UNIVERSITI PUTRA MALAYSIA

EFFECTIVENESS OF THREE SOLID PHASE EXTRACTION ADSORBENTS FOR SAMPLE CLEAN-UP PRIOR TO GAS CHROMATOGRAPHY ANALYSIS OF ORGANOCHLORINE AND PYRETHROID PESTICIDES IN FRUITS AND VEGETABLES

ZAWIYAH SHARIF

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By

ZAWIYAH SHARIF

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master Science

August 2006

UPM

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Dedicated to my beloved mak and abah, and the rest of the family members

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Abstract of thesis presented to Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

EFFECTIVENESS OF THREE SOLID PHASE EXTRACTION ADSORBENTS FOR SAMPLE CLEAN-UP PRIOR TO GAS CHROMATOGRAPHY ANALYSIS OF ORGANOCHLORINE AND PYRETHROID PESTICIDES IN FRUITS AND VEGETABLES

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August 2006

Chairman : Professor Yaakob Che Man, PhD

Faculty : Food Science and Technology

Three solid phase extraction (SPE) cartridges, based on anion exchanger and non-polar interactions, have been evaluated as clean-up columns prior to organochlorine and pyrethroid pesticides analysis in fruits and vegetables samples. Without a clean-up method the interferences in the fruits and vegetables affected the quantitation of organochlorine and pyrethroid pesticides in fruits and vegetables samples. The objective of this study is to compare the effectiveness between SAX/PSA, Florisil and C18 SPE clean-up columns to eliminate matrix interferences from grape, orange, tomato, carrot and green mustard in the determination of organochlorine (gamma-HCH, heptachlor, aldrin, dieldrin, endrin, captafol) and pyrethroid (permethrin,

cypermethrin, fenvalerate) pesticides using gas chromatography with electron capture detection (GC-ECD).

The results showed that SAX/PSA was the most effective clean-up column as compared to Florisil and C18. The mean recoveries were between 70-120% for all samples at fortification levels of 0.01, 0.02 and 0.1 mg/kg, except for captafol that was below 70%. Although Florisil was not effective in removing interferences as significantly as SAX/PSA, the analytical recoveries were between 70 and 120% for all samples at fortification levels of 0.01, 0.02 and 0.1 mg/kg, except for captafol, which was more than 120%. In contrast, the C18 column showed that the mean recovery for captafol was within 70-120% for grape at fortification levels of 0.01, 0.02 and 0.1 mg/kg, and for orange and tomato only at 0.1 mg/kg. In addition, the C18 column resulted in unacceptable range of mean recoveries for heptachlor, aldrin and permethrin from grape at all fortification levels and permethrin from orange at 0.01 and 0.02 mg/kg fortification levels.

The SPE extracts produce cleaner chromatograms allowing quantitation of pesticides by GC-ECD after ethyl acetate extraction with a limit of detection (LOD) between 0.003 and 0.015 mg/kg in grape samples using SAX/PSA clean-up column. The method was confirmed by gas chromatography-mass spectrometry (GC-MS) which able to detect cypermethrin in tomato, chinese parsley, chinese celery, chilli, brinjal, french beans, green mustard and capsicum from the determination of a total of 508 samples obtained from Malaysian markets. Only the mean value of cypermethrin in

brinjal was found to exceed the permissible level according to the Malaysia Food Regulations 1985.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KEBERKESANAN DI ANTARA TIGA PENYERAP PENGEKSTRAKAN FASA PEPEJAL (SPE) UNTUK MEMBERSIH SAMPEL SEBELUM MENGGUNAKAN KROMATOGRAFI GAS UNTUK ANALISA RACUN PEROSAK ORGANOKLORIN DAN PIRETROID DI DALAM BUAHAN DAN SAYURAN

Oleh

ZAWIYAH SHARIF

Ogos 2006

Pengerusi : Profesor Yaakob Che Man, PhD

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Tiga kartrij pengestrakan fasa pepejal (SPE), berasaskan penukaran anion dan interaksi tak-berkutub, telah dibangunkan dan dinilai sebagai turus pencucian sebelum analisis racun perosak organoklorin dan piretroid di dalam sampel buah-buahan dan sayuran. Tanpa kaedah pencucian, matrik di dalam buahan dan sayuran memberi kesan kepada analisis racun perosak organoklorin dan piretroid. Objektif kajian ini adalah untuk membandingkan keberkesanan di antara turus-turus pencucian SAX/PSA, Florisil dan C18 SPE untuk menghapuskan gangguan matrik dari anggur, oren, tomato, lobak merah dan sawi dalam penentuan racun perosak organoklorin (gamma-HCH, heptaklor, aldrin, dieldrin, endrin, captafol) dan pireteroid (pimetrin, cipermetrin, fenvaleret) menggunakan kromatografi gas dengan pengesan penangkap elektron (GC-ECD).

Keputusan kajian menunjukkan bahawa SAX/PSA adalah paling berkesan sebagai turus pencucian berbanding dengan Florisil dan C18. Purata perolehan berada di antara 70-120% untuk semua sampel pada peringkat fortifikasi dari 0.01, 0.02 dan 0.1 mg/kg, kecuali captafol di bawah 70%. Walaupun Florisil tidak berkesan untuk memindahkan gangguan seperti SAX/PSA, tetapi purata pemulihan berada di antara 70 dan120% bagi semua sampel pada peringkat fortifikasi dari 0.01, 0.02 dan 0.1 mg/kg, kecuali captafol melebihi 120%. Namun begitu, turus C18 menunjukkan bahawa purata pemulihan bagi captafol berada di antara 70-120% bagi anggur pada peringkat fortifikasi 0.01, 0.02 dan 0.1 mg/kg, dan untuk oren dan tomato hanya pada 0.1 mg/kg. Walaubagaimanapun, turus C18 juga memberikan keputusan dalam julat yang tidak diterima bagi purata perolehan untuk heptaklor, aldrin dan pimetrin dari anggur pada semua tahap fortifikasi dan pimetrin dari oren pada 0.01 dan 0.02 mg/kg peringkat fortifikasi.

Ekstraksi SPE menghasilkan kromatogram yang lebih bersih membolehkan analisis menggunakan GC-ECD selepas pengekstrakan dengan etil acitet dengan had pengesanan (LOD) di antara 0.003 dan 0.015 mg/kg di dalam sampel anggur menggunakan turus pencuci SAX/PSA. Pengesahan oleh kromatografi gas-spektrometri jisim (GC-MS) mampu untuk mengesan cipermetrin dalam tomato, daun ketumbar, daun sup, cili, terung, kacang buncis, sawi dan cili besar daripada penentuan ke atas sejumlah 508 sampel yang diperolehi daripada pasaran di Malaysia. Hanya nilai purata bagi cipermetrin dalam terung didapati melebihi tahap yang dibenarkan mengikut Peraturan-peraturan Makanan Malaysia, 1985.

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I certify that an Examination Committee has met on 4 August 2006 to conduct the final examination of Zawiyah Sharif on her Master of Science thesis "Effectiveness of Three Solid Phase Extraction Adsorbents for Sample Clean-up Prior to Gas Chromatography Analysis of Organochlorine and Pyrethroid Pesticides in Fruits and Vegetables" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

ZAWIYAH SHARIF

Date: 2 OCTOBER 2006

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AED	Atomic Emission Detector
ECD	Electron Capture Detector
EU	European Union
FAO	Food and Agriculture Organization
FPD	Flame Photometric Detector
FTD	Flame Thermionic Detector
FTIR	Flourier Transform Spectrophotometer Infra-Red Spectrophotometer
GC	Gas Chromatography
GCB	Graphitized Carbon Black
GC-MS	Gas Chromatography-Mass Spectrometry
HPLC	High Pressure Liquid Chromatography
IST	International Sorbent Technology
MRL	Maximum Residue Limit
MS	Mass Spectrometry
NPD	Nitrogen Phophorus Detector
PSA	Primary Secondary Amine
SAX	Secondary Amine Exchange
SCX	Strong Cation Exchange
SIM	Selected Ion Monitoring

SPE	Solid Phase Extraction
TCD	Thermal Conductivity Detector
ULV	Ultra-Low-Volume
USA	United State of America
UV	Ultra Violet

LIST OF SYMBOLS AND UNITS

g	Gram
mL	Milliliter
min	Minute
mg	Milligram
α	Alpha
β	Beta
%	Percent
^{o}C	Degree celcius
µL	Microliter
mm	Millimeter
m	Meter
µm	Micrometer
^{o}C/min	Degree Celcius per minute
mL/min	Milliliter per minute
mg/L	Milligram per liter

v/v	Volume per volume
g/mL	Gram per milliliter
g/L	Gram per liter
mg/mL	Milligram per milliliter
mg/kg	Milligram per kilogram
meq/g	Milliequivalent per gram