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A Multi-Residue Method for Simultaneous Determination of 42 Pesticides in Rice Using QuEChERS Sample Preparation Procedure and Gas Chromatography Mass Spectrometry

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Abstract
The principle of this research is based on the development of multi-residue method by QuEChERS sample preparation follow by gas chromatography with mass spectrometric detection in the selected ion monitoring mode (GC-MS-SIM) for the routine analysis of 42 pesticides in rice samples. The rice samples were initially extracted with acetonitrile, and the targeted pesticides were purified following the dispersive solid phase extraction (d-SPE) cleanup method. The calibration curve for each analyte quantified by matrix-matched calibration was linear over the concentration range of 10.0–1000.0 μg L^{-1} with a correlation coefficient range between 0.990 and 0.999. Mean recoveries from three replicates ranged from 79% to 112%, with satisfactory precision (RSD<7%). The limit of detection and the limit of quantification were in the range of 3.04-12.52 μg L^{-1} and 10.14-41.76 μg L^{-1} respectively, for all 42 pesticides.

Keywords
Gas chromatography; Mass spectrometry; Matrix-matched calibration; Multi-residue; Pesticide; QuEChERS.

1.INTRODUCTION

Rice is a major nutrition source for people all over the world. The application of pesticides in controlling the weeds and pests during planting leads to more growth and increasing in productivity of rice. However, they often residue in final products and may be danger for human and environments. Thus the determination of pesticide residues in food matrices has become a necessity to our living environment and the food. As a result, several government authorities and international organizations established the maximum residue levels (MRLs) for pesticides [1].

The quantification of the pesticides in food samples is required to control the quality of these products, while their higher content and consumption may be toxic. The complexity and the diversity of the samples matrices and the low concentrations of pesticides in samples make performing an efficient sample preparation to enrich and/or separate target material from complex matrices in the presence of some potential interference [2-5].

To reduce the interferences troublesome matrices, different methods that included single drop microextraction (SDME) [6], liquid-liquid extraction (LLE) [7], dispersive liquid–liquid microextraction [8], solid phase extraction (SPE) [7, 9-12], matrix solid phase dispersion (MSPD) [13, 14] and stir bar sorptive extraction (SBSE) [15] have been applied for extraction and subsequent quantification of pesticides in various matrices.

Traditional methods used in pesticide residue analysis are often time and solvent consuming due to steps of sample preparation before the chromatographic analysis. In 2003, a new approach of multi-residues determination named as QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method [16] has been developed based on employing acetonitrile extraction/partitioning and then cleaning up by dispersive solid-phase extraction (d-SPE). The method has the advantages of high recoveries in pesticides with a wide scope of polarity and volatility, high throughput, low cost and smaller use of organic solvent [17, 18]. Generally, primary secondary amine (PSA) was used mostly as the d-SPE sorbent aimed to remove polar organic acids, fatty acids, polar pigments and some sugars [19]. Graphitized carbon black (GCB) was also used as d-SPE sorbent in modified QuEChERS method to remove steroids and pigments [20]. Since then QuEChERS has undergone several modifications and has become well established for multi-residue analyses of pesticides in various food and agricultural samples [21, 22]. Among other beneficial features, the QuEChERS procedure uses acetonitrile, which permits extraction of polar

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analytes and has an elevated degree of selectivity and detectability and direct compatibility with both gas and liquid chromatography coupled with mass spectrometry (MS) [23].The QuEChERS method, when compared with other techniques mentioned above, minimizes the number of sample preparation steps since it only involves two steps, first extraction with acetonitrile and a mixture of salts by partition and then clean-up steps by dispersive solid phase extraction (d-SPE) using a sorbent comprising of primary and secondary amines (PSA). Other advantages of the QuEChERS method compared with other techniques are their excellent recoveries, less time for sample preparation and less solvent consumption [24].

Since the application of pesticides is essential to prevent the loss of production/productivity, it is important to determine the concentrations of pesticide residues in the rice, to determine if the rice is fit for human consumption and in accordance with established maximum residue limits (MRLs). In recent years, the analytical techniques include gas chromatography-mass spectrometry (GC–MS) [6, 14, 15, 25], gas chromatography with electron-capture detection (GC-ECD) [6], liquid chromatography with tandem mass spectrometry (LC–MS/MS) [9], liquid chromatography with ultraviolet detection (LC-UV) [7, 9-11], liquid chromatography with photodiode array detection (LC-DAD) [13] and gas chromatography with thermionic sensitive detection (GC-TSD) [7] were developed and reported in the literature.

In the analysis of pesticides for food samples with gas chromatography (GC), the combination with mass spectral detection is favorable for many applications, allowed simultaneously an increase in speed of analysis by the higher sample throughput, flexibility, selectivity, wide analytical scope, qualitative and quantitative utility and sensitivity [26, 27]. On the other hand, GC-MS is a very appropriate technique for the determination of pesticides in food samples, because it provides sufficient sensitivity and quantification at trace levels from a single injection, minimizing extensively analysis time.

The complex nature of the samples matrix make performing an efficient sample preparation to enrich and/or separate target material from complex matrices in the presence of some potential interference. The under study research focused on the combination rapid, efficient, reliable method based on QuEChERS method with GC-MS detection for simultaneous determination of 42 pesticide residues. The method was designed to accommodate rice matrix and provide good analytical results for the targeted pesticides in the method validation. It has been successfully applied to the analysis of those pesticides in our daily monitoring work.

2.EXPERIMENTAL

2.1. Reagents and material

Certified standards of all pesticides with high purity grade (>98.0%) were acquired from Sigma Aldrich (St. Louis, MO, USA). The internal standard (IS), Tri phenyl phosphate (purity > 98%) was also obtained from Sigma Aldrich (St. Louis, MO, USA). HPLC-grade acetonitrile and methanol were supplied from Sigma Aldrich (St. Louis, MO, USA). Individual stock solutions were prepared at 1000 mgL−1 in acetonitrile or methanol and stored in a freezer at −20˚C. The working solutions were prepared through appropriate dilutions of the stock solutions. Standard stocksolutions of 10 mgL−1 of mixture pesticides were prepared in acetonitrile and stored in freezer (−20◦C). Analytical reagent grade anhydrous magnesium sulfate ($MgSO_4$), sodium chloride (NaCl), anhydrous sodium acetate (NaOAc), Primary secondary amine (PSA) and octadecyl-modified silica (C18) were purchased from Sigma Aldrich (St. Louis, MO, USA).

Intermediate solutions containing 42 pesticides were prepared by adding appropriate amount of individual stock solutions to 10 mL volumetric flask. Standard working solutions at various concentrations were prepared by dilution of the intermediate solutions in acetonitrile or methanol. All stock and working solutions including IS were stored in amber vials with Teflon lined cap and then stored at −20˚C.

2.2. Samples

Representative portion of 1 kg rice sample was taken, shipped to laboratory in an insulated container and stored at 4 ˚C until analysis. Samples from rice free from pesticides were used for the method optimization and validation.

2.3. Apparatus

GC‑MS measurements were performed on an Agilent 6890AGC system, equipped with an Agilent 7683B auto-injector (Agilent, Avondale, PA, USA) and coupled to an Agilent 5975C mass-selective detector. Chromatographic separation was performed using the following column temperature program: the temperature of column oven was programmed from an initial value of 70˚C (hold for 3.0 min), then raised at 25˚C min−1 up to 120 ˚C, and then at 5.0˚C min−1 to 250˚C (hold 14.0 min). The total analysis time was 45.0 min. the carrier gas (helium; purity > 99.996%)

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Table 1. Retention time (RT) with their quantitation and identification ions.

No.	Pesticide name	RT (min)	Selected Ion	Quantitative Ion
1	Phenmedipham	6.23	104-133-167	104
2	Linuron	9.47	187-189-248	187
3	EPTC	10.35	128-132-189	128
4	Carbaryl I,II	12.98-20.10	144-115-116	144
5	Molinate	13.40	187-126-127	187
6	Phorate	16.45	121-75-260	121
7	Trifluralin	16.49	306-264-290	306
8	Dimethoat	16.67	87-93-125	87
9	Atrazine	17.30	200-215-202	200
10	Chlorothalonil	18.30	266-264-268	266
11	Diazinon	18.60	304-152-179	304
12	Pirimicarb	19.30	166-72-238	166
13	Propanil	19.60	161-163-217	161
14	Chlorpyrifos-methyl	20.17	286-288-290	286
15	Acetochlore	20.25	146-162-223	146
16	Alachlor	20.55	160-188-269	160
17	Metalaxyl	20.67	132-160-206	132
18	Fenitrothion	21.08	277-260-125	277
19	Fenthion	21.84	278-109-125	278
20	Dicofol	21.90	251-139-141	251
21	Chlorpyrifos	22.05	314-316-197	314
22	Cyprodinil	22.90	224-225	224
23	Captan	22.99	80-79-149	80
24	Fipronil	23.50	367-369-368	367
25	Methidathion	23.80	145-85-302	145
26	Tricycazol	24.40	189-162-161	189
27	Endosulfanalfa	24.50	337-239-241	337
28	Carboxin	24.94	143-235	143
29	Oxadiazon	25.67	175-177-258	175
30	Endosulfan beta	26.25	337-239-241	337

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31	Ethion	26.9	231-153-384	231
32	Edifenphos	27.65	310-173-218	310
33	Propiconazole	27.90	259-175-373	259
34	Propargite	28.85	135-350-173	135
35	Iprodin	29.47	314-316-245	314
36	Bromopropylate	30.21	341-183-185	341
37	Fenpropathrine	30.32	349-265-181	349
38	Tetradifon	30.92	356-159-111	356
39	Phosalone	30.92	184-182-121	184
40	Permethrin I-II	33.00-	183-163-181	183
41	Fenvalerate	39.67-40.65	167-125-225	167
42	Deltamethrin	43.30	181-253-251	181

Table 2. Characteristic parameters for the regression equation and results of assay of validation for the determination of the pesticides by the proposed method

No.	Pesticide name	Linear range	Coefficient	LOD	LOQ	
1	Phenmedipham	25-1000	0.9947	4.95	16.52	y =0.0036x+0.0369 R^2 = 0.9947
2	Linuron	10-1000	0.9961	3.19	10.64	y = 0.0035x - 0.0418 R^2 = 0.9961
3	EPTC	10-1000	0.9918	3.59	11.97	y = 0.0033x - 0.1222 R^2 = 0.9918
4	Carbaryl I	25-1000	0.9941	3.39	11.33	y = 0.0037x +0.0438 R^2 = 0.9941
5	Molinate	10-1000	0.9956	3.37	12.23	y = 0.0091x + 0.1185 R^2 = 0.9956
6	Phorate	10-1000	0.9983	3.75	12.50	y = 0.0185x - 0.2273 R^2 = 0.9983
7	Trifluralin	10-1000	0.9900	6.56	21.86	y = 0.0017x - 0.0384 R^2 = 0.9900
8	Dimethoat	25-1000	0.9963	3.37	11.23	y = 0.0037x - 0.1474 R^2 = 0.9963
9	Atrazine	10-1000	0.9993	5.57	18.58	y = 0.0053x - 0.0278 R^2 = 0.9993
10	Chlorothalonil	25-1000	0.9964	8.30	27.66	y = 0.0023x - 0.0763 R^2 = 0.9964

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11	Diazinon	10-1000	0.9969	3.10	10.36	y = 0.0031x - 0.0635 R² = 0.9969
12	Pirimicarb	10-1000	0.9997	6.31	21.05	y = 0.0099x - 0.0916 R² = 0.9997
13	Propanil	10-1000	0.9970	4.97	16.57	y = 0.0075x - 0.0203 R² = 0.997
14	Chlorpyrifos-methyl	10-1000	0.9974	3.29	10.96	y = 0.0049x - 0.1039 R² = 0.9974
15	Acetochlore	25-1000	0.9995	3.09	10.31	y = 0.0059x - 0.0621 R² = 0.9995
16	Alachlor	25-1000	0.9996	9.75	32.50	y = 0.0039x - 0.049 R² = 0.9996
17	Metalaxyl	25-1000	0.9996	8.80	29.36	y = 0.0019x - 0.0371 R² = 0.9996
18	Fenitrothion	25-1000	0.9935	7.52	25.08	y = 0.0007x - 0.0176 R² = 0.9935
19	Fenthion	10-1000	0.9990	4.52	15.07	y = 0.0074x - 0.1293 R² = 0.999
20	Dicofol	25-1000	0.9996	9.64	32.14	y = 0.0003x + 0.0039 R² = 0.9996
21	Chlorpyrifos	10-1000	0.9996	3.69	12.32	y = 0.0061x + 0.0526 R² = 0.9996
22	Cyprodinil	10-1000	0.9999	8.92	29.73	y = 0.014x - 0.0793 R² = 0.9999
23	Captan	25-1000	0.9976	7.22	24.07	y = 0.0014x - 0.0477 R² = 0.9976
24	Fipronil	10-1000	0.9995	4.76	15.87	y = 0.0019x - 0.0187 R² = 0.9995
25	Methidathion	25-1000	0.9936	4.48	14.95	y = 0.0063x - 0.2581 R² = 0.9936
26	Tricycazol	25-1000	0.9908	12.52	41.76	y = 0.0054x - 0.1424 R² = 0.9908
27	Endosulfanalfa	10-1000	0.9998	6.32	21.06	y = 0.0007x - 0.0029 R² = 0.9998
28	Oxadiazon	10-1000	0.9990	3.04	10.14	y = 0.0055x - 0.0789 R² = 0.999
29	Carboxin	10-1000	0.9997	8.46	28.21	y = 0.0124x - 0.0875 R² = 0.9997
30	Endosulfan beta	10-1000	0.9946	6.84	22.79	y = 0.0009x + 0.0089 R² = 0.9946
31	Ethion	10-1000	0.9918	3.59	11.97	y = 0.0033x - 0.1222 R² = 0.9918
32	Edifenphos	25-500	0.9962	9.04	31.33	y = 0.0038x - 0.0689 R² = 0.9962

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33	Propiconazole	10-1000	0.9963	8.25	27.51	y = 0.002x - 0.0328 R^2 = 0.9963
34	Propargite	10-1000	0.9996	7.73	25.78	y = 0.0094x - 0.0706 R^2 = 0.9996
35	Iprodin	10-1000	0.9995	4.76	15.87	y = 0.0019x - 0.0187 R^2 = 0.9995
36	Bromopropylate	10-1000	0.9972	3.38	11.27	y = 0.0055x - 0.054 R^2 = 0.9972
37	Fenpropathrine	10-1000	0.9963	5.95	19.84	y = 0.0061x - 0.1317 R^2 = 0.9963
38	Tetradifon	10-1000	0.9992	6.75	22.50	y = 0.0052x - 0.0612 R^2 = 0.9992
39	Phosalone	10-1000	0.9987	8.74	29.14	y = 0.003x + 0.024 R^2 = 0.9987
40	Permethrin I-II	10-1000	0.9998	6.82	22.75	y = 0.0073x - 0.0196 R^2 = 0.9998
41	Fenvalerate	25-1000	0.9975	9.52	31.74	y = 0.0014x - 0.0368 R^2 = 0.9975
42	Deltamethrin	10-1000	0.9936	8.31	27.07	y = 0.0006x - 0.0073 R^2 = 0.9936

was maintained at a constant flow of 1 mL min−1 and the mode of inlet was splitless with injection volume of 1 mL. Separation of pesticides was performed on a capillary column DB1 (Agilent, Middelburg, The Netherlands) with 30 m×0.25 mm I.D.×0.25 μm was utilized. The retention times, target ions, qualifier ions, start times of SIM groups and data acquisition rates for pesticides are given in Table 1. The interface temperature was 250˚C, the electron energy and temperature of EI source were set at 70 eV and 230 ˚C, respectively.

2.4.Sample preparation

Rice samples were prepared based on QuEChERS method described by Anastassiades et al. [16]. Rice samples were homogenized with a blender (Waring Products Co., Torrington, CT, USA) in the presence of CO_2 dry ice for 1 min. A portion of 10 g ground and homogenized sample was weighed into 50 ml Teflon centrifuge tube and covered by 10 ml of water and 10 mL of acetonitrile. Then 4.0 g anhydrous $MgSO_4$, 0.5 g sodium citrate dibasic sesquihydrate, 1.0 g sodium citrate tribasic dehydrate, 4.0 g of sodium bicarbonate and 1.0 g of NaCl were added to the sample and next, the mixture was shaken by the vortex mixer (Nuve NM-110, Ankara, Turkey) for 5 min. The sample extract was centrifuged (Eppendorf 5804, Hamburg, Germany) at 5000 rpm for 5 min. During the clean-up step using d-SPE, 4 ml of upper layer extract was then transferred to a 15 ml centrifuge tube containing 150 mg PSA, 150 mg C18 and 900 mg anhydrous $MgSO_4$. The mixture was vortexed for 2 min and centrifuged at 5000 rpm for 5 min. After centrifugation, 1.5 mL extract was transferred to a glass vial and stored for analysis by GC/MS.

2.5. Matrix-matched calibration

Matrix-matched standards were used in order to avoid quantitative errors. Matrix-matched calibration standard solutions for quantification of pesticide residues in real samples were prepared at various concentrations level of 10-1000 μgL^{-1}. The internal standard was added to all calibration standard solutions. For spiking studies, a 10 g test portion of rice sample with no pesticides was spiked with appropriate standard solutions to a final concentration of 50 and 100 μgkg^{-1}, and the Teflon centrifuge tube was vigorously vortexed to distribute the pesticide residues.

2.6. Validation study

Validation was carried out by using spiked samples and assessed according to European Union SANCO guideline 12571/2013 (Method Validation and Quality Control Procedures for Pesticide Residue Analysis in Food and Feed, 2013). The following parameters were evaluated

during the validation of the analytic method: linearity, limit of quantification (LOQ), accuracy and precision. Seven calibration levels of mixed standards in solvent and matrix have been prepared to investigate the linearity and the matrix effect. The method LOQ (LOQm) was defined as the lowest spiked level which meets the acceptability criteria (mean recoveries were in the range of 70–120%, with a relative standard deviation (RSD) ≤ 20%) of the method performance. The accuracy and precision of the method were tested via recovery experiments which were carried out for each matrix in six replicates at two fortification levels (LOQ and 10 times LOQ). To assess the linearity of the method, the rice extracts from blank materials were spiked with multi-standard solutions containing the 42 pesticides over a 7 concentration range of 10, 25, 50, 100, 200, 300 and 1000 µg kg^{-1}. I.S. concentration was 50 µgL^{-1}. Calibration standards for each concentration level were measured three times, starting with the lowest concentration level.

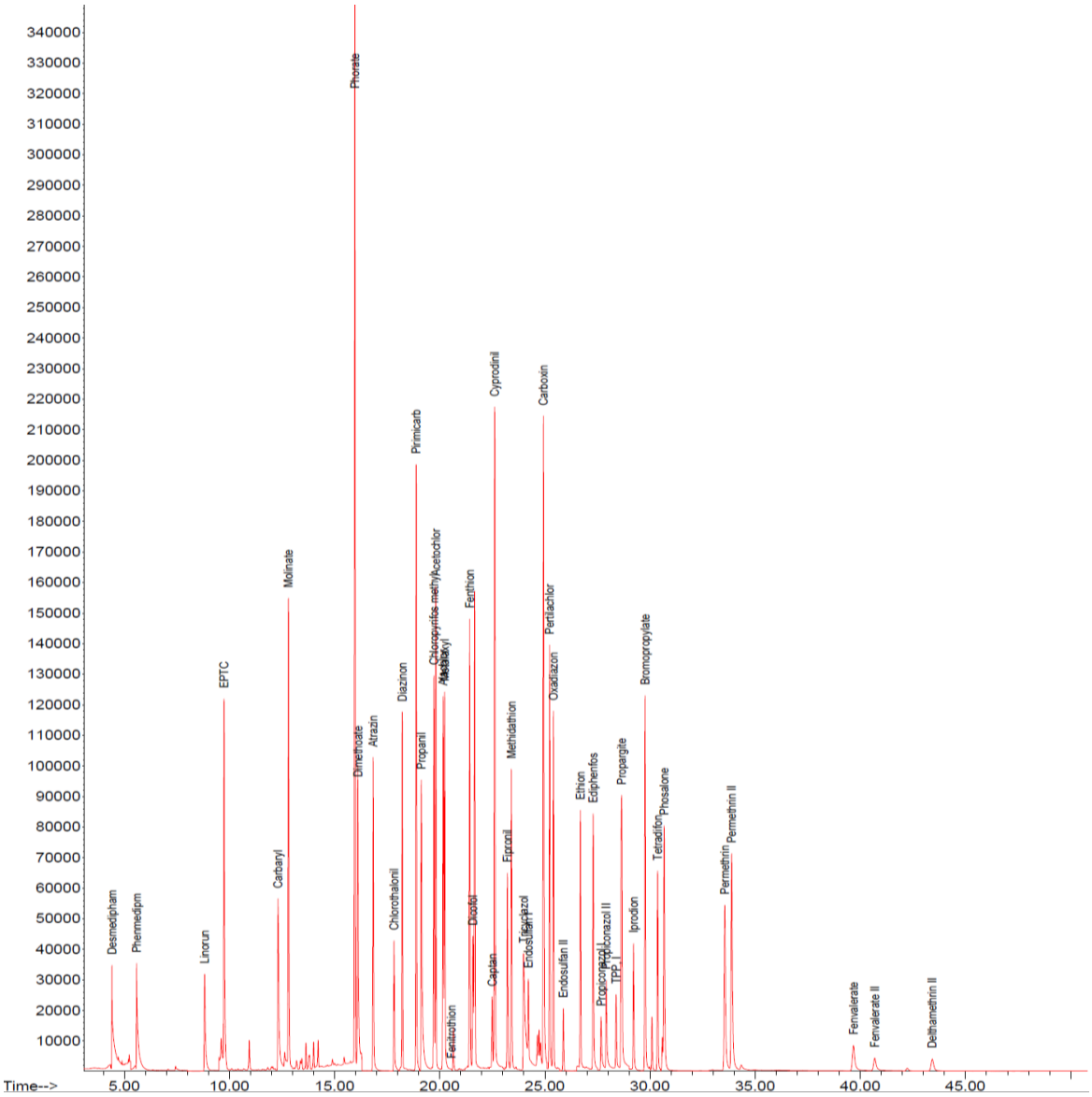

Fig. 1. Chromatograms of 42pesticide by GC-MS at optimum extraction condition

The calibration curves were constructed by using the ratio of peak area of analytes to the peak area of I.S. at seven different concentrations (10, 25, 50, 100, 200, 500 and 1000 µgkg^{-1}) versus the corresponding concentrations in the matrix solution. Least-squares regression analysis was applied to determine equation of each calibration graph. The coefficient of determination (R2) value of >0.99 for each target analytes was acceptable. The LODs and LOQs of the analytical method

were determined according to EURACHEM Guide as the minimum concentration of analyte in the spiked blank samples including SRM traces with a signal-to noise (S/N) ratio of 3 and 10, respectively. The precision was expressed as relative standard deviation (RSD) of replicate measurements.

Recoveries were calculated by comparing the concentrations of the extracted compounds with those from the MMC calibration curves.

3.RESULTS AND DISCUSSION

In this study, 42 pesticides were investigated using the QuEChERS procedure based on Matrix-matched calibration measurement. Table 1 summarizes the studied pesticides with physicochemical parameters and detailed GC–MS acquisition parameters. Typical chromatogram of pesticides is shown in Fig. 1. Because several families of pesticides with different physical and chemical properties were studied, the development of a simple analytical method for the determination of pesticide residues in complex matrices was a challenge.

In order to increase the recoveries and minimize the matrix effects, special attention has been paid to the extraction and cleanup procedure.

3.1. Selection of extraction solvent

An essential requirement to the sample preparation was the applicability to analytes with various physicochemical characteristics, which requires the selection for a suitable solvent. In the original QuEChERS study, acetonitrile was shown to be the best advantageous solvent for the extraction of pesticide residues from many kinds of matrices [28-30].

The extraction solvent has a crucial role in the QuEChERS method via transfer all analytes from the matrix to the extraction solvent and reduce the co-extracted components of matrix as far as possible and produce a good chromatographic pattern. Improvement of solvation ability of extraction solvent was achieved by the addition of water.

3.2. Control of pH

The big challenge in analysis of multi-pesticide residues is the extraction of pH-dependent pesticides. To improve overall satisfactory recoveries for all pesticides, the citrate-buffering version were added (0.5 g sodium citrate dibasic sesquihydrate and 1.0 g sodium citrate tribasic dehydrate). On the other hand, rice is composed of high amount of sugar and carbohydrate.

Under these conditions acetonitrile can be separated more easily from water with the addition of the NaCl to induce phase separation and improve transfer of analytes from aqueous phase to acetonitrile phase via salting-out phenomena resulting in the improved extraction recoveries. Additionally, addition of $MgSO_4$ helps to promote the partitioning of analytes into the acetonitrile phase.

3.3. Dispersive-SPE clean up

After the extraction of pesticides into acetonitrile by partitioning of the analyte molecules in organic solvent, the acetonitrile phase was further cleaned up by mixing with the anhydrous $MgSO_4$ and SPE sorbents (PSA and C18). In QuEChERS method, C18 in place of PSA sorbent was used to remove various co-extractive interferences such the polar organic acids, sugars and fatty acids [31].

3.4. Analytical performance of the method

At optimum experimental conditions, the established QuEChERS method was validated in terms of linearity, LOQ, accuracy and precision. Linearity was investigated using matrix-matched standard solutions at seven concentration levels: 10, 25, 50, 100, 200, 300 and 1000 μgL−1. The corresponding calibration curves were constructed by plotting the relative peak area (analyte/IS) versus the relative concentration. The limit of detection (LOD) also defined as amount of under study compound that generates a ratio more than three for signal to noise. It was calculated based on 3sb m−1, while m is the calibration sensitivity and sb is the standard deviation of blank. Table 2 reports linearity for all pesticides. The calibration curves gave a high level of linearity during 10–1000 μg L^{-1} for all pesticides with correlation coefficients (r) higher than 0.99. The accuracy and precision of the developed method were assessed at two concentration levels for each compound. The repeatability study by performing three parallel replicate extractions (50 and 100 μg L^{-1}) has relative standard deviation lower than 10 %. The actual amount of pesticides in real samples was evaluated by matrix-matched calibration method (Table 3).

The results show that the proposed method is applicable for evaluation of pesticide residue in real sample with relative standard deviations (RSDs, n = 3) less than 10.0 %.

Table 3. Extraction recoveries and RSD in rice sample at spiked level by the QuCHERS-GC-MS method.

No.	Pesticide name	Added (μg L^{-1})	Found (μg L^{-1})	RSD (%)	Recovery (%)
1	Phenmedipham	0.0	0.0	-	-

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		50.0	53.0	3.14	106.0
		100.0	98.0	4.36	98.0
2	Linuron	0.0	0.0	-	-
		50.0	42.0	3.27	84.0
		100.0	86.0	4.33	86.0
3	EPTC	0.0	0.0	-	-
		50.0	44.0	5.86	88.0
		100.0	79.0	6.27	79.0
4	Carbaryl I	0.0	0.0	-	-
		50.0	43.0	5.75	86.0
		100.0	92.0	6.56	92.0
5	Molinate	0.0	0.0	-	-
		50.0	43.0	3.26	86.0
		100.0	89.0	3.72	89.0
6	Phorate	0.0	0.0	-	-
		50.0	41.0	5.45	82.0
		100.0	83.0	5.73	83.0
7	Trifluralin	0.0	0.0	-	-
		50.0	48.0	2.32	96.0
		100.0	97.0	3.25	97.0
8	Dimethoat	0.0	0.0	-	-
		50.0	44.0	4.36	88.0
		100.0	93.0	5.33	93.0
9	Atrazine	0.0	0.0	-	-
		50.0	45.0	4.54	90.0
		100.0	85.0	4.56	85.0
10	Chlorothaloni l	0.0	0.0	-	-
		50.0	41.0	4.45	82.0
		100.0	81.0	4.38	81.0
11	Diazinon	0.0	0.0	-	-
		50.0	44.0	3.32	88.0
		100.0	92.0	2.33	92.0
12	Pirimicarb	0.0	0.0	-	-
		50.0	45.0	4.36	90.0
		100.0	93.0	4.58	93.0
13	Propanil	0.0	0.0	-	-
		50.0	46.0	3.22	92
		100.0	93.0	4.25	93
14	Chlorpyrifos-methyl	0.0	0.0	-	-
		50.0	47.0	3.45	94.0
		100.0	97.0	3.85	97.0
15	Acetochlore	0.0	0.0	-	-
		50.0	46.0	4.22	92.0
		100.0	95.0	6.22	95.0
16	Alachlor	0.0	0.0	-	-
		50.0	41.0	4.45	82.0
		100.0	84.0	5.46	84.0
17	Metalaxyl	0.0	0.0	-	-
		50.0	44.0	4.36	88.0
		100.0	92.0	4.52	92.0
18	Fenitrothion	0.0	0.0	-	-
		50.0	48.0	2.22	96.0
		100.0	98.0	3.26	98.0
19	Fenthion	0.0	0.0	-	-
		50.0	47.0	3.74	94.0
		100.0	96.0	5.56	96.0
20	Dicofol	0.0	0.0	-	-
		50.0	41.0	2.85	82.0
		100.0	83.0	4.65	83.0
21	Chlorpyrifos	0.0	0.0	26.0	-
		50.0	73.0	3.75	94.0
		100.0	130.0	4.66 +	104.0
22	Cyprodinil	0.0	0.0	-	-
		50.0	47.0	3.37	94.0
		100.0	96.0	5.89	96.0
23	Captan	0.0	0.0	-	-
		50.0	46.0	4.85	92.0
		100.0	92.0	5.67	92.0
24	Fipronil	0.0	0.0	-	-

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		50.0	46.0	2.66	92.0
		100.0	96.0	4.57	96.0
25	Methidathion	0.0	0.0	-	-
		50.0	42.0	3.92	84.0
		100.0	96.0	4.25	96.0
26	Tricycazol	0.0	35.0	2.18	-
		50.0	83.0	4.78	96.0
		100.0	142.0	5.28	
27	Endosulfanalfa	0.0	0.0	-	-
		50.0	47.0	3.25	94.0
		100.0	96.0	4.55	96.0
28	Oxadiazon	0.0	0.0	-	-
		50.0	48.0	3.28	96.0
		100.0	99.0	4.75	99.0
29	Carboxin	0.0	0.0	-	-
		50.0	43.0	2.45	86.0
		100.0	88.0	4.63	88.0
30	Endosulfan beta	0.0	0.0	-	-
		50.0	44.0	2.56	88.0
		100.0	99.0	3.45	99.0
31	Ethion	0.0	0.0	-	-
		50.0	52.0	2.12	104.0
		100.0	99.0	3.17	99.0
32	Edifenphos	0.0	0.0	-	-
		50.0	48.0	2.06	96.0
		100.0	95.0	3.47	95.0
33	Propiconazole	0.0	37.0	2.23	-
		50.0	92.0	4.56	110.0
		100.0	146.0	4.45	109.0
34	Propargite	0.0	0.0	-	-
		50.0	49.0	2.25	98.0
		100.0	93.0	3.24	93.0
35	Iprodin	0.0	0.0	-	-
		50.0	53.0	4.27	106.0
		100.0	98.0	4.45	98.0
36	Bromopropylate	0.0	0.0	-	-
		50.0	49.0	4.36	98.0
		100.0	97.0	4.65	97.0
37	Fenpropathrine	0.0	0.0	-	-
		50.0	44.0	2.27	88.0
		100.0	86.0	3.26	86.0
38	Tetradifon	0.0	0.0	-	-
		50.0	48.0	4.38	96.0
		100.0	96.0	5.36	96.0
39	Phosalone	0.0	0.0	-	-
		50.0	46.0	4.56	92.0
		100.0	95.0	4.43	95.0
40	Permethrin I-II	0.0	0.0	-	-
		50.0	56.0	4.26	112.0
		100.0	108.0	4.75	108.0
41	Fenvalerate	0.0	0.0	-	-
		50.0	51.0	4.35	102.0
		100.0	99.0	4.15	99.0
42	Deltamethrin	0.0	0.0	-	-
		50.0	42.0	4.52	84.0
		100.0	86.0	4.56	86.0

4.CONCLUSION

This research focuses on validation of QuEChERS method for the analysis of 42 pesticides by GC–MS in rice samples. The extraction process adopts acetonitrile as extraction solvent in the presence of water coupled with MgSO4 and NaCl to enhance the extraction recoveries. The use of sodium bicarbonate and sodium citrate enable extraction of multi-class pesticides from complex matrices. The d-SPE cleanup stage provided high efficiency of cleanup and low matrix effects following injection of samples to the GC-MS. This method is sensitive and accurate in routine multi-residue analysis in rice samples. The QuEChERS together with GC-MS is comparable for the determination of multi-class pesticides with good sensitivity, high linear range (10–1000 μg L^{-1}), short extraction time and short separation time (45.0 min). The proposed method can be applied for the determination of

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pesticides in rice samples with good recoveries in the range of 79 % to 112 % and RSD less than 10 %.

REFERENCES

[1]E. F. S. Authority, P. Medina Pastor, and G. Triacchini, The 2018 European Union report on pesticide residues in food, *EFSA J.* 18 (2020) e06057.

[2]J. Fenik, M. Tankiewicz, and M. Biziuk, Properties and determination of pesticides in fruits and vegetables, *TrAC Trends Anal. Chem.* 30 (2011) 814.

[3]S. Wahab, K. Muzammil, N. Nasir, M. S. Khan, M. F. Ahmad, M. Khalid, W. Ahmad, A. Dawria, L. K. V. Reddy, and A. M. Busayli, Advancement and new trends in analysis of pesticide residues in food: A comprehensive review, *Plants* 11 (2022) 1106.

[4]M. Bhattu, M. Verma, and D. Kathuria, Recent advancements in the detection of organophosphate pesticides: a review, *Anal. Methods. 13* (2021) 4390.

[5]S. Narenderan, S. Meyyanathan, and B. Babu, Review of pesticide residue analysis in fruits and vegetables. Pre-treatment, extraction and detection techniques. Food Res. Int. 133 (2020) 109141.

[6]J.P. dos Anjos, and J.B. de Andrade, Determination of nineteen pesticides residues (organophosphates, organochlorine, pyrethroids, carbamate, thiocarbamate and strobilurin) in coconut water by SDME/GC–MS, *Microchem. J.* 112 (2014) 119.

[7]N. Brito, S. Navickiene, L. Polese, E. Jardim, R. Abakerli, and M. Ribeiro, Determination of pesticide residues in coconut water by liquid–liquid extraction and gas chromatography with electron-capture plus thermionic specific detection and solid-phase extraction and high-performance liquid chromatography with ultraviolet detection, *J. Chromatogr. A.* 957 (2002) 201.

[8]M. A. Farajzadeh, Z. Fathipour, M. B. Aghdam, M.and R. A. Mogaddam, Evaluation of activated charcoal-infused dental floss combined with dispersive liquid–liquid microextraction for the solid phase extraction of pesticide residues in fruit juices, *J. Food Compost. Anal.* 1 (2023) 105389.

[9]P. Deme, T. Azmeera, S. Kanjilal, P. Jonnalagadda, V. S. Upadhyayula, LC-MS/MS determination of organophosphorus pesticide residues in coconut water, *Food Anal. Methods*. 6 (2013) 1162.

[10]S. Ogawa, N. Brito, M. Silva, M. Ribeiro, L. Leite, H. Dórea, S. Navickiene, R. Abakerli, and J. Ferreira, Determination of carbofuran and 3-hydroxycarbofuran residues in coconut water by solid-phase extraction and liquid chromatography with UV detection, *J. Liq. Chromatogr.* 29 (2006) 1833.

[11]R. Paranthaman, and S. Kumaravel, A reversed-phase high-performance liquid chromatography (RP-HPLC) determination of pesticide residues in tender coconut water (elaneer/nariyal pani), I*nt. J. Chromatogr. Sep. Tech.* 4 (2013) 2.

[12]A. Mohebbi, M. A. Farajzadeh, S. M. Sorouraddin, and M. Abbaspour, Improved magnetic solid-phase extraction based on magnetic sorbent obtained from sand for the extraction of pesticides from fruit juice, *J. Sci. Food Agric.* 102 (2022) 4266.

[13]L.F.S. Santos, N. R. da Silva Souza, J. A. Ferreira, and S. Navickiene, A reversed-phase high-performance liquid chromatography method combined with matrix solid-phase dispersion extraction for the determination of teflubenzuron, lufenuron and bifenthrin residues in lyophilized coconut water, *J. Food Compost. Anal.* 26 (2012) 183.

[14]M. G. D. Silva, A. Aquino, H. S. Dórea, and S. Navickiene, Simultaneous determination of eight pesticide residues in coconut using MSPD and GC/MS, *Talanta* 76 (2008) 680.

[15]E. A. Pfannkoch, J. R. Stuff, and J. A. Whitecavage, Qualitative analysis of coconut water products using stir bar sorptive extraction combined with thermal desorption-GC/MS. *AppNote, Gerstel. 5* (2012).

[16]M. Anastassiades, S. J. Lehotay, D. Štajnbaher, and F. J. Schenck, Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce, *J. AOAC Int.* 86 (2003) 412.

[17]M. C. Bruzzoniti, L. Checchini, R. M. De Carlo, S. Orlandini, L. Rivoira, and M. Del Bubba, QuEChERS sample preparation for the determination of pesticides and other organic residues in environmental matrices: a critical review, *Anal. Bioanal. Chem.* 406 (2014) 4089.

[18]D. I. Kolberg, O. D. Prestes, M. B. Adaime, and R. Zanella, Development of a fast multiresidue method for the determination of pesticides in dry samples (wheat grains, flour and bran) using QuEChERS based method and GC–MS, *Food Chem.* 125 (2011) 1436.

[19]N. Klinsunthorn, A. Petsom, and T. Nhujak, Determination of steroids adulterated in liquid herbal medicines using QuEChERS sample preparation and high-performance liquid chromatography, *J. Pharm. Biomed. Anal.* 55 (2011) 1175.

[20]Y. Han, W. Li, F. Dong, J. Xu, X. Liu, Y. Li, Z. Kong, X. Liang, and Y. Zheng, The behavior of chlorpyrifos and its metabolite 3, 5, 6-trichloro-2-pyridinol in tomatoes during home canning, *Food Control* 31 (2013) 560.

[21]A. A. da Silva, E. Fagnani, and J. Cristale, A modified QuEChERS method for determination of organophosphate esters in milk by GC-MS, *Chemosphere* 1 (2023) 138974.

[22]M. García-Vara, C. Postigo, P. Palma, M. J. Bleda, M. L. de Alda, QuEChERS-based analytical methods developed for LC-MS/MS multiresidue determination of pesticides in representative crop fatty matrices: Olives and sunflower seeds, *Food Chem.* 386 (2022) 132558.

[23]S. J. Lehotay, K. A. Son, H. Kwon, U. Koesukwiwat, W. Fu, K. Mastovska, E. Hoh, and N. Leepipatpiboon, Comparison of QuEChERS sample preparation methods for the analysis of pesticide residues in fruits and vegetables, *J. Chromatogr.* A 1217 (2010) 2548.

[24] Y. Zhang, X. Zhang, and B. Jiao, Determination of ten pyrethroids in various fruit juices: Comparison of dispersive liquid–liquid microextraction sample preparation and QuEChERS method combined with dispersive liquid–liquid microextraction, *Food Chem.* 159 (2014) 367.

[25]J. Yang, X. Zhou, X. Li, X. Li, Y. Gao, and Q. Zhang, Simultaneous determination of 21 organophosphorus flame retardants in rice by gas chromatography quadrupole time-of-flight mass spectrometry, *Talanta* 253 (2023) 124103.

[26]M. Andraščíková, S. Hrouzková, and S. C. Cunha, Combination of QuEChERS and DLLME for GC-MS determination of pesticide residues in orange samples, *Food Addit. Contam. Part A.* 30 (2013) 286.

[27]S. Cunha, J. Fernandes, A. Alves, and M. Oliveira, Fast low-pressure gas chromatography–mass spectrometry method for the determination of multiple pesticides in grapes, musts and wines, *J. Chromatogr.* A 1216 (2009) 119.

[28]A. Melo, S. C. Cunha, C. Mansilha, A. Aguiar, O. Pinho, and I. M. Ferreira, Monitoring pesticide residues in greenhouse tomato by combining acetonitrile-based extraction with dispersive liquid–liquid microextraction followed by gas-chromatography–mass spectrometry, *Food Chem.* 135 (2012) 1071.

[29]O. Golge, and B. Kabak, Evaluation of QuEChERS sample preparation and liquid chromatography–triple-quadrupole mass spectrometry method for the determination of 109 pesticide residues in tomatoes, *Food Chem.* 176 (2015) 319.

[30]J. A. Ferreira, J. M. S. Ferreira, V. Talamini, J. de Fátima Facco, T. M. Rizzetti, O. D. Prestes, M. B. Adaime, R. Zanella, and C. B. G. Bottoli, Determination of pesticides in coconut (Cocos nucifera Linn.) water and pulp using modified QuEChERS and LC–MS/MS, *Food Chem*. 213 (2016) 616.

[31]U. Koesukwiwat, K. Sanguankaew, and N. Leepipatpiboon, Rapid determination of phenoxy acid residues in rice by modified QuEChERS extraction and liquid chromatography–tandem mass spectrometry, *Anal. Chim. Acta.* 626 (2008) 10..

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اندازه‌گیری همزمان باقیمانده ۴۲ آفت‌کش در برنج با آماده سازی نمونه به روش کچرز و کروماتوگرافی گازی–طیف سنجی جرمی

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چکیده

در این کار تحقیقاتی یک روش چندباقیمانده سریع، دقیق و حساس و با هزینه مناسب بر مبنای روش کچرز برای اندازه گیری و پایش باقیمانده سموم در برنج ارائه می شود. جداسازی هم‌زمان آفت‌کش‌ها با دستگاه کروماتوگرافی گازی مجهز به آشکارساز اسپکترومتر جرمی با سرعت جریان گاز حامل ۱/۰ میلیلیتر بر دقیقه، دمای تزریق ۲۵۰ درجه سانتیگراد با مد غیر انشعابی و ستون موئینه به طول ۳۰ متر با سرعت جریان ۱/۰ میلی‌لیتر بر دقیقه انجام گرفت. در این تحقیق استونیتریل به عنوان حلال استخراجی به کار گرفته شد. آنالیت‌های استخراج شده در نهایت با روش استخراج فاز جامد پخشی پاک سازی شد. در شرایط بهینه منحنی درجه‌بندی برای تمامی آفت‌کش‌ها در محدوده غلظتی ۰/۰۰۰۱-۱۰/۰ میکروگرم بر لیتر خطی بوده و مقادیر ضرایب همبستگی بین ۰/۹۹ تا ۰/۹۹۹ بدست آمدند. مقادیر درصد بازیابی بین ۷۹ تا ۱۱۲ درصد با درصد انحراف استاندارد نسبی کمتر از ۷ درصد بدست آمد. همچنین حد تشخیص و حد اندازه‌گیری کمّی مناسبی برای تمامی آفت‌کش ها به دست آمد. مقادیر حد تشخیص بین ۱۲/۵۲-۳/۰۴ میکروگرم بر لیتر و حد اندازه‌گیری کمّی بین ۴۱/۷۶-۱۰/۱۴ میکروگرم بر لیتر بدست آمدند.

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کروماتوگرافی گازی؛ طیف سنجی جرمی؛ آفت‌کش؛ روش چندباقیمانده؛ روش کچرز.

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