DETERMINATION OF MULTICLASS PESTICIDE RESIDUES IN FRUITS AND VEGETABLES WITH HEADSPACE SOLID PHASE MICROEXTRACTION GAS CHROMATOGRAPHY MASS SPECTROMETRY USING EXPERIMENTAL FACTORIAL DESIGN

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FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
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DEDICATION

To Almighty Allah (S.W.T) who has make it possible for me to undertake this research work against all odds and to the founding fathers of Chemistry and the inventors of scientific knowledge, whose labour is not in vain. Also to my father, mother, wife, daughters, son and all family members for their love, understanding, support and continuous prayer for my success in completing this work

ORIGINAL LITERARY WORK DECLARATION

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Field of Study: **ANALYTICAL CHEMISTRY**

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ABSTRACT

The focus of this study is the development and validation of headspace solid phase microextraction and chromatographic techniques for the analysis of pesticide residues in fruit and vegetable samples. The developed method is based on the comparison of the optimized HS-SPME parameters using univariate and multivariate experimental designs. Modern trends in sample preparation and subsequent instrumental analysis are aimed towards reliable and accurate analysis of pesticide residues and other contaminants from food. It is focused on the simplifications, miniaturization, improvement and reduction in volume of sample and solvents used while maintaining high throughput performance. The microextraction techniques have been developed in order to reduce sample preparation time, improve sensitivity and selectivity as well as to corroborate the recent advances in the development of highly sensitive and efficient analytical instrumentation. The method developed was based on the optimization of both GC-MS and SPME parameters using univariate method, followed by the screening for the significant factors using multivariate experimental design. The multivariate experimental design was conducted in two stages. First, the significance of each factor is estimated using the first-order experimental design called the Plackett-Burman (P-B) design, used as a preliminary study for the identification of significant factors. The second stage involves the optimization of the significant factors using second-order models such as central composite design. The multivariate experiment involved the use of Minitab® statistical software for the generation of a 2^{7-4} Plackett-Burman (P-B) and central composite design (CCD) matrices. Factors studied and optimized included, selection of fiber coatings, chromatographic parameters, extraction temperature and time, stirring rate, salt addition, pH, dilution factor and organic solvent addition. A simplex lattice design was employed for the determination of the best combination of organic solvent which enhances extraction efficiency. The optimized conditions for the multivariate design was slightly different from that of the univariate design, this could be due to the fact that the univariate design does not take the possible interaction of factors into consideration. For the validation studies, both the multivariate optimized factors (for significant factors) and univariate conditions obtained were: 100 µm PDMS, 10 % NaCl, optimum dilution varied with sample matrices, extraction temperature and extraction time of 65 ^{0}C and 35 min respectively, stirring rate of 350 rpm at pH 6. The desorption temperature and time were 270 ^{0}C and 7 min respectively. The method produced good analytical figures of merit with linearity ranging from 1 – 500 µg/kg with correlation coefficient greater than 0.99, low limits of detection and quantification which were found between 0.14 and 8.33 µg/kg and 0.38 and 27.76 µg/kg respectively. The recoveries achieved were greater than 74% and less than 120 % with relative standard deviation of less than 15 % for all the investigated pesticides. The use of the multivariate method helps to reduce sampling time and improve analytical throughput. The developed method was used to analyze fourteen multi-class and multi-residue pesticides in 4 fruit and 4 vegetable samples and the results obtained were found to be satisfactory in accordance with various guidelines for the validation of analytical methods.

ABSTRAK

Tumpuan kajian ini ialah pembangunan dan pengesahan headspace mikro fasa pepejal dan teknik kromatografi untuk analisis sisa racun perosak dalam sampel buah-buahan dan sayur-sayuran. Kaedah maju adalah berdasarkan perbandingan dioptimumkan HS-SPME parameter menggunakan reka bentuk eksperimen univariat dan multivariat. Trend moden dalam penyediaan sampel dan analisis memainkan peranan penting berikutnya bertujuan untuk analisis dipercayai dan tepat sisa-sisa racun perosak dan bahan pencemar lain daripada makanan. Ia memberi tumpuan kepada pemudahan, pengecilan, peningkatan dan pengurangan dalam jumlah sampel dan pelarut yang digunakan di samping mengekalkan prestasi pemprosesan yang tinggi. Teknik-teknik mikropengekstrakan telah dibangunkan untuk mengurangkan masa penyediaan sampel, meningkatkan kepekaan dan pemilihan serta untuk menyokong kemajuan terkini dalam pembangunan yang sangat sensitif dan cekap peralatan analitikal. Kaedah maju adalah berdasarkan mengoptimumkan kedua-dua GC-MS dan parameter SPME menggunakan kaedah univariat, diikuti oleh saringan faktor-faktor yang penting menggunakan reka bentuk eksperimen multivariat. Reka bentuk eksperimen multivariat telah dijalankan dalam dua peringkat. Pertama, kepentingan setiap faktor adalah dianggarkan menggunakan reka bentuk yang pertama untuk eksperimen dipanggil Plackett-Burman (PB) reka bentuk, yang digunakan sebagai satu kajian awal untuk mengenal pasti faktor-faktor yang penting. Peringkat kedua melibatkan pengoptimuman faktor penting menggunakan model kedua-perintah seperti reka bentuk komposit pusat. Percubaan multivariat melibatkan penggunaan Minitab ® perisian statistik untuk generasi daripada 2^{7-4} Plackett-Burma (PB) dan reka bentuk komposit pusat (CCD) matriks. Faktor-faktor yang dikaji dan dioptimumkan termasuk, pemilihan lapisan serat, parameter kromatografi, suhu pengekstrakan dan masa, kadar kacau, penambahan garam, pH, faktor pencairan dan penambahan pelarut organik. Satu reka bentuk kekisi simplex telah digunakan untuk menentukan kombinasi yang terbaik pelarut organik yang meningkatkan kecekapan pengeluaran. Syarat-syarat yang optimum untuk reka bentuk multivariat sedikit berbeza daripada reka bentuk univariat, ini mungkin disebabkan oleh hakikat bahawa reka bentuk univariat tidak mengambil interaksi mungkin faktor kira. Bagi kajian pengesahan, kedua-dua faktor dioptimumkan multivariat (faktor-faktor yang penting) dan keadaan univariat diperolehi adalah: 100 μm PDMS, 10% NaCl, pencairan optimum diubah dengan matriks sampel, suhu pengekstrakan dan masa pengeluaran masing-masing 65 ^{0}C dan 35 minit, kacau kadar 350 rpm pada pH 6. Suhu desorption dan masa ialah 270 ^{0}C dan 7 min masing-masing. Kaedah ini menghasilkan angka analitikal yang baik merit dengan kelinearan antara 1-500 μg / kg dengan pekali korelasi yang lebih besar daripada 0.99, had rendah pengesanan dan kuantifikasi yang didapati di antara 0.14 dan 8.33 μg / kg dan 0.38 masing-masing dan 27.76 μg / kg. The pemulihan yang dicapai adalah lebih besar daripada 74% dan kurang daripada 120% dengan sisihan piawai relatif kurang daripada 15% untuk semua racun perosak disiasat. Penggunaan kaedah multivariat membantu mengurangkan masa persampelan dan meningkatkan pemprosesan analitikal. Kaedah yang dibangunkan telah digunakan untuk menganalisis empat belas racun perosak pelbagai kelas dan pelbagai sisa dalam 4 buah-buahan dan sayur-sayuran 4 sampel dan keputusan yang diperolehi didapati memuaskan selaras dengan pelbagai garis panduan untuk pengesahan kaedah analisis

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