

## Evaluation of QuEChERS Method for Determination of pesticide Residues Using GC/NPD and GC/ECD

Tae Hee Cho\*, Young Hye Park, Hye Won Park, Lae Hwong Hwang, In Soon Cho, Min Jung Kim, Hyun Jeong Kim, Mu Sang Kim and Young Zoo Chae

Kangnam Agro-Fishery Products Inspection Center,  
Seoul Metropolitan Government Research Institute of Public Health and Environment, Seoul 138-701, Korea

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**Abstract** The modified QuEChERS method was evaluated for rapid determination of pesticide residues in spinach by gas chromatography-nitrogen phosphorous detector (NPD) and electron capture detector (ECD). Fifty GC-amenable pesticides which were most frequently detected in monitoring were selected in the current study. Matrix-matched calibration was performed. The detector response for all pesticides was linear with determination coefficients higher than 0.995. LODs for most compounds ranged between 0.001 and 0.1 ug/g, and about 90% of the compounds had LODs of less than 0.05 ug/g. LOQs ranged from 0.001 to 0.32 ug/g, which were well below the MRLs permitted for most of pesticides. In the majority of cases, the recoveries (80-120%) and relative standard deviations (RSDs) (less than 20%) were within acceptable levels except for dichlorvos, propamocarb, chlorothalonil, dichlofluanid, cyhalothrin and fenvalerate. Also, this method which is applied to routine samples showed good results when comparing with traditional multi-residue method.

**Key words** GC-ECD, GC-NPD, Pesticide residues, QuEChERS

### Introduction

Nowadays, analysis technology has sought strategies of being eco-friendly and easy to operate. QuEChERS, introduced by USDA scientists in 2003, meet the demands. The QuEChERS, which stands for quick, easy, cheap, effective, rugged, and safe, provided satisfactory results for the wide range of pesticides and the practical benefits desired by all laboratories (Anastassiades et al., 2003). Also, modifications of original method were validated successfully in analysis of over 200 pesticides and standardized as AOAC Official Method 2007.01 and European committee for standardization (CEN) standard method EN15662 (Lehotay et al., 2005). QuEChERS method is very flexible and can be easily modified depending on the analyte properties, matrix composition of sample and analysis equipments (Lehotay et al., 2010). Due to such advantages, QuEChERS method has already applied to the determination of polycyclic aromatic hydrocarbons in fish, acrylamide and mycotoxin in food, drugs in blood and so on (Wilkowska et al., 2011). Three main steps of

QuEChERS procedure involve extraction with acetonitrile followed by liquid-liquid partitioning formed by addition of anhydrous Magnesium Sulfate ( $MgSO_4$ ) plus Sodium Chloride (NaCl), dispersive SPE clean-up with anhydrous  $MgSO_4$  and primary secondary amine (PSA), and analysis by GC/MS and LC/MS/MS (Anastassiades et al., 2003). QuEChERS method is very attractive tool. However, acetonitrile as final solvent is not suitable for GC selective detector like NPD (Anastassiades et al., 2003). And also QuEChERS does not entail concentration step to achieve the desired limits of quantification prior to instrument analysis. Although conventional multi-residue methods are criticized for multiple steps, time consuming and use of high amounts of solvent, many analysts have accustomed to these procedures for a long time and also it is not easy to furnish labs with costly analytical equipments. Therefore, in this study, QuEChERS method was modified to apply to conventional operating systems and the possibility as multi-residues method was examined in comparison with the traditional multi-residue method.

### Material and Methods

#### Reagents and chemicals

Pesticide standards with a purity higher than 97% were

\*Corresponding author

Tel: +82-2-3401-6292, Fax: +82-2-3401-6742

E-mail: bgbright@seoul.go.kr

obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany), Riedel-de Haën (Seelze, Germany) and Wako (Tokyo, Japan). Stock standard solutions at 200 µg/mL were prepared in various solvents and were stored in the dark at 4°C. Working standard pesticide mixtures were prepared freshly by dilution in the matrix-blank extract. All organic solvents were pesticide grade or HPLC grade and purchased from J.T. Baker, USA. 500 mg Sep-Pak Florisil cartridge were purchased from Agilent Technologies. Anhydrous MgSO<sub>4</sub> and NaCl were obtained from Aldrich (Milwaukee, WI, USA). Primary secondary amine (PSA) sorbent was obtained from Varian (Harbor City, CA, USA).

### Sample preparation

#### *Sample preparation for conventional multi-residue method*

Chopped sample (50 g) was extracted with 100 mL acetonitrile for 2 min at high speed with a homogenizer and filtered into a 150 mL glass bottle with a cap containing 10-15 g sodium chloride. The extract was vigorously shaken and allowed to stand for 30 min. Two 10 mL upper phases were transferred into each of two 100 mL beakers and evaporated to dryness in a steam bath at 60°C with a gentle stream of air. The first dried acetonitrile extract was dissolved in 2 mL acetone and then filtered through a 0.2 mm nylon acro-disc for gas chromatography-nitrogen phosphorous detector (GC-NPD). The second residue was dissolved in 2 mL 20% acetone/hexane and loaded onto a 500 mg Sep-Pak Florisil cartridge, which was preconditioned with 5 mL hexane, followed by washing with 5 mL 20% acetone in hexane. The cartridge was eluted with 5 mL 20% acetone/hexane twice. The elution was evaporated at 60°C and dissolved in 2 mL 20% acetone in hexane for gas chromatography-electron capture detector (GC-ECD).

#### *Sample preparation for QuEChERS multi-residue method*

In this study, sample preparation was carried out based on original QuEChERS method (Anastassiades et al., 2003). Chopped sample (10 g) was weighed into 50 mL Teflon centrifuge tube and 10 mL acetonitrile was added. The

centrifuge tube was vigorously shaken for 1 min by using Vortex mixer. 4 g anhydrous MgSO<sub>4</sub> and 1 g NaCl were further added and shaken immediately for 1 min on a Vortex mixer. The extract was centrifuged for 5 min at 3500 rpm. 6 mL upper acetonitrile layer was transferred to 15 mL centrifuge tube containing 300 mg PSA and 900 mg anhydrous MgSO<sub>4</sub>. The centrifuge tube was capped tightly, shaken for 30 s by hand and centrifuged for 5 min at 3500 rpm. 2 mL supernatant was evaporated to dryness in a steam bath at 50°C with a gentle stream of air and the residue was dissolved in 1 mL 20% acetone/hexane for GC/NPD, GC/ECD analysis.

### Instrument analysis

Analysis was performed with the multi-residue method (MRM) No. 2 for pesticide residues according to the Korea Food Code, which is based on MRM of the California Department of Food and Agriculture (CDFA) (Lee et al., 1991). The GC-NPD system for organophosphorous and nitrogen-containing compounds and the GC-ECD system for organochlorine and pyrethroid compounds were used. Agilent 6890 series gas chromatographs equipped with a nitrogen phosphorous detector (NPD) and a <sup>63</sup>Ni electron capture detector (ECD) were employed. The chromatographic separation was performed on an HP-1701 and an HP-5 (Agilent Technologies). Confirmation of residues in field samples was carried out by an Agilent 6890 series gas chromatograph equipped with an HP 5973 mass selective detector. The mass spectrometer was operated in electron-impact ionization mode (ionizing energy = 70 eV) scanning from *m/z* 80 to 400 at 4.45 scan/s. The ion source and quadrupole temperatures were 230 and 150 °C, respectively. The operating conditions for GC and GC-MS are summarized in Table 1.

### Quantification

Calculations were based on the matrix-matched and the standards method. The calibration standards were made from a 2 mg/mL stock solution. Quantification was carried out using peak area. The results were expressed in µg/g (parts per million).

**Table 1.** Analytical conditions of GC-ECD, GC-NPD and GC-MSD

	GC-ECD	GC-NPD	GC-MSD
Column	HP-1701 (30 m × 320 µm × 0.25 µm) HP-5 (30 m × 320 µm × 0.25 µm)	HP-1701 (30 m × 320 × 0.25) HP-5 (30m × 320 × 0.25)	HP-5MS (30 m × 250 µm × 0.25 µm)
Gas Flow	N <sub>2</sub> (1 mL/min)	N <sub>2</sub> (1.4 mL/min) Air (60 mL/min) H <sub>2</sub> (3.5 mL/min)	He (1 mL/min)
Inj. Temp.	230°C	210°C	230°C
Det. Temp.	280°C	270°C	280°C (Interface Temp.)
Oven Temp.	150°C (1 min)-12°C/min- 240°C (2 min)-10°C/min- 280°C (11 min)	100°C (1 min)-15°C/min- 200°C (8 min)-10°C/min- 260°C (7 min)	100°C (2 min)-10°C/min- 280°C (15 min)

## Results and Discussion

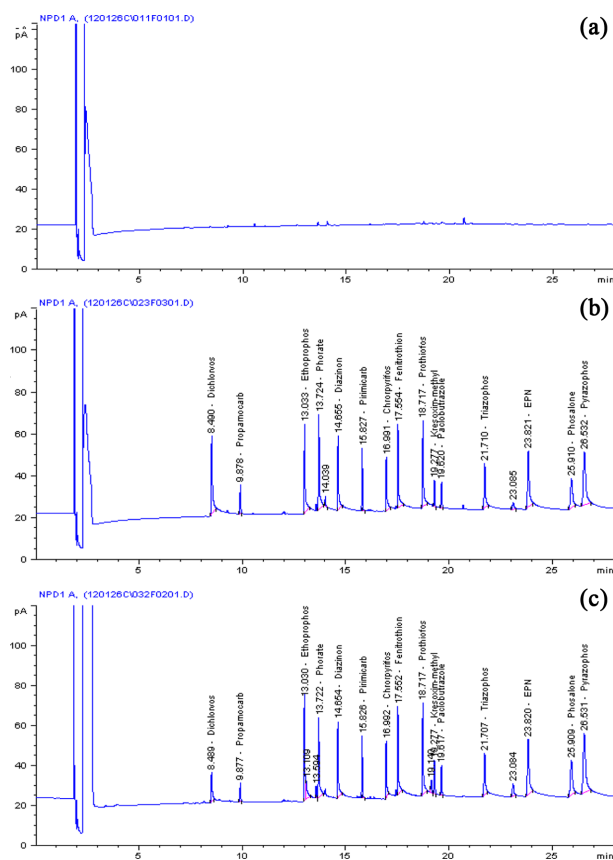
### Validation of QuEChERS method

Pesticide residue monitoring program has been operating for 285 pesticides in our lab under government control. Among them, fifty GC-amenable pesticides which were most frequently detected in previous monitoring were selected in the current study (Cho et al., 2009). Validation was performed by using pesticide-free spinach. Spinach is a representative leafy vegetable with highly pigmented matrix like a chlorophyll. External matrix-matched calibration was carried out to exclude matrix effects. Fig. 1 and 2 show representative chromatogram for blank, matrix-matched standards, and spiked standards in spinach. The detector response for all pesticides was linear at concentrations within the tested interval with determination coefficients higher than 0.995. The limit of detection (LOD) and limit of quantification (LOQ) were determined at signal-to-noise ratios of 3 and 10, respectively. Table 2 and 3 show the LOD and LOQ values of QuEChERS method obtained for each pesticides. LODs for most compounds ranged between 0.001 and 0.1 ug/g, and about 90% of the compounds had LODs of less

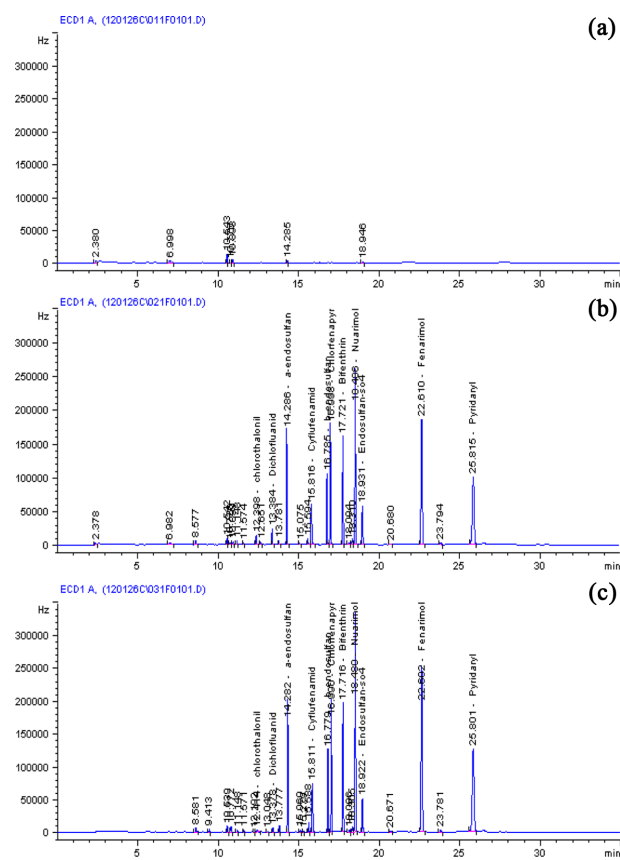
than 0.05 ug/g. LOQs ranged from 0.001 to 0.32 ug/g. LOQs for most of the pesticides were under Korean MRLs, but some pesticides need the concentration to reach into allowable MRLs. Modified method, through concentration step, seems to achieve desirable quantitation limit without large volume injection (LVI) system. (Gilbert-López, 2010) The recovery and reproducibility were evaluated by spiking at two levels of each pesticides. As shown in Table 2 and 3, in the majority of cases, the recoveries (80-120%) and relative standard deviations (RSDs) (less than 20%) were within acceptable levels except for some pesticides.

### Comparison of QuEChERS method Verse conventional multi-residue method

In preliminary test of several agricultural products, the original method showed similar recoveries with other methods such as AOAC and EN methods in most of pesticides. Therefore, in this study, modification based on original QuEChERS method was reviewed in comparing with traditional MRM. Traditional multi-residue method (MRM) was performed with Korea Food Code MRM No. II. The QuEChERS method was modified in order to be compatible



**Fig. 1.** Typical GC-NPD chromatogram (a) blank spinach, (b) matrix-matched standards, and (c) spiked standards in spinach. Levels of pesticide mixtures were prepared ranging from 0.14 to 7.74 ug/g based on the GC signal. Spiking levels were shown in Table 2.



**Fig. 2.** Typical GC-ECD chromatogram (a) blank spinach, (b) matrix-matched standards, and (c) spiked standards in spinach. Levels of pesticide mixtures were prepared ranging from 0.3 to 6.66 ug/g based on the GC signal. Spiking levels were shown in Table 3.

**Table 2.** Recovery results of spiked pesticides in spinach from 2 versions of multi-residue method with GC-NPD

Pesticide	Spiked level (ug/g)	Recovery %(RSD %)		Spiked level (ug/g)	Recovery %(RSD %)		QuEChERS LOD (ug/g)	QuEChERS LOQ (ug/g)
		QuEChERS	Traditional MRM		QuEChERS	Traditional MRM		
Chlorpyrifos	1.22	105.0(3.5)	92.1(5.1)	0.30	84.7(6.0)	93.9(3.0)	0.009	0.029
Chlorpyrifos-methyl	1.42	90.9(5.6)	103.1(7.2)	0.36	82.0(4.6)	78.1(4.5)	0.006	0.020
Diazinon	1.31	107.1(4.2)	84.0(3.4)	0.33	86.1(5.4)	89.3(2.8)	0.007	0.023
Dichlorvos	2.70	72.5(13.4)	13.1(15.1)	0.67	48.7(13.2)	48.0(7.5)	0.037	0.123
Diethofencarb	6.24	102.5(5.9)	101.1(6.2)	1.56	104.2(8.9)	82.0(10.4)	0.062	0.208
EPN	2.66	104.0(2.6)	94.1(9.4)	0.66	92.5(6.1)	93.3(4.5)	0.019	0.064
Ethoprophos	1.59	110.1(1.6)	83.8(6.6)	0.40	98.5(4.2)	90.8(3.2)	0.006	0.020
Fenitrothion	2.00	108(6.7)	93.7(2.3)	0.50	89.8(1.9)	88.8(5.1)	0.009	0.030
Fenobucarb	3.12	90.3(4.8)	105.4(2.1)	0.78	97.7(4.8)	85.0(2.7)	0.022	0.073
Fludioxonil	4.52	106.3(3.1)	98.2(2.7)	1.13	106.3(5.1)	79.7(6.1)	0.044	0.145
Kresoxim-methyl	6.66	107.2(3.4)	95.8(4.5)	1.66	121.7(3.5)	66.8(5.8)	0.079	0.265
Mepanipyrim	1.83	105.7(5.4)	99.3(1.3)	0.46	103.8(3.0)	64.0(3.4)	0.014	0.047
Metalaxyl	1.06	102.9(2.9)	93.2(4.7)	0.27	101.7(2.9)	81.2(5.5)	0.022	0.073
Methidathion	1.98	89.4(5.8)	100.4(6.4)	0.50	84.8(2.1)	75.9(5.4)	0.009	0.031
Paclbutrazole	2.44	115.7(4.0)	94.8(5.6)	0.61	104.9(4.6)	90.0(6.0)	0.033	0.111
Parathion	1.26	105.2(3.8)	97.3(3.9)	0.32	90.9(5.0)	73.1(4.1)	0.005	0.016
Pencycuron	2.20	103.7(4.1)	96.9(3.4)	0.55	106.9(5.4)	77.9(3.8)	0.020	0.066
Phenthoate	1.88	102.3(7.8)	107.3(5.6)	0.47	97.0(6.1)	68.4(3.5)	0.007	0.024
Phorate	1.62	91.1(5.5)	60.2(4.1)	0.41	73.4(7.0)	77.0(4.5)	0.008	0.027
Phosalone	3.25	104.3(3.4)	111.8(3.3)	0.81	108.7(3.5)	93.8(3.1)	0.037	0.124
Pirimicarb	1.89	109.7(2.8)	86.9(6.1)	0.47	93.4(3.0)	87.8(4.3)	0.012	0.040
Propamocarb	1.75	53.9(14.7)	17.4(18.2)	0.44	53.3(10.7)	32.0(13.5)	0.038	0.126
Prothiofos	1.65	101.8(7.9)	84.4(8.5)	0.41	95.3(6.5)	79.1(6.1)	0.007	0.024
Pyrazophos	3.43	101.2(6.5)	101.3(3.0)	0.86	102.3(7.7)	89.7(7.5)	0.023	0.076
Tebufenpyrad	4.20	104.6(4.7)	99.4(4.9)	1.05	108.2(4.1)	78.3(3.9)	0.036	0.122
Triazophos	2.00	104.3(6.1)	104.6(2.9)	0.50	92.0(5.5)	92.6(5.5)	0.019	0.063

with a GC-NPD and a GC-ECD. The QuEChERS method involved extraction with acetonitrile, partitioning by salt and clean-up step with dispersive SPE. Target compounds were extracted only by vortex mixing. QuEChERS sample preparation was achieved only in about 30 minute for ten samples by an analyst when compared with traditional multi-residue method which need over 2 hours. Also, reducing the use of solvents by 1/10 in QuEChERS contribute to economic benefits as well as environmental conservation. However, QuEChERS has limitation of clean-up by only dSPE. As mentioned above, most of pesticides in QuEChERS method gave excellent recoveries (80~120%). However, propamocarb, dichlorvos, chlorothalonil, and dichlofluanid gave low recoveries, (< 75%), whereas fenvalerate and cyhalothrin gave high recoveries (> 140%). In general, polar non-volatile pesticides like a Propamocarb result in poor reproducibility, due to erratic degradation of the analyte in the GC injector (Hiemstra et al., 2002). Thus, propamocarb is moresuitable for LC application and also

propamocarb is rapidly degraded not only in sample but also in standard (Lesueur et al., 2008). Dichlorvos is the most volatile pesticide which seems to be lost during solvent evaporation (Lethoy, 2007). Even though its low recovery make a significant difference with Anastassiades's data (98% in lettuce) without evaporation step, it is better than the traditional MRM (Anastassiades et al., 2003). As mentioned in numerous articles, pesticides are more stable at lower pH. Aalkaline-sensitive pesticides such as chlorothalonil and dichlofluanid degraded rapidly as pH increase. Just like results of the other papers, they showed poor recoveries. Nevertheless, they had higher recovery rates in comparing with the traditional MRM. Meanwhile, fenvalerate gave > 140% and cyhalothrin gave > 200% high recovery. These results are thought to be caused by signal enhancement of instruments with combination target compound and matrix. However, recovery of cyhalothrin showed considerable difference with results of Park in cooked foodstuffs (Park et al., 2011). Nevertheless, pesticides above mentioned

**Table 3.** Recovery results of spiked pesticides in spinach from 2 versions of multi-residue method with GC-ECD

Pesticide	Spiked level (ug/g)	Recovery %(RSD %)		Spiked level (ug/g)	Recovery %(RSD %)		QuEChERS LOD (ug/g)	QuEChERS LOQ (ug/g)
		QuEChERS	Traditional MRM		QuEChERS	Traditional MRM		
Bifenthrin	1.16	102.1(7.1)	103.6(4.6)	0.29	108.2(6.2)	95.7(3.8)	0.002	0.006
Chlorfenapyr	0.59	100.3(5.4)	109.9(3.7)	0.15	111.6(3.3)	96.8(4.6)	0.001	0.002
Chlorfluzuron	3.60	88.4(2.2)	111.0(3.1)	0.90	89.9(3.5)	97.5(6.2)	0.085	0.285
Chlorothalonil	0.57	42.2(10.1)	59.5(13.5)	0.14	ND	ND	0.055	0.182
Cyflufenamid	0.57	104.1(3.8)	93.0(2.6)	0.14	111.2(1.4)	88.7(5.1)	0.001	0.001
Cyhalothrin	1.24	215.2(4.3)	103.2(1.9)	0.31	221.3(5.7)	93.3(4.3)	0.006	0.020
Cypermethrin	4.08	119.2(4.9)	101.9(3.0)	1.02	166.7(8.5)	86.5(11.3)	0.094	0.315
Dichlofluanid	0.58	36.5(13.5)	58.0(16.5)	0.15	ND	ND	0.040	0.135
Diniconazole	1.18	104.3(10.0)	92.9(4.1)	0.29	117.2(8.8)	91.9(14.2)	0.002	0.008
$\alpha$ -Endosulfan	0.20	99.1(3.1)	101.1(3.6)	0.05	109.2(1.5)	90.6(3.3)	0.001	0.002
$\beta$ -Endosulfan	0.15	106.3(5.7)	109.0(4.2)	0.04	123.6(6.5)	85.4(4.3)	0.001	0.002
Endosulfan sulfate	0.40	80.0(5.2)	106.4(6.1)	0.20	96.2(2.8)	89.9(3.4)	0.002	0.008
Fenarimol	1.05	111.1(3.5)	100.3(5.7)	0.26	124.9(4.5)	83.1(4.1)	0.001	0.004
Fenpropathrin	0.53	118.5(3.1)	100.6(2.2)	0.13	128.7(3.0)	94.6(1.5)	0.007	0.024
Fenvalerate	7.44	142.8(4.0)	95.9(3.0)	1.86	148.5(6.5)	89.5(2.9)	0.047	0.158
Fipronil	1.27	101.5(10.0)	107.8(6.8)	0.32	111.1(6.7)	94.5(2.2)	0.012	0.040
Nuarimol	1.02	109.7(2.5)	97.7(1.3)	0.26	122.1(6.5)	87.8(5.5)	0.001	0.003
Ofurace	4.24	113.9(6.3)	90.2(4.4)	1.06	130.5(1.4)	88.4(3.1)	0.017	0.058
Procymidone	2.00	104.8(3.1)	99.5(4.8)	0.50	116.4(6.2)	97.2(2.1)	0.008	0.027
Pyridaben	3.00	96.1(2.7)	91.1(3.1)	0.75	126.4(3.3)	85.1(4.7)	0.039	0.130
Pyridaryl	1.88	107.2(5.3)	99.0(10.4)	0.47	121.5(4.7)	73.1(3.4)	0.004	0.013
Tetraconazole	1.00	108.7(4.6)	82.6(3.5)	0.25	129.1(3.2)	86.3(4.3)	0.002	0.006
Tetradifion	0.57	102.9(1.1)	98.0(3.2)	0.14	125.7(2.5)	93.8(2.8)	0.003	0.009
Vinclozolin	0.65	103.5(6.3)	97.3(4.8)	0.16	124.7(5.4)	94.2(3.2)	0.002	0.007

achieved <20% RSD. Although a few pesticides are problematic, modified method is suitable for routine residue monitoring in agricultural products.

#### Application survey in real samples

The modified QuEChERS method was applied in field samples which were collected under a regulatory pesticide

monitoring programme. As seen in Table 4, six compounds were detected in six items. In case of procymidone, celery and wild garlic showed similar pesticide level, whereas chamnamul showed almost double level of traditional MRM. This may be due to matrix induced enhancement, a phenomenon commonly encountered in the GC analysis of pesticide in foods (Schencket al., 2000). To overcome this

**Table 4.** Comparison of pesticide residues levels detected in monitoring samples from two methods

Product	Pesticide detected	QuEChERS (ug/g)	Traditional MRM (ug/g)	Korean MRL (ug/g)
Celery	Procymidone	2.147	2.053	5.0
Chamnamul	Procymidone	2.419	1.120	5.0
Chamnamul	Pencycuron	1.202	0.956	0.05
Chard	Bifenthrin	0.718	0.694	1.0
Lettuce	Chlorpyrifos-methyl	4.921	6.016	0.2
Perilla Leaves	Procymidone	2.523	2.041	5.0
Perilla Leaves	Chlorpyrifos	0.010	0.010	0.01
Perilla Leaves	Diethofencarb	0.404	0.272	5.0
Wild garlic	Procymidone	1.681	1.522	5.0

effect, matrix-matched standards are usually used. However, it is not easy to prepare matrix-matched blank in routine screening to deal with many kinds of agricultural product. Therefore, quantitation was calculated with solvent -based standards in field sample. In case of diethofencarb, Quechers had a little higher level. This is consistent with recovery result in Table 2. Levels from QuEChERS method, taken as a whole, are a slightly higher than traditional MRM.

## Conclusion

The QuEChERS sample preparation was validated about fifty pesticides which are amenable to gas chromatography-nitrogen phosphorous detector (NPD) and electron capture detector (ECD) in spinach. The recovery and reproducibility, based on matrix spiked standards, were acceptable for determination of pesticide residues in routine practice. Consequently, the proposed method provided excellent results and practice benefits when comparing with traditional multi-residue method.

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## GC/NPD와 GC/ECD를 이용한 잔류농약 정량 분석법으로써의 QuEChERS의 평가

조태희\* · 박영혜 · 박혜원 · 황래홍 · 조인순 · 김민정 · 김현정 · 김무상 · 채영주

강남농수산물검사소 서울특별시보건환경연구원

**요 약** GC-NPD와 GC-ECD를 사용하여 잔류농약을 신속하게 정량 할 수 있는 변형 된 QuEChERS법이 시금치를 이용하여 검토되었다. 본 연구에서는 잔류농약 모니터링에서 주로 검출되며 GC로 측정 가능한 50가지 농약을 대상으로 하였다. 무농약 시금치를 이용하여 검량선을 작성하였으며,  $R^2$  값은 0.995 이상으로 모든 농약이 직선상을 나타내었다. 분석 농약의 검출한계는 0.001~0.1 ug/g로 나타났으며, 분석농약의 90% 이상이 0.05 ug/g 이하를 나타내었다. 정량한계는 0.001~0.32 ug/g로, 이는 농약의 잔류 허용기준치 보다 낮았다. Dichlorvos, propamocarb, chlorothalonil, dichlofluanid, cyhalothrin 그리고 fenvalerate를 제외하고는 대부분의 경우 회수율은 80~120%, RSD는 20% 이하로 나타났다. QuEChers는 기존 다중분석법과 비교해볼 때 일상적인 분석 시료에 응용했을 때 용매 사용량을 획기적으로 줄임으로써 친환경적 일뿐만 아니라 경제적이며 분석시간의 단축을 통해 유통 농산물의 안전성 확보에 기여할 수 있는 바가 크다고 할 수 있겠다.

**색인어** 잔류농약, QuEChERS법, 동시다성분분석