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Analytical Methods

A multiresidue method for the determination of 107 pesticides in cabbage and radish using QuEChERS sample preparation method and gas chromatography mass spectrometry

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Abstract

A rapid, specific and sensitive multiresidue method based on the modified Quick Easy Cheap Effective Rugged and Safe (QuEChERS) sample preparation method and gas chromatography with the electron impact mass spectrometric detection in the selected ion monitoring mode (GC–MS-SIM) using one target and two qualifier ions for the routine analysis of 107 pesticides in cabbage and radish has been developed. The recoveries for all the pesticides studied were from 80% to 115% with relative standard deviation lower than 15% in the concentration range of 0.030–0.360 mg/kg. The limit of quantitation (LOQ) for most compounds met MRLs for pesticides in cabbage and radish in Korea. This method was successfully applied to analysis commercial cabbage and radish samples.

Keywords: QuEChERS; Cabbage; Radish; Pesticide residues; GC–MS-SIM

1. Introduction

Kimchi is an absolute necessity in every Korean meal, it is a kind of food that combines the savor, nutrients and preservability in one environmentally sound food, which Korean are proud of and it is not much to say that Kimchi is the foodstuff of food in Korean culture. There is an abundance of variety of Kimchi but the most usual Kimchi are made from Korean cabbage (*Brassicas rapa var. pekinensis*) and Korean radish (*Raphanus sativus L. var. niger*). Total amount of Kimchi consumption in Korea is estimated at about 1360 thousand metric tons and per capital consumption of Kimchi reaching about 29 kg (Lee, Choi, & Ahn, 2000). Thus it needs large amount of raw materials in which, the farmers used a large number of pesticides to control pest and diseases that damage their crops. The presence of pesticide residues in marketed Korean cabbage and Korean radish is one important concern for not only consumers, but also for the Korean regulatory authorities, due to the popular used of Kimchi in every day meal of Korean. Concern over pesticide residues in food, the regulatory authorities in Korea in particular and in over the World in general provide assurance that any pesticides in or on the food is within established MRLs (Country Report, 2005; Korean Food and Drug Administration, 2005) through monitoring programs of analysis of raw and processed food on the market. To adapt this requirement, a number of methods have been developed for the analysis of pesticide residues in food.

Multiresidue method development is difficult, due to the fact that compounds of different polarity, solubility and volatility have to be extracted and analyzed. Based on the classes of pesticides, several methods using gas chromatography for separation of individual compounds, followed by detection with selective and sensitive detection methods such as electron capture detection (Ismail, Ali, & Habiba, 1993), nitrogen–phosphorus detection (Fenoll, Hellin, Martinez, Miguel, & Flores, 2007) and flame photometric detection (Bolles et al., 1999) have been proposed.

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However, the above mentioned detection methods cover a limited range of pesticide analysis and occurrence of false positive and inaccurate quantitation caused by the interferences of unknown compounds that are co-eluting in the same retention time with analytes. Many of the published methods (Albero, Sánchez-Brunete, & Tadeo, 2005; Gelsomino, Petrovičowá, Tiburtini, Magnani, & Felici, 1997; Hernando, Agüera, Fernández-Alba, Piedra, & Contreras, 2001; Johnson, Rimmer, & Brown, 1997; Lacassie et al., 1998; Štajnbaher & Zupančič-Kralj, 2003) for the pesticide determination in food commodities seem to be complicated while consuming a large volume of solvent and it is very time costly. Therefore, new methods in sample preparation and measurement should be studied and developed.

Recently, the QuEChERS sample preparation method has been introduced (Anastassiades, Lehotay, Štajnbaher, & Schenck, 2003; Lehotay, de Kok, Hiemstra, & van Bodegraven, 2005; Lehotay, Maštovská, & Lightfield, 2005; Nguyen, Lee, Lee, Lee, & Lee, 2007). This method has many advantages such as high recovery for wide polarity and volatility range of pesticides; high sample throughput; the use of smaller amounts of organic solvent and the use of no chlorinated solvents. Very little lab ware is used and there is increased the safety for lab workers.

Many studies have been reported concerning the determination of pesticides by using GC–MS (Albero et al., 2005; Díez, Traag, Zommer, Marinero, & Atienza, 2006; Gelsomino et al., 1997; Hernando et al., 2001; Johnson et al., 1997; Lacassie et al., 1998; Štajnbaher and Zupančič-Kralj, 2003) but this is the first attempt in Korea using gas chromatograph mass spectrometric (GC–MS-SIM) technique to determine of 107 majority pesticides with difference in physio-chemical properties in Korean cabbage and Korean radish. These works are aimed, firstly, to develop a rapid and accurate multiresidues method to determine organohalogen, organonitrogen, pyrethroid, organophosphorus, carbamate pesticides in single run; secondly, to evaluate of the apply of GC–MS-SIM and QuEChERS sample preparation method for analysis pesticide residues in Korean cabbage and Korean radish; and thirdly, to survey the current trend of using pesticides for vegetable in Korea.

This paper describes a simple and effective procedure for sample extraction using a modified QuEChERS sample preparation method and GC–MS-SIM for the simultaneous quantification of 107 pesticides from several classes in Korean cabbage and Korean radish below their respective MRLs in Korea.

2. Experimental

2.1. Materials and standards

The standard pesticides were purchased from Wako (Osaka, Japan), Chemservice (West Chester, PA, USA) and Dr. Ehrenstorfer (Ausberg, Germany). The purities of the standard pesticides were from 97.4% to 99%. Internal standards [Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Fluoranthene-d10, Chrysene-d12, Perylen-d12 and Triphenyl phosphate (TPP)] were purchased from C/D/N Isotopes INC. (Quebec, Canada) and Chemservice (West Chester, PA, USA). Glacial acetic acid (HAc) and solvents of pesticide analytical grade were purchased from J.T. Baker (Philipsburg, NJ, USA). The purified water was 18 MΩ (Ultra-pure water, Sinhan Science Tech, Daejeon, Korea). Anhydrous $MgSO_4$ and NaCl were obtained from Wako (Osaka, Japan). Primary secondary amine (PSA) sorbent was obtained from Varian (Varian, Harbor City, CA).

Stock standard solutions of 2.00 mg/mL were prepared in MeCN and stored at −20 °C. Intermediate and working standard solutions of a mixture of pesticides and internal standard solution was prepared in MeCN.

2.2. Apparatus

A Shimadzu 2010 (Shimadzu, Kyoto, Japan) gas chromatograph equipped with a split-splitless auto-injector model AOC-20i, an auto sampler model AOC-20s and a MS-QP 2010 (Shimadzu, Kyoto, Japan) series mass selective detector was used for the analysis of the pesticides studied. A fused silica capillary column (J&W DB 5MS), 5% phenyl polysiloxane as non-polar stationary phase (30 m × 0.25 mm i.d.) and 0.25 μm film thickness, supplied by Agilent (Palo Alto, CA, USA) was used for the GC separation, with helium as carrier gas at a constant flow at 1.7 mL/min. The temperature program used was as follows: initial temperature, 50 °C held for 1 min, then at the rate of 20 °C/min to 180 °C, 10 °C/min to 190 °C, 3 °C/min to 240 °C and 10 °C/min to 300 °C and then maintaining this temperature 5 min. The temperature of the injection port was 220 °C and a 1 μL volume was injected in splitless mode.

Mass spectronic detector was operated in electron impact ionization mode with an ionizing energy of 70 eV, scanning from m/z 50 to 550 at 0.5 s per scan. The ion source temperature was 200 °C and the MS transfer temperature 280 °C. The electron multiplier voltage (EM voltage) was maintained at 1000 V, and the solvent delay of 5.0 min was employed.

A Glas-Col Multi Pulse Votexer (Glas-Col, Terre Haute, USA) and the Hanil Refrigerated Centrifuge (Hanil Science Industrial, Incheon, Korea) was used for the sample preparation.

An Ecospin 3180C (Biotron, Daejeon, Korea) vacuum concentrator was used to concentrate the sample.

An IlShin DF (IlShin Lab Co, Daejeon, Korea) refrigerator was used to adjust the sample temperature.

2.3. Sample preparation

Korean cabbage and Korean radish samples. Real samples were taken from local markets and supermarkets in the central area of Korea.

Procedure. From the grinded and homogenized sample of cabbage and radish, a 10 g was weighted into a 50 ml Teflon centrifuge tube; mixture of six internal standards (Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Fluoranthene-d10, Chrysene-d12, Perylen-d12) was added and extracted with 10 mL of MeCN (HAc 0.5%) for 1 min with a vortex mixer. Then the sample tubes were kept in a refrigerator for 30 min. When the temperature of the mixed samples reached 4 °C, 4 g $MgSO_4$ and 1 g NaCl were added and then vortexed immediately for 1 min and then the extract was centrifuged for 5 min at 4000 rpm at 4 °C. Two milliliters of prepared aliquot was sampled from the upper layer into a 5 mL micro-centrifuge vial containing 50 mg primary secondary amine (PSA) and 300 mg $MgSO_4$ and again vortexed for 1 min and then centrifuged for 5 min at 4000 rpm at 4 °C. From the upper layer of the prepared sample, an aliquot of 1.2 mL was transferred into a 1.8 mL Eppendox vial and put into a vacuum concentrator to dryness. Finally, 0.4 mL of MeCN containing 0.1 mg/L of triphenyl phosphate (TPP) was added to dissolve the residue and then 1 μL of this solution was injected onto the gas chromatography mass spectrometry system.

2.4. Recovery studies

Cabbage and radish with no pesticides detected previously were used for the fortification experiments. 10 g homogenized sample was spiked prior to the determination procedure by the addition of a mixture of standard pesticides solution to give 0.030, 0.090 and 0.180 mg/kg of each compound. Spiking samples were left to stand for 3 h to allow pesticide absorption onto the sample. They were then prepared according to the determination procedure described above.

2.5. Preparation of calibration standards

Calibration standards in a blank matrix of the cabbage and radish commodities being analyzed were prepared by adding respective spiking solution and internal standard solution to blank extract, to produce a final concentration of 0.030, 0.060, 0.090, 0.180 and 0.360 mg/kg and 0.100 mg/kg for internal standards. Calibration standards in solvent were prepared in the same manner, replacing blank extract with acetonitrile.

3. Results and discussion

3.1. Gas chromatographic determination

Analysis was performed in the SIM mode based on the use of one target and two qualifier ions. Pesticides were identified according to retention times, target and qualifier ions. The quantitation was based on the peak area ratio of the target ion divided by the internal standards. Table 1 summarizes some of the pesticides studied with their target and qualifier ions used in SIM mode to analyze pesticides in Korean cabbage and Korean radish.

Table 1
Quantitation and identification ions for the GC–MS analysis of selected pesticides

Name	Observed ion (*m*/*z*)	Name	Observed ion (*m*/*z*)
Aldrin	263 265 261	Fenobucarb	121 150 207
Alpha-endosulfan	241 195 237	Flucythrinate	199 157 451
BHC-alpha	219 181 183	Folpet	260 295 262
Bifenthrin	181 166 422	Heptachlor	272 100 337
Bromopropylate	341 183 343	Malathion	173 158 125
Captan	79 149 117	Permethrine	183 163 165
Chlorpyrifos	197 199 314	Pirimicarb	166 72 238
Diazinon	179 152 304	Procymidone	96 283 285
Dichlorobenil	171 173 136	Propanil	161 163 217
Dicofol	139 251 250	Sanmarton	167 419 125
Dimethoate	87 229 125	Simazine	201 186 173
Endrine	263 245 281	Tebuconazole	250 125 307
Ethion	231 384 153	Tetradifon	159 75 356

3.2. Quantitation

Calibration curves were constructed for each compound using five different concentration levels. Six internal standards were employed at the beginning of the sample preparation stage to help control the significant losses of the analytes during extraction Adding TPP at the last stage of sample preparation was to control the amount of sample injection in gas chromatography. According to their polarities and volatilities, 107 pesticides were divided into groups to increase the sensitivity of studied pesticides. For identification of pesticides, the retention time and three ions (one for quantitation and two for identification) with the assistance of the NIST's pesticides library were used.

3.3. Method validation

Linearity. Correlation coefficients were greater 0.99 from 0.030 mg/kg to 0.360 mg/kg for all pesticides.

Limit of quantitation. Limits of quantification (LOQs) of the proposed method were calculated by considering a value 10 times that of background noise. For most of the compounds, the LOQs are below their MRLs as shown in Table 2.

Recovery. Satisfactory recoveries (from 80% to 115%) with 52.1% of recovery data ranged from 90% to 105% and 47.9% data ranged from 80% to 90% and from 105% to 115% with RSDs <15% were obtained from two commodities spiked ($n = 5$) at 0.030, 0.090 and 0.180 mg/kg as shown by the data in Table 2.

3.4. Determination in real samples

53 Korean cabbage and 46 Korean radish samples from local markets and supermarkets in the central area of Korea were sampled and analyzed following the sample preparation

Table 2
Calibration data (equation, determination coefficient), MRLs and mean percent recovery ± RSD of 107 pesticides in radish and cabbage samples

Name	Equation	Determination coefficient	MRLs[a] (mg/kg)	LOQ	Recovery[b]					
					Radish (mg/kg)			Cabbage (mg/kg)		
					0.030	0.090	0.180	0.030	0.090	0.180
Alachlor	$y = 1.81 * 10^{-2} x - 1.74 * 10^{-2}$	0.9970	0.100	0.002	85 ± 8	90 ± 3	89 ± 5	84±5	92 ± 1	91 ± 6
Aldrin	$y = 1.30 * 10^{-3} x - 1.00 * 10^{-4}$	0.9997	0.010	0.004	87 ± 4	88 ± 6	87 ± 10	81 ± 13	86 ± 2	84 ± 8
Amitraz	$y = 2.60 * 10^{-3} x - 1.30 * 10^{-2}$	0.9878	0.200	0.01	82 ± 8	92 ± 13	96 ± 8	80 ± 8	85 ± 14	84 ± 8
Benalaxyl	$y = 5.15 * 10^{-2} x - 7.05 * 10^{-2}$	0.9932	0.010	0.002	92 ± 14	91 ± 6	97 ± 6	84 ± 7	91 ± 8	86 ± 4
BHC-alpha	$y = 2.22 * 10^{-2} x - 6.60 * 10^{-3}$	0.9998	0.100[c]	0.002	92 ± 15	90 ± 15	94 ± 12	88 ± 12	85 ± 11	99 ± 9
BHC-beta	$y = 1.84 * 10^{-2} x - 2.80 * 10^{-2}$	0.9955		0.002	82 ± 11	83 ± 12	99 ± 10	82 ± 15	91 ± 10	98 ± 9
BHC-delta	$y = 8.60 * 10^{-3} x - 6.10 * 10^{-3}$	0.9992		0.002	82 ± 9	85 ± 12	99 ± 11	82 ± 6	90 ± 10	102 ± 10
BHC-gamma	$y = 1.66 * 10^{-2} x - 2.23 * 10^{-2}$	0.9961		0.002	95 ± 11	88 ± 9	90 ± 7	90 ± 7	94 ± 6	90 ± 6
Bifenox	$y = 6.20 * 10^{-3} x - 3.42 * 10^{-2}$	0.9866	0.050	0.03	86 ± 6	94 ± 10	96 ± 7	98 ± 13	108 ± 6	87 ± 7
Bifenthrin	$y = 8.77 * 10^{-2} x - 9.55 * 10^{-2}$	0.9958	0.050	0.002	88 ± 9	91 ± 6	102 ± 6	86 ± 5	94 ± 6	93 ± 5
Bromacil	$y = 2.32 * 10^{-2} x - 3.77 * 10^{-2}$	0.9908	0.100	0.02	85 ± 3	95 ± 13	88 ± 9	88 ± 15	92 ± 6	82 ± 5
Bromopropylate	$y = 2.34 * 10^{-2} x - 2.84 * 10^{-2}$	0.9944	0.500	0.01	83 ± 4	89 ± 7	109 ± 6	86 ± 6	93 ± 6	99 ± 5
Buprofezin	$y = 2.18 * 10^{-2} x - 3.77 * 10^{-2}$	0.9904	0.100	0.002	83 ± 6	89 ± 2	101 ± 3	82 ± 9	92 ± 4	95 ± 3
Captan	$y = 2.24 * 10^{-2} x - 9.11 * 10^{-2}$	0.9869	2.000	0.03	87 ± 15	88 ± 11	88 ± 5	81 ± 14	80 ± 9	85 ± 6
Chinomethionat	$y = 1.77 * 10^{-2} x - 1.55 * 10^{-2}$	0.9969	0.050	0.01	90 ± 10	83 ± 9	91 ± 4	90 ± 8	93 ± 10	81 ± 4
Chlofennapyl	$y = 9.70 * 10^{-3} x - 6.10 * 10^{-3}$	0.9982	0.050	0.002	85 ± 8	89 ± 2	101 ± 5	85 ± 6	93 ± 4	95 ± 4
Chlofentezine	$y = 2.50 * 10^{-3} x + 1.20 * 10^{-3}$	0.9975	0.020	0.002	91 ± 9	92 ± 9	82 ± 9	84 ± 5	101 ± 10	94 ± 8
Chlorfenvinphos	$y = 8.60 * 10^{-3} x - 1.31 * 10^{-2}$	0.9909	0.020	0.01	89 ± 8	91 ± 3	86 ± 4	93 ± 4	92 ± 6	82 ± 3
Chlorobenzilate	$y = 3.84 * 10^{-2} x - 1.45 * 10^{-2}$	0.9977	0.200	0.002	80 ± 6	87 ± 3	92 ± 4	82 ± 7	94 ± 3	87 ± 4
Chlorpropham	$y = 5.78 * 10^{-2} x - 4.30 * 10^{-2}$	0.9985	0.050	0.008	88 ± 3	89 ± 10	87 ± 6	93 ± 3	97 ± 11	90 ± 7
Chlorpyrifos	$y = 2.10 * 10^{-3} x - 2.40 * 10^{-3}$	0.9957	0.010	0.003	82 ± 8	87 ± 3	90 ± 6	82 ± 6	89 ± 1	92 ± 4
Chlorpyrifos-methyl	$y = 2.89 * 10^{-2} x - 3.54 * 10^{-2}$	0.9938	0.100	0.002	83 ± 8	90 ± 5	89 ± 15	80 ± 4	95 ± 3	88 ± 15
Cyfluthrine 1	$y = 2.00 * 10^{-4} x - 7.00 * 10^{-4}$	0.9902	0.010	0.008	88 ± 13	91 ± 8	96 ± 3	95 ± 10	94 ± 8	84 ± 5
Cyfluthrine 2	$y = 3.00 * 10^{-4} x - 1.00 * 10^{-4}$	0.9869		0.008	85 ± 10	89 ± 11	99 ± 5	98 ± 10	93 ± 7	94 ± 6
Cyfluthrine 3	$y = 2.00 * 10^{-4} x - 8.00 * 10^{-4}$	0.9871		0.008	88 ± 11	89 ± 13	107 ± 5	102 ± 10	96 ± 7	97 ± 6
Cyfluthrine 4	$y = 2.00 * 10^{-4} x - 5.00 * 10^{-4}$	0.9904		0.008	85 ± 9	89 ± 9	108 ± 5	102 ± 8	95 ± 6	99 ± 6
Cypermethrin 1	$y = 1.10 * 10^{-3} x - 4.60 * 10^{-3}$	0.9895	0.050	0.02	87 ± 11	90 ± 7	96 ± 3	95 ± 9	95 ± 6	87 ± 6
Cypermethrin 2	$y = 6.00 * 10^{-3} x - 2.40 * 10^{-3}$	0.9902		0.02	84 ± 10	89 ± 7	104 ± 4	90 ± 5	93 ± 6	84 ± 6
Cypermethrin 3	$y = 2.00 * 10^{-3} x - 8.00 * 10^{-3}$	0.9858		0.02	84 ± 9	87 ± 10	105 ± 5	84 ± 8	95 ± 5	84 ± 5
Cypermethrin 4	$y = 1.00 * 10^{-4} x - 2.00 * 10^{-4}$	0.9900		0.02	84 ± 7	87 ± 9	98 ± 5	87 ± 13	93 ± 5	82 ± 6
Cyprodinil	$y = 2.50 * 10^{-2} x - 8.00 * 10^{-2}$	0.9872	0.100	0.02	89 ± 1	91 ± 5	100 ± 4	82 ± 5	91 ± 3	98 ± 3
Deltamethrin	$y = 2.13 * 10^{-2} x - 1.26 * 10^{-2}$	0.9897	0.010	0.05	88 ± 10	80 ± 14	94 ± 14	86 ± 13	85 ± 6	99 ± 11
Diazinon	$y = 4.23 * 10^{-2} x - 6.49 * 10^{-2}$	0.9958	0.020	0.004	80 ± 13	84 ± 8	80 ± 5	81 ± 6	83 ± 15	81 ± 6
Dichlorobenil	$y = 6.60 * 10^{-2} x - 2.84 * 10^{-2}$	0.9995	0.150	0.002	90 ± 10	90 ± 7	101 ± 4	88 ± 3	100 ± 4	108±7
Dichlovos	$y = 9.13 * 10^{-2} x + 4.84 * 10^{-2}$	0.9901	0.020	0.002	86 ± 4	81 ± 11	100 ± 4	98 ± 3	93 ± 8	111 ± 5
Dicofol	$y = 4.60 * 10^{-2} x - 6.69 * 10^{-2}$	0.9925	0.100	0.004	84 ± 4	87 ± 4	96 ± 2	92 ± 7	94 ± 3	99 ± 4
Dieldrin	$y = 5.00 * 10^{-4} x + 5.00 * 10^{-4}$	0.9913	0.010	0.002	91 ± 9	81 ± 9	88 ± 8	82 ± 14	88 ± 3	95 ± 8
Difenconazole	$y = 2.09 * 10^{-2} x - 2.75 * 10^{-2}$	0.9904	0.050	0.04	80 ± 10	85 ± 14	101 ± 7	80 ± 8	92 ± 12	81 ± 15
Dimethoate	$y = 5.77 * 10^{-2} x - 1.46 * 10^{-2}$	0.9873	0.050	0.01	80 ± 8	93 ± 8	93 ± 8	110 ± 6	105 ± 5	102 ± 3
Diphenylamine	$y = 2.57 * 10^{-2} x - 1.21 * 10^{-2}$	0.9995	0.010	0.01	84 ± 7	88 ± 11	93 ± 3	85 ± 5	98 ± 12	97 ± 6
Disulfoton	$y = 9.60 * 10^{-3} x - 1.41 * 10^{-2}$	0.9962	0.010	0.002	87 ± 15	84 ± 9	84 ± 6	101 ± 4	87 ± 12	86 ± 5
Edifenphos	$y = 3.35 * 10^{-2} x - 9.45 * 10^{-2}$	0.9860	0.200	0.004	93 ± 14	87 ± 11	100 ± 6	93 ± 10	97 ± 4	96 ± 5
Endosulfan-alpha	$y = 1.60 * 10^{-3} x + 9.00 * 10^{-4}$	0.9961	0.100	0.02	87 ± 6	86 ± 8	90 ± 6	86 ± 11	89 ± 1	91 ± 5
Endosulfan-beta	$y = 6.00 * 10^{-4} x + 1.00 * 10^{-4}$	0.9981		0.02	87 ± 5	88 ± 4	101 ± 4	83 ± 8	89 ± 5	99 ± 4

Endrine	$y = 5.00 * 10^{-4}\ x - 9.00 * 10^{-4}$	0.9903	0.010	0.004	86 ± 7	84 ± 5	96 ± 6	88 ± 10	89 ± 2	92 ± 6
EPN	$y = 1.68 * 10^{-2}\ x - 6.95 * 10^{-2}$	0.9871	0.050	0.01	88 ± 11	93 ± 12	95 ± 7	104 ± 11	100 ± 6	85 ± 7
Ethion	$y = 2.98 * 10^{-2}\ x - 9.34 * 10^{-2}$	0.9858	0.100	0.004	80 ± 6	92 ± 3	103 ± 5	87 ± 4	92 ± 7	91 ± 4
Ethoprophos	$y = 3.90 * 10^{-2}\ x - 3.24 * 10^{-2}$	0.9982	0.005	0.004	86 ± 3	90 ± 8	87 ± 8	88 ± 4	98 ± 9	89 ± 8
Fenarimol	$y = 12.67 * 10^{-1}\ x - 2.06 * 10^{-1}$	0.9908	0.100	0.004	87 ± 14	92 ± 8	104 ± 5	81 ± 3	94 ± 8	94 ± 5
Fenitrothion	$y = 1.48 * 10^{-2}\ x - 5.14 * 10^{-2}$	0.9893	0.050	0.01	81 ± 7	90 ± 7	86 ± 5	89 ± 8	99 ± 4	90 ± 3
Fenobucarb-1	$y = 20.53 * 10^{-1}\ x - 9.74 * 10^{-2}$	0.9994	0.500	0.002	80 ± 6	88 ± 14	90 ± 7	81 ± 8	115 ± 8	101 ± 12
Fenobucarb-2	$y = 2.47 * 10^{-2}\ x - 3.64 * 10^{-2}$	0.9924		0.002	86 ± 2	90 ± 8	102 ± 6	84 ± 3	95 ± 5	105 ± 15
Fenpropathrin	$y = 7.00 * 10^{-3}\ x - 9.40 * 10^{-3}$	0.9923	0.010	0.004	88 ± 9	93 ± 7	98 ± 6	115 ± 12	114 ± 4	102 ± 5
Fensulfothion	$y = 5.01 * 10^{-2}\ x - 5.47 * 10^{-2}$	0.9960	0.020	0.01	80 ± 5	93 ± 10	94 ± 7	105 ± 13	97 ± 8	84 ± 6
Fenthion	$y = 2.55 * 10^{-2}\ x - 5.89 * 10^{-2}$	0.9915	0.050	0.002	84 ± 10	90 ± 4	90 ± 5	85 ± 4	91 ± 2	92 ± 3
Flucythrinate	$y = 7.00 * 10^{-4}\ x - 3.70 * 10^{-3}$	0.9910	0.050	0.02	80 ± 5	90 ± 4	88 ± 1	98 ± 5	95 ± 5	88 ± 7
Fludioxonil	$y = 2.01 * 10^{-2}\ x - 3.40 * 10^{-3}$	0.9913	0.100	0.02	87 ± 5	90 ± 5	107 ± 6	93 ± 6	92 ± 6	94 ± 5
Flufenoxuron	$y = 8.10 * 10^{-3}\ x + 5.00 * 10^{-3}$	0.9901	0.050	0.004	90 ± 15	92 ± 11	102 ± 13	80 ± 13	85 ± 8	92 ± 6
Flusilazole	$y = 8.10 * 10^{-3}\ x - 2.40 * 10^{-3}$	0.9934	0.010	0.002	86 ± 7	92 ± 7	100 ± 6	80 ± 4	92 ± 9	88 ± 4
Fluvalinate 1	$y = 3.20 * 10^{-3}\ x - 1.93 * 10^{-2}$	0.9885	0.010	0.02	87 ± 13	82 ± 13	97 ± 11	94 ± 6	96 ± 5	91 ± 9
Fluvalinate 2	$y = 2.60 * 10^{-3}\ x - 1.70 * 10^{-3}$	0.9901		0.02	81 ± 14	81 ± 14	99 ± 12	90 ± 10	96 ± 5	93 ± 9
Folpet	$y = 6.60 * 10^{-3}\ x - 2.18 * 10^{-2}$	0.9860	0.500	0.1	82 ± 12	86 ± 7	85 ± 8	83 ± 14	81 ± 9	97 ± 15
Heptachlor	$y = 8.00 * 10^{-4}\ x + 6.00 * 10^{-4}$	0.9984	0.010	0.002	91 ± 6	80 ± 9	95 ± 11	84 ± 5	83 ± 4	88 ± 9
Hexaconazole	$y = 3.67 * 10^{-2}\ x - 8.77 * 10^{-2}$	0.9899	0.050	0.002	88 ± 4	92 ± 4	97 ± 5	84 ± 2	90 ± 9	86 ± 3
Imazalil	$y = 10.86 * 10^{-1}\ x - 1.44 * 10^{-1}$	0.9934	0.050	0.01	87 ± 4	91 ± 4	102 ± 6	80 ± 6	88 ± 9	90 ± 4
Iprobenfos	$y = 5.94 * 10^{-2}\ x - 1.08 * 10^{-2}$	0.9952	0.200	0.004	92 ± 3	92 ± 7	93 ± 7	95 ± 10	92 ± 3	96 ± 4
Iprodione	$y = 1.90 * 10^{-2}\ x - 3.16 * 10^{-2}$	0.9901	0.100	0.015	90 ± 15	91 ± 8	106 ± 6	91 ± 9	93 ± 8	97 ± 5
Isoprothiolane	$y = 3.27 * 10^{-2}\ x - 3.15 * 10^{-2}$	0.9966	0.050	0.01	87 ± 6	91 ± 4	100 ± 4	86 ± 3	93 ± 6	93 ± 3
Malathion	$y = 2.95 * 10^{-2}\ x - 3.71 * 10^{-2}$	0.9923	0.300	0.01	82 ± 12	90 ± 6	88 ± 5	88 ± 6	91 ± 2	88 ± 3
Metalaxyl	$y = 1.46 * 10^{-2}\ x - 1.52 * 10^{-2}$	0.9963	0.050	0.002	89 ± 1	92 ± 8	98 ± 6	82 ± 8	92 ± 3	102 ± 4
Methidathion	$y = 2.74 * 10^{-1}\ x - 3.16 * 10^{-1}$	0.9954	0.200	0.004	81 ± 9	88 ± 2	95 ± 3	89 ± 7	95 ± 2	95 ± 4
Methoxychlor	$y = 2.20 * 10^{-2}\ x - 2.90 * 10^{-2}$	0.9955	1.000	0.02	92 ± 10	95 ± 12	108 ± 7	93 ± 10	93 ± 12	94 ± 6
Metribuzin	$y = 2.14 * 10^{-2}\ x - 6.01 * 10^{-2}$	0.9906	0.500	0.004	85 ± 6	90 ± 5	93 ± 6	83 ± 5	91 ± 1	96 ± 4
Mevinphos	$y = 1.16 * 10^{-1}\ x - 9.71 * 10^{-2}$	0.9989	0.050	0.01	88 ± 2	91 ± 7	91 ± 2	96 ± 5	101 ± 6	96 ± 3
Myclobutanil	$y = 2.41 * 10^{-2}\ x - 6.16 * 10^{-2}$	0.9889	0.100	0.002	83 ± 12	87 ± 12	104 ± 6	86 ± 7	89 ± 11	93 ± 5
Napropamide	$y = 2.12 * 10^{-2}\ x - 1.76 * 10^{-2}$	0.9904	0.100	0.015	94 ± 7	91 ± 2	93 ± 5	94 ± 4	93 ± 5	88 ± 4
op-DDD	$y = 6.40 * 10^{-2}\ x - 1.00 * 10^{-2}$	0.9972	0.100[d]	0.002	84 ± 3	88 ± 5	97 ± 3	88 ± 7	93 ± 2	96 ± 4
op-DDT	$y = 9.60 * 10^{-3}\ x - 8.70 * 10^{-3}$	0.9915		0.002	87 ± 5	88 ± 3	88 ± 3	87 ± 8	91 ± 4	83 ± 3
Oxadiazone	$y = 1.75 * 10^{-2}\ x + 1.50 * 10^{-3}$	0.9982	0.050	0.002	83 ± 5	92 ± 1	99 ± 3	81 ± 10	98 ± 2	94 ± 3
Oxyfluorfen	$y = 7.70 * 10^{-3}\ x - 3.49 * 10^{-2}$	0.9873	0.050	0.01	85 ± 2	91 ± 7	104 ± 6	106 ± 6	99 ± 4	93 ± 6
Pachlobutrazol	$y = 2.61 * 10^{-2}\ x - 1.99 * 10^{-2}$	0.9949	0.050	0.002	101 ± 12	93 ± 5	94 ± 5	95 ± 13	97±8	88 ± 6
Parathion	$y = 9.90 * 10^{-3}\ x - 4.05 * 10^{-2}$	0.9901	0.300	0.01	82 ± 8	87 ± 10	97 ± 5	107 ± 10	100 ± 5	100 ± 2
Penconazole	$y = 3.48 * 10^{-2}\ x - 1.03 * 10^{-2}$	0.9870	0.100	0.002	89 ± 2	95 ± 12	89 ± 8	82 ± 14	90±8	84 ± 4
Pendimethalin	$y = 1.84 * 10^{-2}\ x - 7.60 * 10^{-3}$	0.9908	0.050	0.004	84 ± 7	90 ± 7	91 ± 5	99 ± 7	96 ± 3	90±3
Penthoate	$y = 2.31 * 10^{-2}\ x - 3.05 * 10^{-2}$	0.9942	0.050	0.004	80 ± 11	87 ± 4	101 ± 4	86 ± 10	95 ± 2	102 ± 2
Permethrine	$y = 5.32 * 10^{-2}\ x - 8.61 * 10^{-2}$	0.9916	0.100	0.004	88 ± 11	92 ± 8	107 ± 5	99 ± 8	98 ± 5	99 ± 5
Phorate	$y = 1.24 * 10^{-1}\ x - 1.51 * 10^{-2}$	0.9974	0.050	0.002	82 ± 7	89 ± 10	88 ± 8	92 ± 4	96±7	87 ± 3
Phosalone	$y = 2.09 * 10^{-2}\ x - 8.39 * 10^{-2}$	0.9894	0.050	0.01	88 ± 12	93 ± 9	97 ± 5	96 ± 11	94 ± 9	88 ± 5
Phosmet	$y = 5.79 * 10^{-2}\ x - 2.26 * 10^{-2}$	0.9864	0.020	0.015	88 ± 8	89 ± 11	90 ± 5	112 ± 8	91 ± 10	86 ± 5
Pirimicarb	$y = 3.80 * 10^{-2}\ x - 5.49 * 10^{-2}$	0.9963	0.050	0.002	91 ± 4	89 ± 3	89 ± 3	82±4	89 ± 2	90 ± 3
Pirimiphosethyl	$y = 8.00 * 10^{-3}\ x - 1.00 * 10^{-3}$	0.9917	0.020	0.002	83 ± 8	92 ± 4	91 ± 4	86 ± 7	91 ± 3	92±3
Pirimiphos-methyl	$y = 2.38 * 10^{-2}\ x - 4.10 * 10^{-2}$	0.9905	0.050	0.002	82 ± 10	90 ± 3	87 ± 6	84 ± 4	90 ± 2	90 ± 5

(*continued on next page*)

Table 2 (*continued*)

Name	Equation	Determination coefficient	MRLs[a] (mg/kg)	LOQ	Recovery[b]					
					Radish (mg/kg)			Cabbage (mg/kg)		
					0.030	0.090	0.180	0.030	0.090	0.180
pp-DDD	$y = 4.17 * 10^{-2}\ x - 2.02 * 10^{-2}$	0.9970	0.100[d]	0.002	82 ± 10	91 ± 2	94 ± 4	84 ± 8	94 ± 5	88 ± 3
pp-DDE	$y = 1.94 * 10^{-2}\ x + 1.28 * 10^{-2}$	0.9940		0.002	83 ± 6	83 ± 7	84±5	83 ± 12	91 ± 2	85 ± 3
pp-DDT	$y = 3.04 * 10^{-2}\ x - 4.38 * 10^{-2}$	0.9911		0.002	88 ± 3	91 ± 3	95±6	93 ± 6	92 ± 7	86 ± 6
Procymidone	$y = 3.85 * 10^{-2}\ x + 1.76 * 10^{-2}$	0.9965	0.200	0.002	83 ± 8	86 ± 4	92±3	81 ± 11	92 ± 2	93 ± 3
Profenofos	$y = 1.03 * 10^{-2}\ x - 1.06 * 10^{-2}$	0.9928	0.050	0.01	89 ± 5	91 ± 3	95 ± 4	98 ± 6	93 ± 6	92 ± 2
Propanil	$y = 2.94 * 10^{-2}\ x - 2.78 * 10^{-2}$	0.9961	0.200	0.02	86 ± 15	89 ± 5	98 ± 5	80 ± 6	88 ± 3	96 ± 4
Propargite	$y = 2.57 * 10^{-2}\ x - 7.44 * 10^{-2}$	0.9883	0.100	0.005	87 ± 9	91 ± 6	102 ± 7	92 ± 6	96 ± 5	92 ± 4
Pyrazophos	$y = 1.94 * 10^{-2}\ x - 2.69 * 10^{-2}$	0.9922	0.050	0.02	83 ± 6	92 ± 8	99 ± 4	91 ± 6	92 ± 9	88 ± 5
Pyridaben	$y = 6.66 * 10^{-2}\ x - 2.81 * 10^{-2}$	0.9878	0.050	0.002	88 ± 12	92 ± 7	104 ± 4	91 ± 8	93 ± 8	92±5
Quintozene	$y = 3.80 * 10^{-3}\ x - 2.90 * 10^{-3}$	0.9961	0.010	0.01	90 ± 14	83±12	101 ± 8	95 ± 5	92 ± 12	92 ± 12
Sanmarton 1	$y = 2.90 * 10^{-2}\ x - 1.27 * 10^{-2}$	0.9863	0.050	0.03	82 ± 5	89 ± 5	98 ± 3	106 ± 8	95 ± 5	90 ± 6
Sanmarton 2	$y = 5.62 * 10^{-2}\ x - 2.71 * 10^{-2}$	0.9904		0.03	82 ± 5	86 ± 12	105 ± 5	106 ± 8	91 ± 7	94±8
Simazine	$y = 3.38 * 10^{-2}\ x - 5.25 * 10^{-2}$	0.9955	0.100	0.01	82 ± 6	90 ± 7	96 ± 6	80 ± 5	97 ± 6	100 ± 7
Tebuconazole	$y = 1.26 * 10^{-2}\ x - 5.02 * 10^{-2}$	0.9850	0.050	0.004	85 ± 9	91 ± 8	108 ± 6	91 ± 7	92 ± 8	97 ± 5
Terbufos	$y = 6.91 * 10^{-2}\ x - 1.18 * 10^{-2}$	0.9967	0.050	0.004	82 ± 7	89 ± 9	88 ± 6	85 ± 4	94 ± 7	88 ± 5
Tetradifon	$y = 1.65 * 10^{-2}\ x - 2.10 * 10^{-3}$	0.9988	1.000	0.002	87 ± 7	91 ± 7	107 ± 6	87 ± 6	94 ± 6	97 ± 5
Thiobencarb	$y = 8.30 * 10^{-2}\ x - 7.16 * 10^{-2}$	0.9976	0.050	0.002	84 ± 8	89 ± 3	89 ± 4	82 ± 4	89 ± 2	90 ± 4
Tolclofos-methyl	$y = 6.11 * 10^{-2}\ x - 4.55 * 10^{-2}$	0.9981	0.050	0.002	84 ± 8	89 ± 3	80 ± 7	84 ± 5	91 ± 1	84 ± 3
Tralomethrine	$y = 2.56 * 10^{-2}\ x - 1.05 * 10^{-2}$	0.9981	0.050	0.02	82 ± 6	88 ± 3	92 ± 3	85 ± 7	95 ± 3	87 ± 5
Triadimefon	$y = 1.54 * 10^{-2}\ x - 3.67 * 10^{-2}$	0.9884	0.100	0.002	91 ± 10	91 ± 7	90 ± 3	85 ± 10	91 ± 3	88 ± 4
Triadimenol	$y = 3.30 * 10^{-3}\ x - 5.50 * 10^{-3}$	0.9896	0.050	0.002	87 ± 7	92 ± 5	107 ± 6	81 ± 10	92 ± 8	97 ± 4
Triazophos	$y = 1.67 * 10^{-2}\ x - 5.98 * 10^{-2}$	0.9870	0.020	0.01	85 ± 7	92 ± 8	95 ± 4	93 ± 11	93 ± 8	91 ± 5
Triflumizole	$y = 3.30 * 10^{-2}\ x - 1.77 * 10^{-2}$	0.9855	1.000	0.004	88 ± 7	94 ± 7	107 ± 3	84 ± 8	89 ± 13	94 ± 3
Trifluralin	$y = 1.20 * 10^{-3}\ x - 6.40 * 10^{-3}$	0.9904	0.050	0.01	83 ± 5	89 ± 10	95 ± 10	114 ± 4	91 ± 6	106 ± 5
Vinclozoline	$y = 4.50 * 10^{-3}\ x - 4.30 * 10^{-3}$	0.9971	0.050	0.004	84 ± 8	89 ± 3	86 ± 5	89 ± 4	93 ± 2	91 ± 6

[a] MRLs in Korea for vegetables.
[b] Mean percent recovery ± RSD of pesticides in radish and cabbage samples at 0.030, 0.090 and 0.180 mg/kg fortification levels ($n = 5$).
[c] Total BHC (alpha, beta, gamma and delta).
[d] Total DDD (op, pp′), DDT (op, pp′) and pp′ DDE.

Table 3
Pesticide residues in Korean cabbage samples and their concentrations

Sample ID	Pesticides found	Concentration (mg/kg)	Class
G-18	Procymidone	0.185	Fungicide
	Sanmarton	0.064	Pyrethroid
HA-06	Metalaxyl	0.010	Fungicide
HE-05	Alpha-endosulfan	0.047	OCPs
HE-18	Procymidone	0.010	Fungicide
LO-01	Procymidone	0.083	Fungicide
	Bifenthrin	0.081	Pyrethroid
	Fenpropathrin	0.009	Pyrethroid
LO-05	Diazinon	0.420	OPPs
LO-18	Procymidone	2.02	Fungicide
P-07001	pp′-DDE	0.002	OCPs

OCP, organochlorine pesticides; OPP, organophosphorus pesticides.

method described above. The residue was detected in 8.1% of the total samples (8 from 99 samples). The residues were found in 8 Korean cabbage but Korean radish samples. Pesticide levels encountered in the analyzed samples are shown in Table 3. Procymidone was detected in 4 samples at concentrations ranging from 0.010 to 2.02 mg/kg. Alpha-endosulfan, Bifenthrin, Diazinon, Fenpropathrin, Metalaxyl, pp′-DDE and Sanmarton were detected in one sample each. The most common pesticide residue found was procymidone. Procymidone was detected in 4% of analyzed samples. These findings indicate that procymidone is one of the most used pesticides in Korean cabbage's cultivation.

The diversity of classes of pesticide residues such as organochlorine (Alpha-endosulfan, pp′-DDE), organophosphorus (Diazinon), fungicide (Metalaxyl, Procymidone) and pyrethroid (Bifenthrin, Fenpropathrin, Sanmarton) detected in this study show that the proposed method, to determine residues of pesticides in various classes of pesticides is rapid, simple, sensitive and uses smaller amount of organic solvents, reducing the risk for workers and the environment.

4. Conclusions

A simple and rapid method was developed to determine residues of 107 pesticides in Korean cabbage and Korean radish, the two main materials for making Kimchi. This method using QuEChERS sample preparation and GC–MS-SIM analysis showed a high sensitivity and confirmatory power necessary for the determination of pesticide residues at the levels required in Korea's MRL for Kimchi materials. The proposed method not only allowed the simultaneous determination and confirmation of very large number of pesticides with good recoveries and low detection limits but also showed useful in routine analysis due to its fast and easy to carry out.

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