette. Synergistic extraction of cobalts(II) from cesium containing aqueous solution with mixtures of 4-acyl-pyrazol-5-ols and crown ethers. *Talanta*, 1993, **40**, 805-809.

14. Sigit, G. J. Goetz-Grandmont and J.-P. Brunette. Liquid-liquid extraction of cadmium and cobalt with mixtures of 1-phenyl-3-methyl-4-stearoyl-5-hydroxypyrazole (HPMSP) and n-dodecylamine (DDA) in toluene. *Monatsh. Chem.*, 1998, **129**, 787-797.

15. A. Tong, Y. Akama and S. Tanaka. Pre-concentration of copper, cobalt and nickel with 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone loaded on silica gel. *Analyst*, 1990, **115**, 947-949.

16. A. Tong and Y. Akama. Preconcentration of trace metals with 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone loaded on silica gel. *Anal. Sci.*, 1991, **7**, 83-86.

17. A. Intasiri. *4-Acylpyarazolone doped silica: synthesis, characterization, metal complexation and application to preconcentration.* Doctoral Dissertation, Department of Chemistry, Faculty of Science, Université Louis Pasteur, 2000.

18. A. Boos, A. Intasiri, J.-P. Brunette and M. J. F. Leroy. Surfactant-templated silica doped with 1-phenyl-3-methyl-4-stearoylpyrazole-5-one (HPMSP) as a new sorbent. *J. Mater, Chem.*, 2002, **12**, 886-889.

19. R. Yucha. *1-Phenyl-3-methyl-4-stearoyl-5-pyrazolone doped porous silica for solid phase extraction of metal from aqueous solution.* Master's Thesis, Department of Chemistry, Faculty of Science, Chulalongkorn University. 2003.

20. V. Camel. Solid phase extraction of trace elements. *Spectrochimica Acta Part B*, 2003, **58**, 1177-1233.

21. N. J. K. Simpson. *Solid-phase extraction: principle, techniques, and applications.* New York: Marcel Dekker, 2000, 2-3, 6.

22. Y. Shiraishi, G. Nishimuru, T. Hirai and I. Komasawa. Separation of transition metal using inorganic adsorbents modified with chelating ligands. *Ind. Eng. Chem. Res.*, 2002, **41**, 5065-5070.

23. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.*, 1985, **57**, 603-619.

24. E. M. Thurman and M. S. Mills. *Solid-phase extraction.* New York: John Wiley & Sons, 1998, 29.

25. A. Berthod. Silica: backbone material of liquid chromatographic column packings. *J. chromatrogr.*, 1991, **549**, 1-28.

26. R. K. Iler. *The Chemistry of silica.* New York: John Wiley & Sons, 1998, 186, 660.

27. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck. Ordered mesoporous molecular sieves synthesised by a liquid-crystal template mechanism. *Nature*, 1992, **359**, 710-712.

28. D. Kumar, S. Varma, G. K. Dey and N. M. Gupta. Hydrothermal synthesis characterization and catalytic properties of urano-silicate mesoporous molecular sieves. *Microporous Mater.*, 2004, **73**, 181-189.

29. K. Y. Ho, G. Mckay and K. L. Yeung. Selective adsorbents from ordered mesoporous silica. *Langmuir.*, 2003, **19**, 3019-3024.

30. X. S. Zhao, G. Q. Lu and G. J. Millar. Advances in mesoporous molecular sieves MCM-41. *Ind. Eng. Chem. Res.*, 1996, **35**, 2075-2090.

31. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker. A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J. Am. Chem. Soc.*, 1992, **114**, 10834-10843.

32. C.-Y. Chen, S. L. Burkett, H.-X. Li and M. E. Davis. Studies on mesoporous materials II. Synthesis mechanism of MCM-41. *Micropor. Mater.*, 1993, **2**, 27-34.

33. Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. Petroff, F. Schuth and G. D. Stucky. Generalized synthesis of periodic surfactant inorganic composite-materials. *Nature*, 1994, **368**, 317-321.

34. Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schuth and G. D. Stucky. Organization of organic molecules with inorganic molecular species into nanocomposite biphase arrays. *Chem. Mater.*, 1994, **6**, 1176-1191.

35. S. Mitra. *Sample preparation techniques in analytical chemistry*. New York: John Wiley & Sons, 2003, 227.

36. J. R. Dean. *Methods for environmental trace analysis*. New York: John Wiley & Sons, 2003, 50-51.

37. D. A. Skoog, D. M. West, F. J. Holler and S. R. Crouch. *Fundamentals of analytical chemistry*. 8th edition, California: Thomson Learning, 2004, 1044-1045.

38. E. Prichard, G. M. Mackay and J. Points. *Trace analysis: a structured approach to obtaining reliable results*. Cambridge: Hartnolls Ltd., 1996, 72.

39. D. C. Montgomery. *Design and analysis of experiments*. 5th ed, New York: John Wiley & Sons, 2001, 218-286.

40. E. Morgan. *Chemometric: experimental design*. New York: John Wiley & Sons, 1991, 49-113.

41. W. Stumm. *Chemistry of the solid-water interface processes at the mineral-water and particle-water interface in natural systems*. New York: John Wiley & Sons, 1992, 90-96.

42. K. W. Kolasinski. *Surface science*. New York: John Wiley & Sons, 2002, 192-193.

43. A. W. Adamson and A. P. Gast. *Physical Chemistry of surfaces*. 6th ed, New York: John Wiley & Sons, 1997, 390-398.

44. W. Mickler, A. Reich, E. Uhlemann and H. J. Bart. Liquid membrane permeation of zinc, cadmium and nickel with 4-acyl-5-pyrazolones and β-diketones. *J. Membrane. Sci.*, 1996, **119**, 91-97.

45. J. Seneviratne and J. A. Cox. Sol-gel materials for the solid phase extraction of metals from aqueous solution. *Talanta*, 2000, **52**, 801-806.

46. A. Khan, S. Ahmed, F. Mahmood, M. Y. Khokhar and M. Riaz. Efficacy of a new tan doped sol-gel sorbent for uptake of zinc. *Radichim. Acta*, 2003, **91**, 413-418.

47. C. Sizun, J. Raya, A. Intasiri, A. Boos and K. Elbayed. Investigation of the surfactants in CTAB-templated mesoporous silica by ^{1}H HRMAS NMR. *Micropor. Mesopor. Mater.*, 2003, **66**, 27-36.

48. B. S. Jensen. The synthesis of 1-phenyl-3-methyl-4-acyl-pyrazolones-5. *Acta Chem. Scand.*, 1959, **13**, 1668-1670.

49. L. H. Larry and J. H. West. The sol-gel process. *Chem. Rev.*, 1990, **90**, 32-72.

50. K. Sato, Y. Akama and T. Nakai. Liquid-liquid extraction separation of zinc and cadmium with 1-phenyl-3-methyl-4-acyl-5-pyrazolones and tri-n-octyl phosphine oxide. *Anal. Chim. Acta*, 1988, **207**, 367-372.

51. B. S. Jensen. Solvent extraction of metal chalets II. An investigation on some 1-phenyl-3-methyl-4-acyl-pyrazolones-5. *Acta Chem. Scand.*, 1959, **13**, 1890-1896.

52. J. A. Dean. *Lange's Handbook of chemistry.* New York: Mcgraw-hill book company, 1979, 54.

53. M. E. Mahmoud, M. M. Osman and M. E. Amer. Selective preconcentration and solid phase extraction of mercury(II) from natural water gel-loaded dithizone phases. *Anal. Chim. Acta,* 2000, **415,** 33-40.

54. M. E. Mahmoud and M. S. M. Al Saadi. Selective solid phase extraction and preconcentration of iron(III) based on silica gel-chemically immobilized purpurogallin. *Anal. Chim. Acta,* 2001, **450,** 239-246.

55. A. Goswami, A. K. Singh. Silica gel functionalized with resacetophenone: synthesis of a new chelating matrix and its application as metal ion collector for their flame atomic absorption spectrometric determination. *Anal. Chim. Acta,* 2002, **454,** 229-240.

56. A. Goswami, A. K. Singh. 1,8-Dihydroxyanthraquinone anchored on silica gel: synthesis and application as solid phase extractant for lead(II), zinc(II) and cadmium(II) prior to their determination by flame atomic absorption spectrometry. *Talanta,* 2002, **58,** 669-678.

57. A. R. Sarkar, P. K. Datta, M. Sarkar. Sorption recovery of metal ions using silica gel modified with salicylaldoxime. *Talanta,* 1996, **43**, 1857-1862.

58. P. Lessi, N. L. D. Filho, J. C. Moreira and J. T. S. Campos. Sorption and preconcentration of metal ions on silica gel modified silica with 2,5-dimercapto-1,3,4-thiadiazole. *Anal. Chim. Acta,* 1996, **327,** 183-190.

59. E. Matoso, L. T. Kubota and S. Cadore. Use of silica gel chemically modified with zirconium phosphate for preconcentration and determination of lead and copper by flame atomic absorption spectrometry. *Talanta*, 2003, **60**, 1105-1111.

60. M. Shamsipur, A. R. Ghiasvand, H. Sharghi and H. Naeimi. Solid phase extraction of ultra trace copper(II) using octadecyl silica membrane disks modified by a naphthol-derivative Schiff's base. *Anal. Chim. Acta*, 2000, **408**, 271-277.

61. L. T. Pryde. *Chemistry of the water environment.* Califonia: Commings Publishing Company, 973, 213.

62. Y. Akama, K. Sato, M. Ukaji, T. Kawata and M. Kajitani. Studies on extraction of copper(II) with 1-phenyl-3-methyl-4-acyl-5-pyrazolone. *Polyhedron*, 1985, **4**, 59-63.

63. B. J. Alloway and D. C. Ayres. *Chemistry principles of environmental pollution.* Ukraine: Blackie academic & professional, 1993, 140-150.

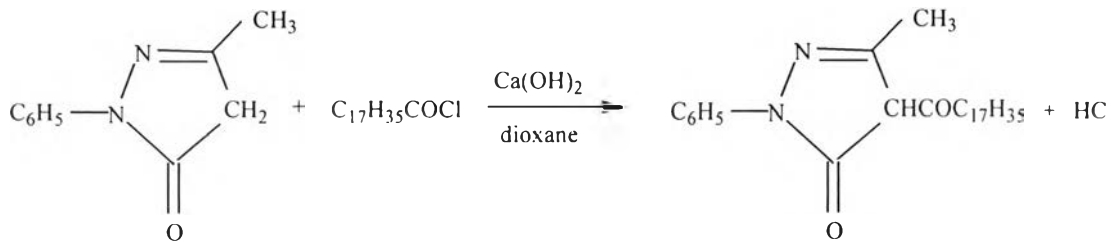
64. W. Viessman and M. J. Hammer. *Water supply and pollution Control.* 4th ed. New York: Happer & Row, 1985, 220-235.

APPENDICES

APPENDIX A

SYNTHESIS OF 1-PHENYL-3-METHYL-4-STEAROYL -5-PYRAZOLONE (HPMSP)

HPMSP was synthesized via the reaction given below [48]:



H_2PMP HPMSP

15 g (86.10 mmol) of 1-phenyl-3-methyl-pyrazolone was dissolved in 70 mL of dioxane at 60 °C. Then 12 g (161.94 mmol) of calcium hydroxide was added to the mixture and 30 mL (89.13 mmol) of stearoyl choride was added dropwise within 1 min. The reaction mixture was refluxed at 100 °C for 30 min. The excess calcium hydroxide was decomposed by pouring 200 mL of 2 M hydrochloric acid into the mixture which caused cream coloured crystals to separate. The products were filtered and washed with dilute hydrochloric acid and water. The crystals were recrystallized from ethanol/toluene (9 : 1 v/v) solution. Yield 75.20%, m.p. 66–67 °C. ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.85-7.29 (m, 5H, Ph-H), 2.76 (t, 2H, C(O)-CH_2),-2.51 (s, 3H, CH_3, pyrazolone), 1.78 (quint., 2H, $C(O)CH_2CH_2$-$(CH_2)_{14}$-CH_3), 1.29-1.44 (m, 28H, -$(CH_2)_{14}$-), 0.91 (t, 3H, $C(O)(CH_2)_{16}$-CH_3).

APPENDIX B

^{1}H-NMR spectrum of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP)

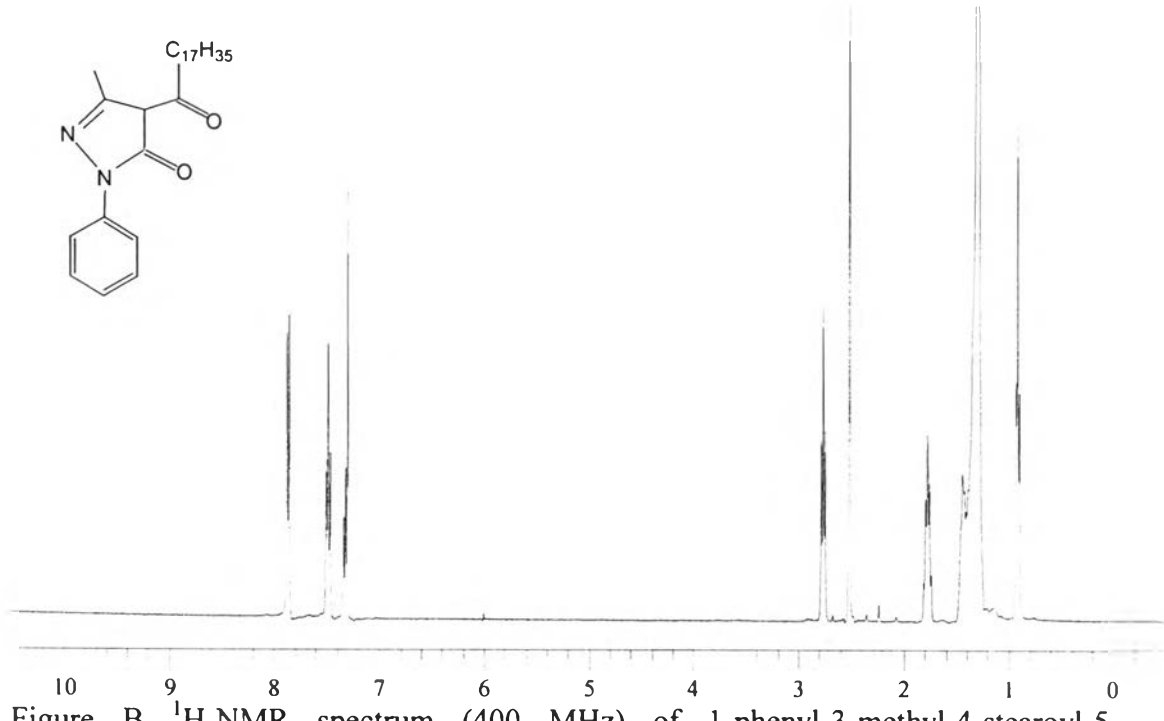


Figure B ^{1}H-NMR spectrum (400 MHz) of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone in $CDCl_3$.

APPENDIX C

CALCULATION OF ORGANIC MATTER CONTENTS IN MESOPOROUS SILICA

The organic matter contents in mesoporous silica could be determined from the composition of starting materials tabulated in Table C. And the calculation details were described below.

Table C The amounts of starting materials used for the synthesis of non-doped and HPMSP doped mesoporous silica.

Starting materials	Non-doped silica		HPMSP doped silica	
	(g)	(mmol)	(g)	(mmol)
TEOS	5.2295	25.102	5.1679	24.806
H_2O*	63.020	3501.1	63.540	3530.0
CTAB	1.6412	4.5031	1.6439	4.5105
MeOH	10.428	325.47	10.491	327.43
HPMSP	-		0.6556	1.4900

*H_2O was introduced to the mixture in the form of 0.1 M NaOH.

1. Non-doped mesoporous silica

   TEOS 25.102 mmol provides SiO_2 25.102 mmol

   $= 25.102 \times 10^{-3} \times 60.0843$ g $= 1.5082$ g

   CTAB 1.6412 g provided CTA^+ $= (1.6412/364.46) \times 284.56$ g $= 1.2814$ g

   Organic matter contents in non-doped mesoporous silica $= 1.2814$ g

   Mass of non-doped mesoporous silica $= 1.5082 + 1.2814$ g $= 2.7896$ g

   Therefore, organic matter contents in non-doped mesoporous silica

   $= (1.2814/2.7896) \times 100$ % $= 45.93$ %

2. HPMSP doped mesoporous silica

   TEOS 24.806 mmol provided SiO_2 24.806 mmol

   $= 24.806 \times 10^{-3} \times 60.0843$ g $= 1.4905$ g

   CTAB 1.6439 g provided CTA^+ $= (1.6439/364.46) \times 284.56$ g $= 1.2835$ g

   Amount of HPMSP in silica $= (1.4900 \times 10^{-3}) \times 440$ g $= 0.6556$ g

Organic matter contents in HPMSP doped mesoporous silica

= 1.2835 + 0.6556 g = 1.9391 g

Mass of HPMSP doped mesoporous silica

= 1.4905 + 1.2835 + 0.6556 g = 3.4296 g

Therefore, organic matter contents in HPMSP doped mesoporous silica

= (1.9391/3.4296) x 100 % = 56.54 %

APPENDIX D

CALCULATION OF ESTIMATED EFFECTS

The estimated effects of each variable and their interaction on the Cu(II) desorption could be calculated using the data from Table D as described below.

Table D The expanded design matrix and the Cu(II) desorption results.

Run	A	E	V	AE	AV	EV	AEV	Desorption of Cu(II) (mol/kg)
1	-	-	-	+	+	+	-	0.0309
2	+	-	-	-	-	+	+	0.0327
3	-	+	-	-	+	-	+	0.0343
4	+	+	-	+	-	-	-	0.0402
5	-	-	+	+	-	-	+	0.0255
6	+	-	+	-	+	-	-	0.0346
7	-	+	+	-	-	+	-	0.0335
8	+	+	+	+	+	+	+	0.0382
Estimated effect ($x10^{-3}$)	5.375	5.625	-1.575	-0.075	1.525	0.175	-2.125	

Main effect

$$A = \frac{-0.0309 + 0.0327 - 0.0343 + 0.0402 - 0.0255 + 0.0346 - 0.0335 + 0.0382}{4}$$

$$= 5.375x10^{-3}$$

$$E = \frac{-0.0309 - 0.0327 + 0.0343 + 0.0402 - 0.0255 - 0.0346 + 0.0335 + 0.0382}{4}$$

$$= 5.625x10^{-3}$$

$$V = \frac{-0.0309 - 0.0327 - 0.0343 - 0.0402 + 0.0255 + 0.0346 + 0.0335 + 0.0382}{4}$$

$$= -1.575x10^{-3}$$

Two-factor interaction

$$AE = \frac{0.0309 - 0.0327 - 0.0343 + 0.0402 + 0.0255 - 0.0346 - 0.0335 + 0.0382}{4}$$

$$= -0.075x10^{-3}$$

$$AV = \frac{0.0309 - 0.0327 + 0.0343 - 0.0402 - 0.0255 + 0.0346 - 0.0335 + 0.0382}{4}$$

$$= 1.525 \times 10^{-3}$$

$$EV = \frac{0.0309 + 0.0327 - 0.0343 - 0.0402 - 0.0255 - 0.0346 + 0.0335 + 0.0382}{4}$$

$$= 0.175 \times 10^{-3}$$

Three-factor interaction

$$AEV = \frac{-0.0309 + 0.0327 + 0.0343 - 0.0402 + 0.0255 - 0.0346 - 0.0335 + 0.0382}{4}$$

$$= -2.125 \times 10^{-3}$$

APPENDIX E

THE REPRODUCIBILITY RESULTS OF METAL EXTRACTION

The amounts of Cu(II) extracted by HPMSP doped mesoporous silica resulted from 16 replicate extraction experiments via column method were tabulated in Table E.

Table E The Cu(II) extraction results of the reproducibility study.

Number of run	Amounts of Cu(II) extracted (mol/kg)	
	20 ppm	40 ppm
1	0.0337	0.0548
2	0.0366	0.0514
3	0.0371	0.0519
4	0.0306	0.0492
5	0.0312	0.0492
6	0.0359	0.0508
7	0.0366	0.0493
8	0.0347	0.0443
9	0.0328	0.0496
10	0.0358	0.0493
11	0.0361	0.0449
12	0.0396	0.0433
13	0.0376	0.0459
14	0.0374	0.0497
15	0.0361	0.0448
16	0.0381	0.0457
Average	**0.0356**	**0.0484**
SD	**0.0025**	**0.0032**
RSD	**6.91**	**6.66**

CURRICULUM VITAE

Miss Tuanjai Yubolpas was born on November 4th, 1976 in Kalasin, Thailand. She received a Bachelor's degree of Science in Chemistry from Mahasarakham University in 1999. Since 2002, she has been a graduate student at Department of Chemistry, Faculty of Science, Chulalongkorn University and become a member of the solid-phase extraction research group under the supervision of Dr. Amarawan Intasiri. She earned the Master of Science in Chemistry in 2005. Her permanent address is 44 Moo 2, Dongling, Kamalasai, Kalasin, 46130, Thailand.