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SIMULTANEOUS DETERMINATION OF CARBARYL AND
CARBOFURAN IN VEGETABLE SAMPLES USING
SPECTROPHOTOMETRY

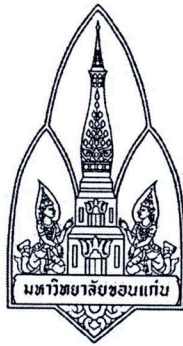
MR. SUKSANT KARNSA-ARD

A THESIS FOR THE DEGREE OF MASTER OF SCIENCE
KHON KAEN UNIVERSITY

2010

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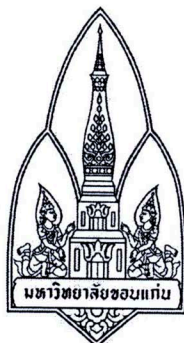
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MR. SUKSANT KARNSA-ARD

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIEMENTS FOR THE DEGREE OF MASTER OF SCIENCE
IN ANALYTICAL CHEMISTRY
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IN ANALYTICAL CHEMISTRY

Thesis Title: Simultaneous determination of carbaryl and carbofuran in vegetable samples using spectrophotometry

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สุขสันต์ การสะอาด. 2553. การหาปริมาณคาร์บาริล และคาร์โบฟูรานพร้อมกัน ในตัวอย่างผัก โดยวิธีสเปกโทรโฟโตเมทรี. วิทยานิพนธ์ปริญญาวิทยาศาสตรมหาบัณฑิต สาขาวิชาเคมีวิเคราะห์ บัณฑิตวิทยาลัย มหาวิทยาลัยขอนแก่น.

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บทคัดย่อ

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ได้พัฒนาเทคนิคทางสเปกโทรโฟโตเมทรีเพื่อหาปริมาณคาร์บาริล (CBR) และคาร์โบฟูราน (CBF) พร้อมกันในตัวอย่างผัก โดยเทคนิคนี้ประกอบด้วยการเตรียมตัวอย่างและการตรวจวัดโดยใช้เครื่องสเปกโทรโฟโตมิเตอร์ การเตรียมตัวอย่างใช้เทคนิค QuEChERS และเพิ่มความเข้มข้นด้วยเทคนิคการสกัดแบบจุดชุ่ม (CPE) โดยใช้ Triton X-114 (TX-114) เป็นสารสกัด ได้ศึกษาสภาวะที่เหมาะสมของ CPE ในเทคนิคสเปกโทรโฟโตเมทรีใช้ 4-aminoantipyrine (AP) ในการเตรียมอนุพันธ์ของ CBR และ CBF ซึ่งสภาวะที่เหมาะสมในการเตรียมอนุพันธ์ คือ AP และ $K_3Fe(CN)_6$ เข้มข้น 5.0 มิลลิโมลต่อลิตร และ 9.6 มิลลิโมลต่อลิตร ตามลำดับ หลังจากนั้นปรับพีเอช เป็น 9.5 ด้วย สารละลายบัฟเฟอร์ สำหรับการหาปริมาณของคาร์บาริล และคาร์โบฟูราน ได้ทำการตรวจวัดค่าการดูดกลืนแสงที่ 480 นาโนเมตร และ 510 นาโนเมตร ตามลำดับ ใช้เทคนิค simultaneous equations และ เทคนิค zero-crossing เพื่อหาปริมาณของ CBR และ CBF พร้อมกัน ได้ทดสอบความน่าเชื่อถือของวิธีโดยใช้สภาวะที่เหมาะสม การใช้วิธีสเปกโทรโฟโตเมทรี ร่วมกับ CPE เป็นวิธีที่ง่าย เชื่อถือได้ และมีความไวในการตรวจวัด CBR และ CBF โดยสามารถตรวจวัด CBR และ CBF ในระดับ 0.5 มิลลิกรัมต่อกิโลกรัม นอกจากนี้ได้เปรียบเทียบค่าร้อยละการกลับคืนกับเทคนิค HPLC พบว่า ค่าร้อยละการกลับคืนไม่แตกต่างกันอย่างมีนัยสำคัญทางสถิติกับเทคนิค HPLC ที่ระดับความเชื่อมั่น 95%

Suksant Karnsa-ard. 2010. **Simultaneous Determination of Carbaryl and Carbofuran in Vegetable Samples Using Spectrophotometry**. Master of Science Thesis in Analytical Chemistry, Graduate School, Khon Kaen University.

Thesis Advisor: Assoc. Prof. Dr. Supalax Srijaranai

ABSTRACT

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The simultaneous determination of carbaryl (CBR) and carbofuran (CBF) in vegetables using spectrophotometry was developed. The method consisted of sample preparation and detection. Quick Easy Cheap Effective Rugged and Safe (QuEChERS) and cloud-point extraction (CPE) were used as the sample preparation step. Triton X-114 (TX-114) was used as the extractant in CPE. The conditions for CPE were optimized. For spectrophotometry, 4-aminoantipyrine (AP) was used as the derivatizing agent. The optimum condition for the derivatization of CBR and CBF with AP was as follow: 5.0 mmol L⁻¹ AP, 9.6 mmol L⁻¹ K₃Fe(CN)₆ and 5.0 mmol L⁻¹ borate buffer pH 9.5. The absorbances of the derivatives were measured at 480 nm and 510 nm for CBR and CBF, respectively. Simultaneous equations and zero-crossing techniques were applied for the simultaneous analysis of CBR and CBF. The proposed method was validated under the optimum conditions. The spectrophotometric method using AP as derivatizing agent coupled to CPE is a simple, reliable and sensitive for the detection of CBR and CBF at 0.5 mg kg⁻¹. In addition, the proposed method gave insignificantly different results with HPLC at 95% confidence level.

**The good aspects of the present thesis are dedicated
to my parents and entire teaching staff**

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LIST OF ABBREVIATIONS

1 st -value	first-derivative value
ACN	acetonitrile
ANSA	2-aminonaphthalene sulfonic acid
AP	4-aminoantipyrine
AQ	aqueous phase
Abs	Absorbance
AU	Absorbance unit
BDC	bendiocarb
BF	2,3-dihydro-2,2-dimethyl-7-benzofuran
C ₁₈	octadecylsilane
CBF	carbofuran
CBR	carbaryl
CE	capillary electrophoresis
CPE	cloud-point extraction
DMA	2,4-dimethoxyaniline
Eqn	Equation
F _C	preconcentration factor
g	gram
GCB	graphitized carbon black
HPLC	high performance liquid chromatography
IPC	isoprocarb
LLE	liquid-liquid extraction
LOD	limit of detection
LOQ	limit of quantitation
MCP	monocrotophos
MeOH	methanol
mg L ⁻¹	milligram per litre
min	minus
mL	millilitre
MME	micelle-mediated extraction

LIST OF ABBREVIATIONS (Cont.)

mmol	millimole
mol	mole
MRLs	maximum residues limits
MS	mass spectrometer (mass spectrometry)
PDA	photodiode array detector
PLE	pressurized liquid extraction
PLS	partial least squares
PMC	promecarb
PPX	propoxur
PSA	primary secondary amine
PTO	parathion
QuEChERS	quick easy cheap effective rugged and safe
RSD	relative standard deviation
rpm	round per minus
SD	standard deviation
SDS	sodium dodecyl sulfate
SLE	solid-liquid extraction
SPE	solid-phase extraction
SRP	surfactant-rich phase
TMA	trimethylaniline
t_R	retention time
TX-114	triton X-114
UPLC	ultra performance liquid chromatography
UV	ultraviolet
Vis	visible
w/v	weight by volume
ϵ	molar absorptivity
λ_{\max}	maximum absorption wavelength
μL	microlitre
μm	micrometre