

นางสาว กิตติมา ฉัตรวงศ์วาน

วิทยานิพนธ์นี้ เป็นส่วนหนึ่งของการศึกษาหลักสูตรปริญญาวิทยาสาสตรมหาบัณฑิต ภาควิชา เคมี บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย พ.ศ. 2531 ISBN 974-569-853-9 ลิขสิทธิ์ของบัญฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

MICROEXTRACTION OF THE PHENOL AND SOME DERIVATIVES

IN WATER

Miss Kittima Chatrewongwan

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

Department of Chemistry

Graduate School

Chulalongkorn University

1988

ISBN 974-569-853-9

Copyright of the Graduate School . Chulalongkorn University

Thesis Title

Microextraction of The Phenol And Some

Derivatives in Water.

Name

Miss Kittima Chatrewongwan

Department

Chemistry

Thesis Advisor Sittichai Leepipatpiboon . Ph.D.

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

(Professor Thavorn Vajrabhaya , Ph.D.)

Thesis Comittee

M. Amorasit ... Chairman

(Associate Professor Maen Amorasit)

K. Pronghetchara Member

(Rucha Phongbetchara , Ph. D.)

Pipat Karitray Member

(Associate Professor Pipat Karntiang , Ph.D.)

S. Le spopstpoboon Member

(Sittichai Leepipatpiboon , Ph.D.)



กิตติมา ฉัตรวงศ์วาน : การสกัดระบบจุลภาคของพีนอลและอนุพันธ์บางชนิดในน้ำ (MICROEXTRACTION OF THE PHENOL AND SOME DERIVATIVES IN WATER อ.ที่ปรีกษา ดร.สิทธิชัย ลีพิพัฒน์ไพบูลย์, 201 หน้า.

การพัฒนาการสกัดระบบจุลภาค เพื่อใช้ในการสกัดสารประกอบพีนอล เช่น พีนอล 2-ไนโทรพีนอล 2,4-ไดคลอโรพีนอล 2,4,6-ไทรคลอโรพีนอล 4-คลอโร-3-ครีชอล จากตัวอย่างน้ำ ก่อนที่จะนำไปวิเคราะห์หาปริมาณโดยใช้เครื่องแก๊สโครมาโทกราฟ ซึ่งใช้เฟลมไอออไนเชชั่นดีเทคเตอร์ (FID) โดยศึกษาบัจจัยต่าง ๆ ที่มีอิทธิพลต่อประสิทธิภาพของการสกัด ได้แก่ ความเป็นกรด ระยะเวลาที่ เหมาะสมในการสกัด ชนิดของตัวทำลายอินทรีย์ในการสกัดซึ่งรวมถึง เมธิลีน คลอไรด์ คาร์บอน ไดซัลไฟด์ และเชกเชน อัตราส่วนของสารตัวอย่างต่อตัวทำลายนั้นคือ 9:1 5:5 และ 2:8 และผลจากการเติม เกลือโชเดียมคลอไรด์ เกลือโชเดียมชัลเฟต สภาวะที่เหมาะสมที่สุดสำหรับ การสกัดระบบจุลภาคของสาร ประกอบพีนอลและอนุพันธ์บางชนิดของฟันอลในตัวอย่างน้ำ คือการสกัดที่ pH 2 ด้วยเมธิลีน คลอไรด์ อัตรา ส่วนสารละลาย ตัวอย่างต่อตัวทำละลาย 9:1 และใช้เกลือโชเดียมชัลเฟตปริมาณ 2.0 กรัม โดยทำการ สกัดเป็นเวลา 20 นาที ประสิทธิภาพของการสกัดซึ่งได้จากการศึกษาอยู่ในช่วง 17.74-106.30% และมีค่า เบี่ยงเบนมาตราฐานระหว่าง 0.08-9.95% ปีดจำกัดต่ำสุดของสารประกอบพีนอลสามารถวัดปริมาณในสาร ตัวอย่างน้ำได้อยู่ในช่วง 0.45-1.70 ppm นอกจากนี้ยังได้ศึกษาความถูกต้องของเทคนิกการฺวิเคราะห์ใน สภาวะที่เหมาะสมที่สุด ผลปรากฏว่าเปอร์เซนต์ความผิดพลาดอยู่ในช่วง 0.53-4.97%

กาควิชา	เคมี		Andra	1		
สาขาวิชา	(And 10/1:11					
ปีการศึกษา	2531	ลายมือชื่ออาจารย์ที่	ปริกษา	Fulle	Lynn	/~



KITTIMA CHATREWONGWAN: MICROEXTRACTION OF THE PHENOL AND SOME DERIVATIVES IN WATER. THESIS ADVISOR: DR. SITTICHAL LEEPIPATPIBOON, 201 pp.

Microextraction technique has been developed for the determination of trace phenolic compounds, i.e., phenol; 2-nitrophenol, 2,4-dinitrophenol, 2,4,6-trichlorophenol, and 4-chloro-3-cresol from water samples prior to analyze by gas chromatograph equipped with flame ionization detector (FID). The various effects on percent recovery ,i.e., the pHs, the shaking times, the salting out with sodium chloride and anhydrous sodium sulfate, the sample-to-solvent ratios, i.e., 9:1, 5:5, 2:8, and the extracting organic solvents including methylene chloride, carbon disulfide, and hexane were investigated and evaluated. The suitable condition for the microextraction of phenolic compounds from water samples is the pH of 2, the equilibration time of 20 minute, the methylene chloride, the sample-to-solvent ratio of 9:1 and salting out with 2.00 g anhydrous sodium sulfate. The percent recoveries are in the range of 17.74-106.30% with the percent RSD of 0.08-9.95%. accuracy of these techniques was studied and the percent error was in the range of 0.53-4.97%. The aqueous samples contained as low as 0.45-1.70 ppm of these phenolic compounds could be eassily detected,

ภาควิชา	102	 ลายมือชื่อนิสิต	Δ.	2
	ואיניסורילמן			4
ปีการศึกษา	2531	 ลายมือชื่ออาจารย์	ที่ปรึกษา	22 35. 94



ACKNOWLEDGEMENTS

The author would like to take this opportunity to convey the most sincere thanks and appreciation to her advisor Dr. Sittichai Leepipatpiboon. This thesis will not be successfull without the kindness, guidance, and assistance from him.

A note of appreciation is also extented to Mrs. Nongyow Thongtan, The Director of Agricultural Chemistry Division, Department of Agriculture, Ministry of Agriculture and Cooperatives for her permission of using the gas chromatograph in the first period of this thesis and the microcomputor.

She is also grateful to Miss Pornpimal Kongthip, Mr. Vinai Pitiyon, Mr. Adul Suvannate, and Mr. Charun Pornkuntham for their invaluable suggestions and helpfuls. In addition, appreciations are also expressed to her friends and her officemates for their encouragement.

She would also like to thanks the Graduate School , Chulalongkorn University for their financial support for this thesis , the thesis comittee for their comments , the laboratory of Environmental Quality Standard Division , Office of the National Environment Broad for the standard , and the laboratory of Metropolitan Water Work Authority at the Samsen Station for the water samples.

Finally, Special appreciate is acknowledged to her dear family for their encouragement, and understanding throughout the entire study.



CONTENTS

		PAGE	
ABSTRACT	(IN	THAI) iv	
ABSTRACT	(IN	ENGLISH) v	,
ACKNOWLED	GEME	NTS vii	-
CONTENTS.	••••	1x	
LIST OF T	ABLE	s xii	
LIST OF F	IGUF	ES xv111	
CHAPTER 1	. :	INTRODUCTION 1	
1	.1	THE PURPOSE OF THE STUDY	,
1	. 2	HISTORICAL 5	
CHAPTER 2	2 :	THEORY 18	
2	2.1	GIBBS'PHASE RULE	
2	2.2	NERNST DISTRIBUTION LAW 19	
	2.3	THERMODYNAMIC DERIVATION OF THE	
	3		
		DISTRIBUTION LAW 20	•
2	2.4	DISTRIBUTION LAW 22	
2	2.5	EXTRACTION EFFICIENCY 23	,
2	2.6	EFFECT OF ph 26	
2	2.7	SALTING EFFECT 28	,
2	8.8	CHOICE OF SOLVENT)
CHAPTER 3	3 :	EXPERIMENT	3
3	3.1	APPARATUS 33	3
		CHEMICALS 33	
		3.2.1 Standard of phenolic compounds 33	

	3.2.2	Organic Solvents 34
	3.2.3	Reagents 34
3.3	PREPAR	ATION OF STANDARD SOLUTIONS 34
	3.3.1	The Stock Standard Solution
		of Phenolic Compounds in 2-
		Propanol 34
	3.3.2	The Stock Standard Solutions
		of Phenolic Compounds in Organic
		Solvents 35
	3.3.3	The Internal Standard Solution
		of Phenolic Compounds in Organic
true et al.		Solvents 35
з. и	THE V	ARIOUS EFFECTS ON % RECOVERY
OF MICKOLAIN		Study on the pH
		Study on the Shaking Time 37
		Study on the Salting Out 38
	3.4.4	Study on the Sample-to-
		Solvent Ratio 40
3.5	INTERN	AL STANDARDIZATION METHOD 41
3.6	THE CA	LIBRATION CURVES OF EACH
PHENOLIC COM	POUND I	N EACH ORGANIC SOLVENT 36
3.7	GAS CH	ROMATOGRAPHIC CONDITIONS 44
	3.7.1	Gas Chromatographic Conditions
		for Studying the Single
		Component Solutions 44
	3.7.2	Gas Chromatographic Conditions
		for Studying the Mixture

		Solutions 46
CHAPTER	4:	RESULT AND DISCUSSION 60
	4.1	THE STUDY OF pH
	4.2	THE STUDY OF THE SHAKING TIME 74
	4.3	THE SALTING OUT EFFECT 87
	4.4	THE EFFECT OF SAMPLE-TO-SOLVENT
		RATIOS 129
	4.5	THE EFFECT OF ORGANIC SOLVENT 151
	4.6	THE EFFECT OF CONCENTRATIONS 152
	4.7	THE MINIMUM DETECTABLE LEVEL (MDL)
		OF PHENOLIC COMPOUNDS 153
	4.8	THE ACCURACY OF MICROEXTRACTION
		TECHNIQUE 154
	4.9	THE DETERMINATION OF PHENOLIC COMPOUNDS
		IN REAL WATER SAMPLES 156
CHAPTER	5:	CONCLUSION 162
		REFERENCES 165
		VTTA

LIST OF TABLES

TABLE		PAGE
4.1	The effect of pH on % recovery of 10.00 ppm	
	of phenol in standard aqueous solution with	
	the various organic solvents	. 62
4.2	The effect of pH on % recovery of 10.00 ppm	
	of 2-nitrophenol in standard aqueous solution	on
	with the various organic solvents	. 63
4.3	The effect of pH on % recovery of 10.00 ppm	of
	2.4-dichlorophenol in standard aqueous solu-	tion
	with the various organic solvents	. 64
4.4	The effect of pH on % recovery of 10.00 ppm	of
	2.4-trichlorophenol in standard aqueous solu	ition
	with the various organic solvents	. 65
4.5	The effect of pH on % recovery of 10.00 ppm	of
	4-chloro-3-cresol in standard aqueous solut:	lon .
	with the various organic solvents	. 66
4.6	The effect of pH on % recovery of 10.00 ppm	
	of phenol in standard mixture aqueous solut:	Lon
	with the various organic solvents	. 68
4.7	The effect of pH on % recovery of 10.00 ppm	
	of 2-nitrophenol in standard mixture aqueous	3
	solution with the various organic solvents.	. 69
4.8	The effect of pH on % recovery of 10.00 ppm	
	of 2,4-dichlorophenol in standard mixture	
	sausaus salution with the ventous organic	

	solvents 70
4.9	The effect of pH on % recovery of 10.00 ppm
	of 2,4,6-trichlorophenol in standard mixture
	aqueous solution with the various organic
	solvents 73
4.10	The effect of pH on % recovery of 10.00 ppm
	of 4-chloro-3-cresol in standard mixture
	aqueous solution with the various organic
	solvents 72
4.11	The effect of shaking time on % recovery of
	10.00 ppm of phenol in standard aqueous
	solution with the various organic solvents. 75
4.12	The effect of shaking time on % recovery of
	10.00 ppm of 2-nitrophenol in standard aqueous
	solution with the various organic solvents 70
4.13	The effect of shaking time on % recovery of
	10.00 ppm of 2.4-dichlorophenol in standard
	aqueous solution with the various organic
	solvents 77
4.14	The effect of shaking time on % recovery of
	10.00 ppm of 2,4,6-trichlorophenol in standard
	aqueous solution with the various organic
	solvents 78
4.15	The effect of shaking time on % recovery of
	10.00 ppm of 4-chloro-3-cresol in standard
	aqueous solution with the various organic
	solvents 79
	The state of the state of the state of

	10.00 ppm of phenol in standard mixture
	aqueous solution with the various organic
	solvents 83
4.17	The effect of shaking time on % recovery of
	10.00 ppm of 2-nitrophenol in standard mixture
	aqueous solution with the various organic
	solvents 82
4.18	The effect of shaking time on % recovery of
	10.00 ppm of 2,4-dichlorophenol in standard
	mixture aqueous solution with the various
	organic solvents
4.19	The effect of shaking time on % recovery of
	10.00 ppm of 2.4.6-trichlorophenol in standard
	mixture aqueous solution with the various
	organic solvents 84
4.20	The effect of shaking time on % recovery of
	10.00 ppm of 4-chloro-3-cresol in standard
	mixture aqueous solution with the various
	organic solvents
4.21	The effect of salting out on % recovery of
	phenol in standard aqueous solution with
	the various organic solvents
4.22	The effect of salting out on % recovery of
4.22	2-nitrophenol in standard aqueous solution
	with the various organic solvents 93
4.23	The effect of salting out on % recovery of
	2,4-dichlorophenol in standard aqueous
	ROLLICON WILD LOW VARIOUS OFFMILE

	solvents 93
4.24	The effect of salting out on % recovery of
	2.4.6-trichlorophenol in standard aqueous
	solution with the various organic
	solvents 95
4.25	The effect of salting out on % recovery of
	4-chloro-3-cresol in standard aqueous solution
	with the various organic solvents 97
4.26	The effect of salting out on % recovery of
	phenol in standard mixture aqueous solution
	with the various organic solvents 109
4.27	The effect of salting out on % recovery of
	2-nitrophenol in standard mixture aqueous
	solution with the various organic
	solvents 111
4.28	The effect of salting out on % recovery of
	2.4-dichlorophenol in standard mixture
	aqueous solution with the various
	organic solvents
4.29	The effect of salting out on % recovery of
	2.4.6-trichlorophenol in standard aqueous
	mixture solution with the various organic
	solvents 115
4.30	The effect of salting out on % recovery of
	4-chloro-3-cresol in standard mixture aqueous
	solution with the various organic
	solvents 117
4.31	The effect of sample-to-solvent ratios on %

	recovery of phenol in standard aqueous solution
	with the various organic solvents 131
4.32	The effect of sample-to-solvent ratios on %
	recovery of 2-nitrophenol in standard aqueous
	solution with the various organic solvents. 132
4.33	The effect of sample-to-solvent ratios on %
	recovery of 2.4-dichlorophenol in standard
	aqueous solution with the various organic
	solvents 133
4.34	The effect of sample-to-solvent ratios on %
,	recovery of 2.4.6-trichlorophenol in standard
	aqueous solution with the various
	organic solvents
4.35	The effect of sample-to-solvent ratios on %
	recovery of 4-chloro-3-cresol in standard
	aqueous solution with the various
	organic solvents
4.36	The effect of sample-to-solvent ratios on %
	recovery of phenol in standard mixture
	aqueous solution with the various organic
	solvents 141
4.37	The effect of sample-to-solvent ratos on %
	recovery of 2-nitrophenol in standard
	mixture aqueous solution with the various
	organic solvents 142
4.38	The effect of sample-to-solvent ratios on %
	recovery of 2,4-dichlorocresol in standard
	The second of th

	organic solvents 143
4.39	The effect of sample-to-solvent ratios on %
	recovery of 2,4,6-trichlorophenol in standard
	mixture aqueous solution with the various
	organic solvents 144
4.40	The effect of sample-to-solvent ratios on %
	recovery of 4-chloro-3-cresol in standard
	mixture aqueous solution with the various
	organic solvents 145
4.41	The minimum detectable level of phenolic
	compounds in the various organic solvents 153
4.42	The analysis of phenolic compounds in the
	unknown synthetic mixture solutions 155



LIST OF FIGURES

FIGURE	S	PAGE
2.1	The effect of the solvent to water ratio	
	on both the % recovery and the relative	
	concentration of analytes with difference	
	distribution coefficients	. 25
3.1	Relative calibration curve	. 42
3.2	The calibration curves of phenol in the vari	ous
	organic solvents	. 47
3.3	The calibration curves of 2-nitrophenol in	
	the various organic solvents	. 48
3.4	The calibration curves of 2,4-dichlorophenol	
	in the various organic solvents	. 49
3.5	The calibration curves of 2,4,6-trichlorophe	nol
	in the various organic solvents	. 50
3.6	The calibration curves of 4-chloro-3-cresol	
	in the various organic solvents	. 51
3.7	Gas chromatograms of phenol in the various	
	organic solvents	. 52
3.8	Gas chromatograms of 2-nitrophenol in the	
	various organic solvents	. 53
3.9	Gas chromatograms of 2,4-dichlorophenol in the	he
	various organic solvents	. 54
3.10	Gas chromatograms of 2,4,6-trichlorophenol in	n
	the various organic solvents	. 55
2 11	God obnometogness of 1-oblono-3-onegol in	

	the various organic solvents 56
3.12	Gas chromatogram of the mixture of phenolic
	compounds in methylene chloride 57
3.13	Gas chromatogram of the mixture of phenolic
	compounds in carbon disulfide 58
3.14	Gas chromatogram of the mixture of phenolic
	compounds in hexane 59
4.1	The effect of pH on % recovery of 10.00 ppm
	of each phenolic compounds in standard aqueous
	solution with the various organic solvents 67
4.2	The effect of pH on % recovery of 10.00 ppm
	of each phenolic compounds in standard mixture
	aqueous solution with the various organic
	solvents 73
4.3	The effect of shaking time on % recovery of
	10.00 ppm of each phenolic compounds in standard
	aqueous solution with the various organic
	solvents 80
4.4	The effect of shaking time on % recovery of
	10.00 ppm of each phenolic compounds in standard
	mixture aqueous solution with the various
	organic solvents 86
4.5A	The effect of salting out on % recovery of
	10.00 ppm of phenol in standard aqueous
	solution with the various organic
	solvents 99
	The effect of salting out on % recovery of
	1 00 npm of phenol in standard aqueous

	solution with the various organic
	-solvents 100
4.6A	The effect of salting out on % recovery of
	10.00 ppm of 2-nitrophenol in standard aqueous
	solution with the various organic
	solvents 101
4.6B	The effect of salting out on % recovery of
	1.00 ppm of 2-nitrophenol in standard aqueous
	solution with the various organic
	solvents 102
4.7A	The effect of salting out on % recovery of
	10.00 ppm of 2.4-dichlorophenol in standard
	aqueous solution with the various organic
	solvents 103
4.7B	The effect of salting out on % recovery of
	1.00 ppm of 2.4-dichlorophenol in standard
	aqueous solution with the various organic
	solvents 104
4.8A	The effect of salting out on % recovery of
	10.00 ppm of 2.4.6-trichlorophenol in standard
	aqueous solution with the various organic
	solvents 105
4.8B	The effect of salting out on % recovery of
	1.00 ppm of 2,4,6-trichlorophenol in standard
	aqueous solution with the various organic
	solvents 106
4.9A	The effect of salting out on % recovery of
	as as were as hearteness amount in standard

	aqueous solution with the various organic
	solvents 107
4.9B	The effect of salting out on % recovery of
	1.00 ppm of 4-chloro-3-cresol in standard
	aqueous solution with the various organic
	solvents 108
4.10A	The effect of salting out on % recovery of
	10.00 ppm of phenol in standard mixture
	aqueous solution with the various organic
	solvents 119
4.10B	The effect of salting out on % recovery of
	1.00 ppm of phenol in standard mixture
	aqueous solution with the various organic
	solvents 120
4.11A	The effect of salting out on % recovery of
	10.00 ppm of 2-nitrophenol in standard mixture
	aqueous solution with the various organic
	solvents 121
4.11B	The effect of salting out on % recovery of
	1.00 ppm of 2-nitrophenol in standard mixture
	aqueous solution with the various organic
	solvents 122
4.12A	The effect of salting out on % recovery of
	10.00 ppm of 2,4-dichlorophenol in standard
	mixture aqueous solution with the various
	organic solvents 123
4.12B	
	1 00 mm of 2 % dishlemenhanal in standard

	mixture aqueous solution with the various
	organic solvents 124
4.13A	The effect of salting out on % recovery of
	10.00 ppm of 2.4.6-trichlorophenol in standard
	mixture aqueous solution with the various
	organic solvents 125
4.13B	The effect of salting out on % recovery of
	1.00 ppm of 2.4,6-trichlorophenol in standard
	mixture aqueous solution with the various
	organic solvents 126
4.14A	The effect of salting out on % recovery of
	10.00 ppm of 4-chloro-3-cresol in standard
	mixture aqueous solution with the various
	organic solvents 127
4.14B	The effect of salting out on % recovery of
	1.00 ppm of 4-chloro-3-cresol in standard
	mixture aqueous solution with the various
	organic solvents 128
4.15	The effect of sample-to-solvent ratios on
	% recovery of phenol in standard aqueous
	solution with the various organic
	solvents 136
4.16	The effect of sample-to-solvent ratios on
	% recovery of 2-nitrophenol in standard
	aqueous solution with the various organic
	solvents 137
4.17	The effect of sample-to-solvent ratios on
	* recovery of 2 /-dichlerenherel in standard

	aqueous solution with the various organic
	solvents
4.18	The effect of sample-to-solvent ratios on
	% recovery of 2,4,6-trichlorophenol in
	standard aqueous solution with the various
	organic solvents 139
4.19	The effect of sample-to-solvent ratios on
	% recovery of 4-chloro-3-cresol in standard
	aqueous solution with the various organic
	solvents 140
4.20	The effect of sample-to-solvent ratios on
	% recovery of phenol in standard mixture
	aqueous solution with the various organic
	solvents 146
4.21	The effect of sample-to-solvent ratios on
	% recovery of 2-nitrophenol in standard
	mixture aqueous solution with the various
	organic solvents
4.22	The effect of sample-to-solvent ratios on
	% recovery of 2,4-dichlorophenol in standard
	mixture aqueous solution with the various
	organic solvents
4.23	The effect of sample-to-solvent ratios on
	% recovery of 2,4,6-trichlorophenol in
	standard mixture aqueous solution with the
	various organic solvents
4.24	The effect of sample-to-solvent ratios on
	% recovery of 4-chloro-3-cresol in standard

	mixture aqueous solution with the various	
	organic solvents 1	.50
4.25	Gas chromatogram of the real sample	
	No. 1* 1	57
4.26	Gas chromatogram of the real sample	
	No. 2* 1	58
4.27	Gas chromatogram of the real sample	
	No. 3* 1	59
4.28	Gas chromatogram of the real sample	
	No. 4* 1	60
4.29	Gas chromatogram of the real sample	
	No. 5 1	61