



UNIVERSITI PUTRA MALAYSIA

**EFFECTIVENESS OF DISPERSIVE SOLID PHASE EXTRACTION
SORBENTS FOR SAMPLE CLEAN-UP BY QuEChERS
METHOD FOR ORGANOCHLORINE PESTICIDES
DETERMINATION IN PACIFIC WHITE SHRIMP**

NORAZLINA OMAR

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IN PACIFIC WHITE SHRIMP**

By

NORAZLINA OMAR

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

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**Dedicated to my beloved husband, mak, abah, abang
and
the rest of family members.**

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

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June 2013

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Organochlorine pesticides (OCPs) are persistent in the environments and have the ability to bioaccumulate in the food chain and are capable of causing various health hazards. The sample preparation techniques used for monitoring of OCPs in food are usually complicated, time consuming, use large volume of solvents and expensive. An ideal multi-residue method with high recoveries should be rapid, easy to perform, accurate, low cost and safer to the analyst due to less exposure to organic solvent and waste. The Quick Easy Cheap Effective Rugged and Safe (QuEChERS) is one of such methods. The objectives of this study are to evaluate the effectiveness of dispersive solid phase extraction (DSPE) sorbents in removing matrix interferences in

Pacific white shrimp, to validate the most effective sorbent using the QuEChERS method and compare to the modified AOAC Official method 983.21. Thus, the QuEChERS sample preparation method DSPE and gas chromatography mass spectrometry (GC-MS) with selected ion monitoring mode (SIM) has been improved and applied for the analysis of common OCPs (α -HCH, β -HCH, γ -HCH, δ -HCH, *trans*-chlordane, *cis*-chlordane, *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT) in Pacific white shrimp (*Litopenaeus vannamei*). The combination of primary and secondary amine (PSA), octadecyl (C18) and/or graphitized carbon black (GCB) have been evaluated as clean-up sorbents to samples collected from the state of Kedah, Selangor and Terengganu. Sampling was conducted twice a year between February - June and July - November 2011 at two selected farms from each state. The results have shown the mean recoveries for PSA:C18, PSA:GCB and PSA:C18:GCB ranged between 93–100%, 98-105% and 98-105%, respectively. The relative standard deviations (RSD) of <14%, <15% and <10% were obtained for PSA:C18, PSA:GCB and PSA:C18: GCB, respectively. The PSA:C18 was not able to remove matrix interference, such as cholesterol. The sorbent efficiency to minimize matrix interferences was PSA:C18:GCB > PSA:GCB > PSA:C18. In the validation study, PSA:C18:GCB was validated for selectivity, limit of detection (LOD), limit of quantification (LOQ), linearity and working range, matrix effect, recovery, trueness and precision using the QuEChERS method. The range for LOD and LOQ were 0.9 - 4.5 ng/g and 3 - 15 ng/g, respectively. The correlation coefficients for matrix-matched calibration curves >0.99 were

obtained. All analytes had matrix enhancement effects with mild effect for γ -HCH, medium for α -HCH, β -HCH, δ -HCH, *trans*-chlordane, *cis*-chlordane and strong effect for *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT. Mean recoveries of 98 – 105% with associated RSD of <4.2% had been obtained for the QuEChERS method. By using the modified AOAC Official Method 983.21, LOD and LOQ values for all OCPs were between 15 – 30 ng/g and 50 – 100 ng/g, respectively. The correlation coefficients for matrix-matched calibration curves >0.96 were obtained for the modified AOAC Official Method 983.21. All OCPs had mild signal suppression effects for the modified AOAC Official Method 983.21. Mean recoveries of 76 – 110% with associated RSD <6% were obtained. In term of LOD, LOQ, linearity, trueness and precision, the results indicated that the QuEChERS method was better than the modified AOAC Official Method 983.21. The validated QuEChERS method had been applied for the determination of nine OCPs in 65 samples from selected farms in Malaysia. OCPs were not detected in all samples. The results have indicated that this method could be adopted in routine analysis to reduce inspection time and cost of analysis and be used towards the International Standard requirements for laboratory accreditation.

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

**KEBERKESANAN PENJERAP PENGEKSTRAKAN SERAKAN FASA
PEPEJAL UNTUK PEMBERSIHAN SAMPEL DENGAN KAEDAH
QuEChERS UNTUK PENENTUAN RACUN PEROSAK ORGANOKLORIN
DALAM UDANG PUTIH PASIFIK**

Oleh

NORAZLINA OMAR

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Racun perosak organoklorin (OCPs) adalah berterusan dalam persekitaran mempunyai keupayaan untuk berkumpul dalam rantai makanan dan mampu menyebabkan pelbagai bahaya kesihatan. Teknik penyediaan sampel yang digunakan untuk pemantauan OCPs dalam makanan biasanya adalah rumit, memakan masa, menggunakan jumlah pelarut yang banyak dan mahal. Kaedah pelbagai residu yang ideal harus cepat, mudah untuk dilaksanakan, mempunyai pemulihan yang tinggi, tepat, murah dan selamat untuk jurunalisa kerana kurang terdedah kepada pelarut organik dan sisa buangan. Pantas Mudah Murah Berkesan Lasak dan Selamat (QuEChERS) adalah salah satu kaedah tersebut. Objektif kajian ini ialah untuk menilai keberkesanan penjerap

DSPE dalam menghapuskan gangguan matrik di dalam udang putih Pasifik, menjalankan validasi kaedah untuk penjerap yang paling berkesan menggunakan kaedah QuEChERS dan membandingkannya dengan kaedah rasmi AOAC 983.21 diubahsuai. Oleh itu, kaedah penyediaan sampel QuEChERS yang melibatkan pengekstrakan serakan fasa pepejal dan gas kromatografi spektrometri jisim (GC-MS) dengan mod pemantauan ion terpilih (SIM) telah diperbaiki dan digunakan untuk analisis organoklorin (α -HCH, β -HCH, γ -HCH, δ -HCH, *trans*-klordan, *cis*-klordan, *p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT) dalam udang putih Pasifik (*Litopenaeus vannamei*). Gabungan amina primer dan sekunder (PSA), C18 dan/atau karbon hitam bergrafit (GCB) telah dinilai sebagai penjerap pembersih untuk sampel yang diambil dari negeri Kedah, Selangor dan Terengganu. Persampelan telah dijalankan dua kali setahun iaitu antara bulan Februari dan November 2011 di dua ladang terpilih dari setiap negeri. Keputusan menunjukkan bahawa purata pemulihan untuk PSA:C18, PSA:GCB dan PSA:C18:GCB masing-masing berada di dalam julat 93–100%, 98-105% dan 98-105%. Sisihan piawai relatif (RSD) <14%, <15% dan <10% masing-masing telah diperolehi untuk PSA:C18, PSA:GCB dan PSA:C18:GCB. PSA:C18 tidak berupaya untuk menghapuskan gangguan matrik seperti kolesterol. Kecekapan penjerap untuk meminimumkan gangguan matrik adalah seperti berikut; PSA:C18:GCB > PSA:GCB > PSA:C18. Dalam kajian validasi, PSA:C18:GCB telah disahkan untuk parameter seperti selektiviti, had pengesanan (LOD), had kuantifikasi (LOQ), kelinearan, kesan matrik, pemulihan, ketepatan dan kejituan menggunakan

kaedah QuEChERS. LOD dan LOQ masing-masing berada pada julat 0.9 - 4.5 ng/g dan 3 - 15 ng/g. Korelasi pekali >0.990 telah diperolehi. Semua analit mempunyai kesan peningkatkan matrik dengan kesan yang rendah untuk γ -HCH, sederhana untuk α -HCH, β -HCH, δ -HCH, *trans*-klordan, *cis*-klordan dan kesan yang tinggi untuk *p,p'*-DDE, *p,p'*-DDD dan *p,p'*-DDT. Purata pemulihan berjulat antara 98 – 105% dengan RSD < 4.2% telah diperolehi untuk kaedah QuEChERS. Dengan menggunakan kaedah rasmi AOAC 983.21 diubahsuai, nilai LOD dan LOQ masing-masing ialah di antara 15 – 30 ng/g and 50 – 100 ng/g. Pekali korelasi bagi matriks dipadankan keluk penentukuran >0.96 telah diperolehi bagi semua OCP untuk kaedah rasmi AOAC 983.21 diubahsuai. Kesemua OCP mempunyai kesan matrik dengan penindasan isyarat yang rendah untuk kaedah rasmi AOAC 983.21 diubahsuai. Purata pemulihan antara 76 – 110% dengan nilai RSD <6% telah diperolehi. Dari segi LOD, LOQ, kelinearan, ketepatan dan kejituan, keputusan menunjukkan bahawa kaedah QuEChERS adalah lebih baik berbanding kaedah rasmi AOAC 983.21 diubahsuai. Kedah QuEChERS yang disahkan telah digunakan untuk penentuan sembilan OCP dalam 65 sampel dari ladang terpilih di Malaysia. Semua sampel dikesan tidak mengandungi residu organoklorin. Keputusan menunjukkan bahawa kaedah ini boleh digunakan dalam analisis rutin untuk mengurangkan masa pemeriksaan dan kos analisis dan digunakan ke arah memenuhi keperluan Piawaian Antarabangsa bagi akreditasi makmal.

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I certify that a Thesis Examination Committee has met on (24 June 2013) to conduct the final examination of Norazlina Omar on her thesis entitled “Effectiveness of Dispersive Solid Phase Extraction Sorbents During Clean-up in QuEChERS Technique for Analysis of Organochlorine Pesticides in Pacific White Shrimp (*Litopenaeus vannamei*)” in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science

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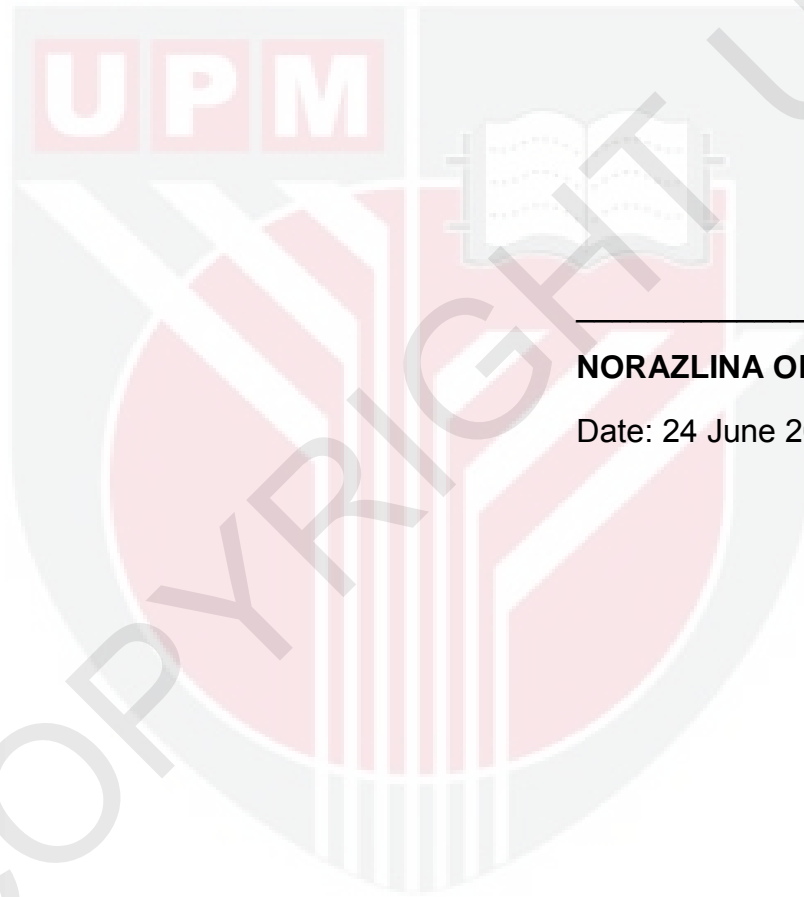
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DECLARATION

I declare that the thesis is my original work except for quotations and citation which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.



NORAZLINA OMAR

Date: 24 June 2013



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