

การประยุกต์เมโซพอร์ซซิลิกาโดยด้าย 1-เฟนิล-3-เมทิล-4-สเตียโรอิล-5-ไพราโซโลน  
ในการหาปริมาณโลหะ



นางสาวเดือนใจ ยบุลพาศ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชาเคมี ภาควิชาเคมี

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2548

ISBN 974-53-2481-7

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

**APPLICATION OF 1-PHENYL-3-METHYL-4-STEAROYL-5-PYRAZOLONE  
DOPED MESOPOROUS SILICA TO THE DETERMINATION OF METAL**

**Miss Tuanjai Yubolpas**

**A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Chemistry**

**Department of Chemistry**

**Faculty of Science**

**Chulalongkorn University**

**Academic Year 2005**


**ISBN 974-53-2481-7**

**481899**


Thesis Title            Application of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone  
                                 doped mesoporous silica to the determination of metal  
By                            Miss Tuanjai Yubolpas  
Field of study            Chemistry  
Thesis Advisor          Amarawan Intasiri, Ph.D.

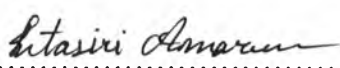
---


Accepted by the Faculty of Science, Chulalongkorn University in  
Partial Fulfillment of the Requirements for the Master's Degree


  
.....Dean of the Faculty of Science  
(Professor Piamsak Menasveta, Ph.D.)


THESIS COMMITTEE

  
.....Chairman  
(Associate Professor Siri Varothai, Ph.D.)

  
.....Thesis Advisor  
(Amarawan Intasiri, Ph.D.)

  
.....Member  
(Assistant Professor Aroonsiri Shitangkoon, Ph.D.)

  
.....Member  
(Assistant Professor Thammarat Aree, Ph.D.)

  
.....Member  
(Assistant Professor Yongsak Sritana-anant, Ph.D.)

เตือนใจ ยุบลพาศ : การประยุกต์เมโซพอร์ซิลิกาโดปด้วย 1-ฟีนิล-3-เมทิล-4-สเตียโรอิล-5-ไพราโซโลนในการหาปริมาณโลหะ (APPLICATION OF 1-PHENYL-3-METHYL-4-STEAROYL-5-PYRAZOLONE DOPED MESOPOROUS SILICA TO THE DETERMINATION OF METAL) อ. ที่ปรึกษา : ดร.อมรवारณ อินทศิริ, 86 หน้า. ISBN 974-53-2481-7

สมบัติในการสกัดโลหะของเมโซพอร์ซิลิกาโดปด้วย 1-ฟีนิล-3-เมทิล-4-สเตียโรอิล-5-ไพราโซโลน (HPMSP) ที่เตรียมผ่านกระบวนการโซล-เจลที่มีสารต้นแบบร่วมอยู่ด้วยได้รับการตรวจสอบทั้งในรูปแบบแบทช์และรูปแบบคอลัมน์ จากผลการทดลองในรูปแบบแบทช์พบว่าความสามารถในการสกัดโลหะของสารดูดซับปรับแต่งชนิดนี้ไม่เพียงขึ้นอยู่กับ pH ของสารละลายโลหะเท่านั้น แต่ยังขึ้นอยู่กับเกลือร่วมอยู่ด้วยในสารละลายโลหะ ความสามารถในการสกัด Cd(II), Pb(II) และ Zn(II) ที่ภาวะเหมาะสมที่สุดของซิลิกาชนิดนี้ พบว่ามีค่า 0.21, 0.12 และ 0.32 mol/kg ตามลำดับ การออกแบบการทดลองเชิงแฟคทอเรียลแบบสองยกกำลังสามที่นำมาใช้ในการหาปัจจัยหลักที่มีผลต่อประสิทธิภาพในการคาย Cu(II) ของสารดูดซับชนิดนี้ ได้ผลสรุปว่าปัจจัยที่มีความสำคัญได้แก่ ปริมาณของ Cu(II) และความเข้มข้นของกรดไนตริกที่ใช้เป็นตัวชะ ความสามารถในการสกัด Cu(II) ในรูปแบบคอลัมน์ของซิลิกาชนิดนี้มีค่าเท่ากับ 0.0998 mol/kg การนำเมโซพอร์ซิลิกาโดปด้วย HPMSP ไปใช้ในการเพิ่มความเข้มข้นของ Cu(II) จากสารละลายเอเควียสประสบความสำเร็จเป็นอย่างดี โดยสามารถเพิ่มความเข้มข้นได้ถึง 40 เท่า การศึกษาเรื่องการสกัดและการคายโลหะได้แสดงให้เห็นถึงความสามารถในการนำสารดูดซับกลับมาใช้ใหม่ได้โดยปราศจากการสูญเสียความสามารถในการดูดซับสาร นอกจากนี้ สารดูดซับโดปด้วย HPMSP นี้ยังสามารถนำไปประยุกต์กับการสกัดโลหะจากเมทริกซ์ที่เป็นอาหารทะเลได้อีกด้วย

ภาควิชา.....เคมี..... ลายมือชื่อนิสิต.....  
 สาขาวิชา.....เคมี..... ลายมือชื่ออาจารย์ที่ปรึกษา.....  
 ปีการศึกษา.....2548.....


# # 457 23036 23 : MAJOR CHEMISTRY

KEY WORD: HPMSP / MESOPOROUS SILICA / SOLID-PHASE EXTRACTION/  
DOPED SILICA / METAL EXTRACTION

TUANJAI YUBOLPAS : APPLICATION OF 1-PHENYL-3-METHYL-4-  
STEAROYL-5-PYRAZOLONE DOPED MESOPOROUS SILICA TO THE  
DETERMINATION OF METAL. THESIS ADVISOR : AMARAWAN  
INTASIRI, Ph.D., 86 pp. ISBN 974-53-2481-7.

The metal extraction properties of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP) doped mesoporous silica prepared by a template-tailored sol-gel process were investigated in both batch and column methods. The metal sorption capacities of the modified sorbent determined by batch experiments were governed not only by the pH of metal solution but also the presence of salts in metal solution. The capacities of the modified silica at optimum conditions for the extraction of Cd(II), Pb(II) and Zn(II) were found to be 0.21, 0.12 and 0.32 mol/kg, respectively. A  $2^3$  factorial design served for the determination of principal parameters on the Cu(II) desorption efficiency of the sorbent reached the conclusion that the significant factors were the amount of Cu(II) and the concentration of HNO<sub>3</sub> as eluent. The Cu(II) sorption capacity of the modified silica determined by column process was found to be 0.0998 mol/kg. The potential application of the HPMSP doped mesoporous silica to the preconcentration of Cu(II) from aqueous solution was accomplished with the maximum preconcentration factor of 40. The study of metal adsorption-desorption cycles showed the reusability of the sorbent without considerable loss of adsorption capacity. The HPMSP doped sorbent was also successfully applied for the extraction of metal ions contained in seafood matrix.

Department.....Chemistry..... Student's signature.....

Field of study.....Chemistry.....Advisor's signature.....

Academic year.....2005.....

## ACKNOWLEDGEMENTS

First of all, I wish to express the highest appreciation to my thesis advisor, Dr. Amarawan Intasiri for her invaluable guidance, kind supervision, profound assistance, encouragement and especially sincere forgiveness for my mistakes throughout my course of study. Thanks are also extended to Assoc. Prof. Dr. Siri Varothai, Assist. Prof. Dr. Aroonsiri Shitangkoon, Assist. Prof. Dr. Thammarat Aree and Assist. Prof. Dr. Yongsak Sritana-anant for being members of the thesis committee and for their worthy comments and suggestions.

This thesis would not be completed without kindness and help from many people. I gratefully acknowledge the Thailand Research Fund and the Office of Commission for Higher Education-CU Graduate Thesis Grant for their financial supports. Research facilities provided by the Solid-Phase Extraction Research Group and the Organic Synthesis Research Unit (OSRU) of Chulalongkorn University are greatly appreciated.

Finally, I am grateful and thankful to my parents and family members for their love, kindness, encouragement, great support and other assistance throughout the entire course of study. Also, I would like to express my special thanks to all members of the Solid-Phase Extraction Research Group for their kind assistance, cheerful moral and social support.

## CONTENTS

	<b>PAGE</b>
<b>ABSTRACT (IN THAI)</b> .....	iv
<b>ABSTRACT (IN ENGLISH)</b> .....	v
<b>ACKNOWLEDGEMENTS</b> .....	vi
<b>CONTENTS</b> .....	vii
<b>LIST OF FIGURES</b> .....	x
<b>LIST OF TABLES</b> .....	xiii
<b>LIST OF ABBREVIATION</b> .....	xv
<b>CHAPTER I : INTRODUCTION</b> .....	1
<b>CHAPTER II : THEORY AND LITERATURE REVIEW</b> .....	3
2.1. Solid-phase extraction.....	3
2.1.1. Principle.....	3
2.1.2. Mechanism of solid-phase extraction.....	4
2.1.3. Type of solid support.....	5
2.2. Silica.....	5
2.2.1. General.....	5
2.2.2. Functionalization of silica.....	6
2.3. Mesoporous silica.....	7
2.4. Sample preparation for metal analysis.....	11
2.5. Factorial design.....	12
2.6. Adsorption isotherms.....	15
2.7. Doping molecule.....	16
2.8. Literature review.....	17
2.9. Objectives of this study.....	19
<b>CHAPTER III : EXPERIMENTAL SECTION</b> .....	20
3.1. Reagents.....	20
3.2. Equipments.....	20
3.3. Experimental.....	20
3.3.1. Synthesis of materials.....	21
3.3.2. Characterization of materials.....	22
3.3.2.1. Determination of organic matter contents.....	22

	<b>PAGE</b>
3.3.2.2. Crystallinity, mesoporosity, surface area and pore size.....	22
3.3.3. Extraction properties of materials.....	23
3.3.3.1. Batch method.....	23
3.3.3.2. Column method.....	23
3.3.4. Application of HPMSP doped mesoporous silica to the metal extraction from food sample.....	24
<b>CHAPTER IV : RESULTS AND DISCUSSION.....</b>	<b>25</b>
4.1. Synthesis of materials.....	25
4.2. Characterization of materials.....	25
4.2.1. Determination of organic matter contents.....	25
4.2.2. Crystallinity of materials.....	26
4.2.3. Mesoporosity, surface area and pore size.....	27
4.3. Extraction properties of materials.....	29
4.3.1. Batch method.....	29
4.3.1.1. Reproducibility of materials for the extraction of metal.....	29
4.3.1.2. Effect of pH.....	31
i) Extraction of Cd(II) .....	31
ii) Extraction of Pb(II) .....	32
iii) Extraction of Zn(II) .....	33
4.3.1.3. Effect of salts present in metal solution.....	34
i) Extraction of Cd(II) .....	34
ii) Extraction of Pb(II) .....	36
iii) Extraction of Zn(II) .....	38
4.3.1.4. Effect of NaNO <sub>3</sub> concentration.....	40
4.3.1.5. Comparison with other sorbents.....	41
4.3.2. Column method .....	42
4.3.2.1. Reproducibility of material.....	42
4.3.2.2. Optimization of metal desorption.....	43
4.3.2.3. Column capacity.....	46
4.3.2.4. The effect of sample volume.....	47



	<b>PAGE</b>
4.3.2.5. Reusability of material.....	48
4.4. Application of HPMSP doped mesoporous silica to the metal extraction from food sample.....	49
4.4.1. The determination of metal ions contaminated in seafood sample....	49
4.4.2. The influence of acetate buffer on the metal extraction properties of HPMSP doped mesoporous silica.....	50
4.4.3. The metal extraction of HPMSP doped mesoporous silica from mixture solution in acetate buffer medium.....	51
4.4.4. The extraction of metal in seafood matrix.....	52
<b>CHAPTER V : CONCLUSIONS.....</b>	<b>55</b>
<b>REFERENCES.....</b>	<b>57</b>
<b>APPENDICES.....</b>	<b>63</b>
APPENDIX A Synthesis of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP).....	64
APPENDIX B <sup>1</sup> H-NMR spectrum of 1-phenyl-3-methyl-4-stearoyl-5- pyrazolone (HPMSP).....	65
APPENDIX C Calculation of organic matter contents in mesoporous silica.....	66
APPENDIX D Calculation of estimated effects.....	68
APPENDIX E The reproducibility results of metal extraction.....	70
<b>CURRICULUM VITAE.....</b>	<b>71</b>

## LIST OF FIGURES

FIGURES	PAGE
2.1	Structure of a silica gel showing siloxane bond, single free silanol, geminal silanols and vicinal silanols..... 6
2.2	Two possible mechanistic pathways for the formation of MCM-41: (1) liquid crystal initiated and (2) silicate anion initiated..... 8
2.3	Assembly of silicate-encapsulated rods proposed by Davis <i>et al.</i> ..... 8
2.4	Schematic diagram of the cooperative organization of silicate-surfactant mesophases as proposed by Stucky <i>et al.</i> ..... 10
2.5	A general scheme for the self-assembly reaction of different surfactant and inorganic species as proposed by Huo <i>et al.</i> ..... 10
2.6	Geometric view of the 2 <sup>3</sup> factorial design..... 13
2.7	The adsorption isotherms: (a) linear sorption isotherm (b) Langmuir isotherm (c) Freundlich isotherm..... 15
2.8	Chemical structure of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone (HPMSP)..... 16
3.1	Schematic diagram for the synthesis of HPMSP doped and non-doped mesoporous silica..... 21
3.2	The thermal profile for calcination of HPMSP doped and non-doped mesoporous silica..... 22
4.1	The XRD patterns of (a) non-doped mesoporous silica and (b) HPMSP doped mesoporous silica (black: as-synthesized silica, gray: calcined silica)..... 26
4.2	N <sub>2</sub> adsorption-desorption isotherms of (a) non-doped mesoporous silica and (b) HPMSP doped mesoporous silica (—●—: adsorption, —○—: desorption)..... 27
4.3	BJH pore size distribution of (a) non-doped mesoporous silica and (b) HPMSP doped mesoporous silica..... 28
4.4	Effect of pH on the Cd(II) extractability of non-doped and HPMSP doped mesoporous silica..... 31
4.5	Effect of pH on the Pb(II) extraction efficiency of non-doped and HPMSP doped mesoporous silica..... 32

<b>FIGURES</b>	<b>PAGE</b>
4.6 Effect of pH on the Zn(II) extractability of non-doped and HPMSP doped mesoporous silica.....	33
4.7 Effect of salts present in metal solution on the Cd(II) extraction efficiency of non-doped and HPMSP doped mesoporous silica from aqueous solution.....	35
4.8 Effect of salts present in metal solution on the Cd(II) extraction efficiency of non-doped and HPMSP doped mesoporous silica when the experiments were performed at (a) pH 3 and (b) pH 2.....	36
4.9 Effect of salts present in metal solution on the Pb(II) extraction efficiency of non-doped and HPMSP doped mesoporous silica from aqueous solution.....	36
4.10 Effect of salts present in metal solution on the Pb(II) extraction efficiency of non-doped and HPMSP doped mesoporous silica when the experiments were performed at (a) pH 3 and (b) pH 2.....	37
4.11 Effect of salts present in metal solution on the Pb(II) extractability of non-doped and HPMSP doped mesoporous silica at pH 2 using Pb(OAc) <sub>2</sub> as metal source.....	38
4.12 Effect of salts present in metal solution on the Zn(II) extraction of non-doped and HPMSP doped mesoporous silica from aqueous solution using (a) Zn(NO <sub>3</sub> ) <sub>2</sub> and (b) Zn(OAc) <sub>2</sub> as zinc sources.....	39
4.13 Effect of salts present in metal solution on the Zn(II) extraction of non-doped and HPMSP doped mesoporous silica performed at pH 3 and used (a) Zn(NO <sub>3</sub> ) <sub>2</sub> and (b) Zn(OAc) <sub>2</sub> as zinc sources.....	40
4.14 Effect of salts present in metal solution on the Zn(II) extraction of non-doped and HPMSP doped mesoporous silica performed at pH 2 and used (a) Zn(NO <sub>3</sub> ) <sub>2</sub> and (b) Zn(OAc) <sub>2</sub> as zinc sources.....	40
4.15 Effect of NaNO <sub>3</sub> concentration on the extraction of Zn(II) by non-doped and HPMSP doped mesoporous silica using (a) Zn(NO <sub>3</sub> ) <sub>2</sub> and (b) Zn(OAc) <sub>2</sub> as zinc sources.....	41
4.16 The normal probability plot of estimated effect.....	46

<b>FIGURES</b>	<b>PAGE</b>
<b>4.17</b> The amounts of Cu(II) extracted by HPMSP doped mesoporous silica using column method as a function of initial concentration of Cu(II).....	46
<b>4.18</b> (a) Adsorption isotherms of Cu(II) on HPMSP doped mesoporous silica and (b) linearization of the adsorption isotherm.....	47
<b>B</b> <sup>1</sup> H-NMR spectrum (400 MHz) of 1-phenyl-3-methyl-4-stearoyl-5-pyrazolone in CDCl <sub>3</sub> .....	65

## LIST OF TABLES

TABLES	PAGE
2.1	Design matrix for $2^3$ factorial design..... 13
2.2	The columns of contrast coefficients for the $2^3$ design..... 14
4.1	Amount of organic matters in non-doped and HPMSP doped mesoporous silica..... 26
4.2	The d-spacing values of as-synthesized and calcined mesoporous silica... 27
4.3	The textural properties of calcined non-doped and HPMSP doped mesoporous silica ..... 28
4.4	The reproducibility results of Cu(II) extraction by HPMSP doped mesoporous silica from different lots..... 30
4.5	The reproducibility results of Zn(II) extraction by non-doped and HPMSP doped mesoporous silica from different lots..... 30
4.6	Comparison of sorption capacities (mol/kg)..... 42
4.7	Experimental variables, levels, design matrix and results (amounts of Cu(II) desorped) in the $2^3$ factorial design for Cu(II) desorption..... 43
4.8	The estimated effects of the variables and their interaction..... 44
4.9	Analysis of variance for the Cu(II) desorption efficiency of HPMSP doped mesoporous silica..... 45
4.10	Effect of sample volume on the Cu(II) desorption efficiency of HPMSP doped mesoporous silica..... 48
4.11	The Cu(II) adsorbed and desorbed on HPMSP doped mesoporous silica, using 20 ml of 3 M HNO <sub>3</sub> as eluent in the column method..... 49
4.12	The amounts of metals contained in mussel and fish samples determined by AAS after wet digestion process..... 50
4.13	The amounts of metal ions extracted by HPMSP doped mesoporous silica from acetate buffer medium at pH 4.5..... 51
4.14	The amounts of each extracted metal ion from mixture solution in acetate buffer medium at pH 4.5..... 52
4.15	The percent recovery results for metal ions added to the blank, mussel and fish samples..... 53

<b>TABLES</b>	<b>PAGE</b>
<b>4.16</b> Effect of sample matrix on the amounts of metal extracted by HPMSP doped mesoporous silica in each mixture.....	54
<b>C</b> The amounts of starting materials used for the synthesis of non-doped and HPMSP doped mesoporous silica.....	66
<b>D</b> The expanded design matrix and the Cu(II) desorption results.....	68
<b>E</b> The Cu(II) extraction results of the reproducibility study.....	70

**LIST OF ABBREVIATION**

ANOVA	analysis of variance
APD	average pore diameter
BET	Brunauer-Emmet-Teller
BJH	Barrett-Joyner-Halenda
CTAB	Cetyltrimethylammonium bromide
H <sub>2</sub> PMP	1-phenyl-3-methyl-pyrazolone
HPMSP	1-phenyl-3-methyl-4-stearoyl-5-pyrazolone
IUPAC	International Union of Pure and Applied Chemistry
LCT	liquid crystal templating
LLE	liquid-liquid extraction
SPE	solid-phase extraction
TEOS	tetraethylorthosilicate
XRD	x-ray diffraction