

A Multiresidue Method for the Determination of 118 Pesticides in Vegetable Juice by Gas Chromatography–Mass Spectrometry and Liquid Chromatography–Tandem Mass Spectrometry

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An analytical method has been developed for measuring 118 pesticides in vegetable juice. The extraction of pesticides was carried out based on dispersive solid-phase extraction, and determination was performed using gas chromatography with mass spectrometric detection (GC-MS-SIM) and liquid chromatography electrospray ionization tandem mass spectrometry (LC/ESI-MS/MS). Pesticides were confirmed by their retention time and their quantification and identification ions by GC-MS-SIM or multiple reaction monitoring of two fragment ions by LC/ESI-MS/MS, respectively. Spiking experiments from 10 to 120 $\mu\text{g}/\text{kg}$ were carried out to determine the recovery, precision, and limit of quantification (LOQ) of the method. The overall recoveries of all pesticides were between 77 and 114% with relative standard deviations lower than 14%. The LOQ for most compounds was below 5 $\mu\text{g}/\text{kg}$. The proposed method was applied successfully for the residue determination of the 118 pesticides in commercial vegetable juice samples.

KEYWORDS: QuEChERS; vegetable juice; pesticide residues; GC-MS-SIM; LC/ESI-MS/MS

INTRODUCTION

Vegetable juice is praised for its dietary benefits all over the world. The vegetable juice market in South Korea in particular and in the world in general has been boosted by growing consumer incomes, increased health consciousness, and changes in taste.

Pesticide residues represent one of the most important factors of chemical contamination in vegetable juice, as the vegetable juices are obtained from raw vegetables by juicing. Pesticide residues in vegetables are expected to enter vegetable juices during the juicing process. Therefore, rapid and reliable controls are a must to ensure that the residual levels in vegetable juices are under safety levels because maximum residue limits (MRLs) of vegetable juice have not been set up by the Korea Food and Drug Administration and a guide for the authorities to make their decision regarding MRLs for vegetable juice is required in the forthcoming future.

The determination of pesticide residues is generally performed by gas chromatography using specific detectors such as electron capture (ECD) (1), nitrogen phosphorus (2), flame photometric (3), and mass selective detection (4), as well as by liquid chromatography diode array detection (5) and liquid chromatography mass spectrometry (LC-MS) (6). The current and traditional sample preparation method for determining pesticides in food samples such as solid-phase extraction (4–7), gel permeation

chromatography (8), supercritical fluid extraction (9), and fluidized bed extraction (10) seems to be complicated, both time and solvent consuming. For this reason, a new method in sample preparation and measurement should be taken into consideration. Various methods have been developed for the analysis of pesticide residues in fruits and vegetables (2, 4–8, 11, 15), but to the best of our knowledge, no publication has documented a method of analysis of pesticide residues in vegetable juice using gas chromatography with mass spectrometric detection (GC-MS-SIM) and liquid chromatography electrospray ionization tandem mass spectrometry (LC/ESI-MS/MS).

The objective of this work was the development and validation of a multiresidue method for the determination of 118 pesticides commonly used in vegetable grooves in Korea. The QuEChERS method (12–15) was selected as the most suitable method for routine analysis of pesticide traces in vegetable juice with the advantages of low cost, easy implementation, and nonspecific instrumentation demands. The developed method was applied to the analysis of pesticide residues in vegetable juice samples.

MATERIALS AND METHODS

Materials and Standards. Pesticide analytical standards were purchased from Wako (Osaka, Japan), Chemservice (West Chester, PA), and Dr. Ehrenstorfer (Augsburg, Germany). The purity of the standard pesticides was from 97.4 to 99%. Internal standards [naphthalene-*d*₈, acenaphthene-*d*₁₀, phenanthrene-*d*₁₀, fluoranthene-*d*₁₀, and triphenyl phosphate (TPP)] were purchased from C/D/N Isotopes Inc. (Quebec, Canada) and Chemservice. Glacial acetic acid and acetonitrile of pesticide analytical grade were obtained from J. T. Baker (Philipsburg, NJ).

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Methanol (HPLC grade) was purchased from Aldrich (WI). Formic acid (HPLC grade) was purchased from Merck (Darmstadt, Germany). The purified water was 18 M Ω (Ultrapure water, Sinhan Science Tech, Daejeon, Korea). Anhydrous MgSO₄ and NaCl were purchased from Wako. Primary secondary amine (PSA) sorbent was purchased from Varian (Varian, Harbor City, CA). Graphite carbon black (GCB) was purchased from Supelco (Bellefonte, PA).

Individual pesticide stock solution (2.00 mg/mL) was prepared in acetonitrile or methanol and stored in -20 °C. Working standard solutions of a mixture of pesticides and internal standard solution were prepared in acetonitrile or methanol.

Apparatus. Sample Preparation Equipments. A Glas-Col Multi Pulse Votexer (Glas-Col, Terre Haute, IN) and the Hanil Refrigerated Centrifuge (Hanil Science Industrial, Incheon, Korea) were used for the sample preparation. An Ecospin 3180C (Biotron, Daejeon, Korea) vacuum concentrator was used for concentration works.

GC-MS Analysis. GC-MS analyses were run on a Shimadzu 2010 (Shimadzu, Kyoto, Japan) gas chromatograph equipped with a split-splitless autoinjector model AOC-20i, an autosampler model AOC-20s, and a MS-QP 2010 (Shimadzu) series mass selective detector. Analytes were separated in a fused silica capillary column (J&W DB5 MS), with 5% phenyl polysiloxane as the nonpolar stationary phase (30 m \times 0.25 mm i. d.) and 0.25 μ m film thickness, supplied by Agilent (Palo Alto, CA). The helium carrier gas flow was maintained at 1.7 mL/min. The oven temperature program was 1.0 min at 50 °C, 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 (keeping 300 °C for 5 min). The temperature of the injection port was 250 °C, and a 1 μ L volume was injected in splitless mode.

Mass spectrometric parameters were as follows: Electron impact mass spectra were obtained at 70 eV of electron energy, the ion source temperature was 200 °C, and the MS transfer temperature was 280 °C. The scan mode was performed from *m/z* 50 to 650 at 0.5 s per scan. The solvent delay time was 5.0 min.

GC-ECD Analysis. GC-ECD analyses were run on a Shimadzu GC 2010 (Shimadzu) gas chromatograph coupled with ECD systems operated at 300 °C and J&W DB5 MS capillary column of the same dimension as described above. The injector was operated in the splitless mode (220 °C, 60 s, and 1 μ L). The carrier gas and makeup gases were helium and nitrogen, respectively. The oven temperature program was as follows: 50 °C, hold for 1 min; 5 °C/min to 190 °C; 3 °C/min to 290 °C; and hold 10 min.

LC/ESI-MS/MS Analysis. LC/ESI-MS/MS used was an Agilent 1200 series, equipped with a binary pump, autosampler, and an Agilent 6410 triple Quad MS/MS. Chromatographic separations were performed using a Zorbax eclipse XDB C18 column (5 cm \times 4.6 mm i.d., 1.8 μ m particle size) purchased from Agilent. The mobile phase flow rate was set at 0.8 mL/min. The injection volume was 5 μ L for all standards and samples. Mobile phases A and B were water with 0.1% formic acid and methanol, respectively. A gradient elution was made using a binary gradient of LC as follows: isocratic conditions for 1.5 min at 20% B, then linear gradient from 20 to 90% of solvent B, from 1.5 to 10 min, and maintained 90% solvent B from 10 to 12 min.

The detection was achieved using an Agilent 6410 triple Quad MS/MS system operating in the positive ionization mode. The capillary voltage and nebulizer pressure were 4.0 kV and 10 psi, respectively. The desolvation gas flow (N₂) and temperature were set at 10 L/min and 350 °C, respectively.

Sample Preparation. Sampling. Vegetable juice samples were received from vegetable juice manufacturers located in South Korea. Vegetable juice samples were randomly collected from the manufacturers' batch and were analyzed on the day of sampling. The characteristics of vegetable juice samples are presented in **Table 1**. The 68 vegetable juice samples were continuously analyzed in a period of 34 days.

Extraction Procedure. Ten grams of vegetable juice was put into a 50 mL Teflon centrifuge tube; a mixture of internal standards and 10 mL of acetonitrile (acetic acid 0.5%) was added, and the sample was shaken vigorously for 1 min using a vortex mixer; the sample tube was then put into a refrigerator for 30 min; 4 g of MgSO₄ and 1 g of NaCl were added and vortexed immediately for 1 min; the extract was centrifuged for 5 min at 4000 rpm in 4 °C; a 2 mL aliquot of the upper layer was transferred into a 5 mL microcentrifuge vial containing 50 mg of PSA, 300 mg of MgSO₄,

Table 1. Composition of Vegetable Juice Samples

| sample A | % | sample B | % |
|---|----|---------------|----|
| carrot | 52 | carrot | 23 |
| celery | 1 | kale | 45 |
| lettuce | 2 | keiskei koidz | 17 |
| spinach | 1 | wild parsley | 15 |
| tomato | 42 | | |
| broccoli, cabbage, cauliflower, cucumber, | 2 | | |
| dropwort, green bell pepper, kale, | | | |
| leaf beet, pumpkin, red bell pepper, wild parsley | | | |

and 30 mg of GCB and then vortexed for 1 min, and the extracts were centrifuged for 5 min at 4000 rpm in 4 °C.

For LC/ESI-MS/MS analysis, a 0.1 mL amount of the upper layer was transferred directly to an autosampler vial for LC/ESI-MS/MS analysis. For GC-MS-SIM analysis, a 1.2 mL amount of the upper layer was transferred into an 1.8 mL Eppendox vial and put into a vacuum concentrator to concentrate to dryness; 0.4 mL of acetonitrile that contained 0.1 mg/L of TPP was added to dissolve the residue and then transferred to an autosampler vial for GC-MS analysis.

Recovery Study. For recovery studies, 10 g of vegetable juice with no pesticides detected previously was spiked by the addition of a mixture of standard pesticides solution to give 10, 40, and 120 μ g/kg (except for bifenox, captan, chlorothalonil, deltamethrin, and sanmarton, the spiked concentrations were 20, 80, and 240 μ g/kg). They were then prepared according to the extraction procedure described above.

Matrix-Matched Calibration. The calibration standards were prepared in matrix-matched solutions in which standards and internal standards were added to the blank extracts. The calibration concentrations were 10, 20, 40, 80, 120, and 160 μ g/kg and 10, 25, 50, 100, and 150 μ g/kg for GC-MS-SIM and LC/ESI-MS/MS, respectively (for bifenox, captan, chlorothalonil, deltamethrin, difenconazole, and sanmarton, the standard concentrations were 20, 40, 80, 160, 240, and 320 μ g/kg).

RESULTS AND DISCUSSION

Chromatographic Determination. GC-MS-SIM. Pesticides were identified according to retention times and the quantification and identification ions. The quantification was based on the peak area ratio of the quantification ion divided by the internal standards. **Table 2** summarizes some pesticides studied with their quantification and identification ions used in SIM mode to analyze pesticides in vegetable juice. The pp'-DDE at the ppb level was also analyzed for comparison purposes using GC-ECD.

LC/ESI-MS/MS Data Acquisition. All of the compounds analyzed were detected with the ESI source in positive ion mode. Full-scan spectra were acquired first to optimize the collision-induced dissociation fragmentation applied at the source via the fragmentor voltage to obtain the maximum sensitivity for the protonated molecule (in general, the protonated molecule was used as a precursor ion). Second, MS/MS spectra in product ion mode of operation were acquired to obtain information on fragment ions. Once the product ions (two) had been selected for every compound, a MRM (multiple reaction monitoring) experiment was carried out to select the optimum collision energy for every specific transition. Various collision energies (from 2 to 30 eV) were investigated. The optimum energies were those that gave the best sensitivity for every transition, and they were selected as optimum ones. **Table 3** summarizes the most relevant MS settings such as fragmentor voltage and collision energies used for each one of the 21 compounds investigated, as well as all of the MRM transitions selected for screening, quantification, and confirmation. These were the MRM transitions selected in the validation study with vegetable juice matrices. The first transition shown was used for quantification, and the second transition was used for confirmatory purposes.

Table 2. Quantification and Identification Ions of Some Pesticides Analyzed by GC-MS

| pesticide's name | observed ions (<i>m/z</i>) (ion ratio) ^a | pesticide's name | observed ions (<i>m/z</i>) (ion ratio) ^a |
|------------------|---|-------------------|---|
| aldrin | 263, 265 (73), 261 (70) | EPN | 157, 185 (104), 169 (42) |
| captan | 79, 149 (20), 117 (11) | fenitrothion | 277, 125 (183), 260 (53) |
| chlorfenvinphos | 267, 323 (71), 269 (64) | iprodione | 314, 187 (26), 316 (66) |
| chlorothalonil | 266, 264 (75), 268 (47) | malathion | 173, 158 (39), 125 (153) |
| chlorpropham | 127, 213 (41), 154 (23) | metalaxyl | 206, 234 (46), 249 (63) |
| cyhalothrin | 181, 197 (80), 449 (52) | metribuzin | 198, 214 (5), 199 (29) |
| diazinon | 179, 152 (64), 304 (54) | myclobutanil | 179, 288 (15), 150 (54) |
| dicofol | 139, 251 (4), 250 (27) | pendimethalin | 252, 191 (13), 281 (18) |
| dieldrin | 263, 261 (68), 277 (87) | pirimiphos-methyl | 290, 305 (82), 276 (82) |
| endosulfan | 241, 195 (110), 237 (74) | pp'-DDE | 318, 246 (145), 316 (78) |

^a Percentage of identification-to-quantification ratios.

Table 3. Retention Times, MRM Transitions, and MS Operating Parameters Selected for Analysis of the 21 Pesticides

| compound | RT ^a (min) | fragmentor voltage | MRM transition (<i>m/z</i>) | collision energy (eV) | ion ratios ^b (%) |
|-----------------|-----------------------|--------------------|-------------------------------|-----------------------|-----------------------------|
| acetamiprid | 6.383 | 110 | 223 > 126 | 20 | 28 |
| | | 70 | 223 > 70 | 10 | |
| azaxystrobin | 14.124 | 70 | 404 > 372 | 5 | 47 |
| | | 70 | 404 > 344 | 20 | |
| boscalid | 14.491 | 90 | 343 > 307 | 15 | 40 |
| | | 90 | 343 > 140 | 10 | |
| clothianidin | 5.259 | 70 | 250 > 169 | 5 | 87 |
| | | 70 | 250 > 132 | 10 | |
| cyazofamid | 18.312 | 110 | 325 > 108 | 10 | |
| diethofencarb | 13.397 | 70 | 268 > 226 | 5 | 87 |
| | | 70 | 268 > 152 | 15 | |
| dimethomorph | 12.242 | 150 | 388 > 301 | 15 | 80 |
| | | 165 | 388 > 165 | 30 | |
| fenobucarb | 12.933 | 50 | 208 > 95 | 10 | 5 |
| | | 90 | 208 > 152 | 3 | |
| fluquinconazole | 14.655 | 90 | 376 > 349 | 15 | |
| imidacloprid | 5.735 | 70 | 256 > 175 | 15 | |
| isoprocarb | 11.429 | 70 | 194 > 95 | 5 | 20 |
| | | 70 | 194 > 137 | 3 | |
| methomyl | 3.202 | 50 | 163 > 88 | 2 | 62 |
| | | 50 | 163 > 106 | 3 | |
| pencycuron | 21.581 | 130 | 329 > 125 | 30 | 1 |
| | | 110 | 329 > 218 | 5 | |
| pyrimethanil | 9.527 | 90 | 200 > 107 | 20 | 42 |
| | | 110 | 200 > 82 | 25 | |
| tebufenozide | 17.617 | 70 | 297 > 133 | 5 | 39 |
| | | 70 | 297 > 105 | 30 | |
| tebupirimfos | 26.959 | 90 | 319 > 277 | 5 | 86 |
| | | 110 | 319 > 153 | 25 | |
| tetraconazole | 14.678 | 90 | 372 > 159 | 25 | 60 |
| | | 90 | 372 > 70 | 15 | |
| thiacloprid | 7.690 | 70 | 253 > 126 | 20 | 14 |
| | | 90 | 253 > 186 | 5 | |
| thiamethoxam | 4.229 | 70 | 292 > 211 | 5 | 79 |
| | | 70 | 292 > 181 | 15 | |
| tricyclazole | 6.562 | 100 | 190 > 136 | 20 | 52 |
| | | 110 | 190 > 163 | 20 | |
| trifloxystrobin | 24.486 | 110 | 409 > 186 | 15 | 14 |
| | | 90 | 409 > 206 | 5 | |

^a RT, retention time. ^b Intensity of qualifying ion/intensity of quantifying ion.

Method Validation. *Linearity.* The GC-MS-SIM and LC-MS/MS responses for all pesticides were linear in the concentration assayed (10–160 µg/kg) with determination coefficients ≥ 0.99 for all pesticides.

Limits of Quantification (LOQ). The LOQs of the proposed method were calculated by considering a value 10 times that of background noise for the individual pesticides in vegetable juice. For most of the compounds, the LOQs were below 5 and 0.5 µg/kg for GC-MS-SIM and LC/ESI-MS/MS, respectively (**Table 4**).

Recovery. The recovery obtained for all pesticides ranged from 77 to 114%. The precision of the method, expressed as the RSDs of analyte recoveries, was good, < 14% (**Table 4**).

Application to Real Samples. Sixty-eight vegetable juice samples were continuously analyzed in a period of 34 days following the sample preparation methods described above. Analysis results showed that almost all of the samples were free from pesticide residues. pp'-DDE was detected in one sample with a concentration of 4 µg/kg. Analysis of real samples showed the validity of

Table 4. LOQs, Retention Time, and Recovery of Spiked Vegetable Juice Samples

| name | LOQs ($\mu\text{g}/\text{kg}$) | retention time (min) | recovery ^a | | |
|---------------------|----------------------------------|----------------------|----------------------------|----------------------------|-----------------------------|
| | | | 10 $\mu\text{g}/\text{kg}$ | 40 $\mu\text{g}/\text{kg}$ | 120 $\mu\text{g}/\text{kg}$ |
| GC-MS-SIM | | | | | |
| alachlor | 2 | 12.165 | 95 \pm 3 | 97 \pm 4 | 99 \pm 7 |
| aldrin | 4 | 13.166 | 84 \pm 7 | 105 \pm 5 | 100 \pm 7 |
| benalaxyl | 4 | 19.752 | 94 \pm 4 | 99 \pm 4 | 101 \pm 5 |
| BHC- α | 1 | 9.839 | 95 \pm 5 | 96 \pm 4 | 96 \pm 8 |
| BHC- β | 1 | 10.351 | 91 \pm 6 | 100 \pm 5 | 99 \pm 5 |
| BHC- δ | 1 | 10.994 | 82 \pm 5 | 89 \pm 4 | 93 \pm 8 |
| BHC- γ | 1 | 10.485 | 96 \pm 3 | 95 \pm 5 | 100 \pm 7 |
| bifenox | 15 | 23.533 | 96 \pm 8 | 92 \pm 4 | 101 \pm 7 |
| bifenthrin | 2 | 22.983 | 90 \pm 3 | 97 \pm 4 | 100 \pm 6 |
| bromacil | 4 | 12.872 | 97 \pm 6 | 94 \pm 4 | 97 \pm 8 |
| bromopropylate | 4 | 22.577 | 94 \pm 4 | 97 \pm 4 | 98 \pm 7 |
| buprofezin | 2 | 17.161 | 98 \pm 4 | 93 \pm 4 | 97 \pm 6 |
| captan | 15 | 14.617 | 84 \pm 9 | 99 \pm 9 | 94 \pm 9 |
| chlofennapyl | 2 | 17.890 | 92 \pm 7 | 97 \pm 4 | 102 \pm 5 |
| chlofentezine | 2 | 5.951 | 90 \pm 7 | 92 \pm 7 | 95 \pm 6 |
| chlorfenvinphos | 4 | 14.762 | 98 \pm 4 | 94 \pm 3 | 95 \pm 7 |
| chlorobenzilate | 2 | 18.183 | 91 \pm 4 | 96 \pm 4 | 98 \pm 6 |
| chlorothalonil | 15 | 11.108 | 87 \pm 6 | 92 \pm 4 | 91 \pm 8 |
| chlorpropham | 4 | 9.285 | 94 \pm 4 | 97 \pm 6 | 101 \pm 7 |
| chlorpyrifos | 3 | 13.371 | 93 \pm 6 | 93 \pm 5 | 92 \pm 7 |
| chlorpyrifos-methyl | 2 | 11.965 | 88 \pm 4 | 91 \pm 4 | 94 \pm 7 |
| cyfluthrin | 4 | 28.414 | 83 \pm 8 | 80 \pm 9 | 91 \pm 6 |
| cyhalothrin | 4 | 25.443 | 80 \pm 9 | 84 \pm 5 | 94 \pm 9 |
| cypermethrin | 5 | 28.901 | 81 \pm 7 | 81 \pm 8 | 90 \pm 12 |
| deltamethrin | 20 | 31.201 | 80 \pm 14 | 82 \pm 8 | 90 \pm 10 |
| diazinon | 4 | 10.776 | 105 \pm 4 | 101 \pm 3 | 102 \pm 7 |
| dichlofluanid | 5 | 12.971 | 82 \pm 6 | 83 \pm 6 | 81 \pm 8 |
| dichlorobenil | 2 | 7.129 | 96 \pm 4 | 99 \pm 5 | 97 \pm 9 |
| dicofol | 4 | 13.443 | 89 \pm 4 | 89 \pm 4 | 96 \pm 8 |
| dieldrin | 2 | 16.705 | 87 \pm 8 | 99 \pm 4 | 97 \pm 6 |
| dimethoate | 4 | 10.072 | 93 \pm 6 | 92 \pm 4 | 93 \pm 4 |
| diphenylamine | 4 | 9.088 | 102 \pm 7 | 99 \pm 5 | 101 \pm 6 |
| disulfoton | 2 | 10.917 | 105 \pm 4 | 98 \pm 3 | 98 \pm 7 |
| edifenphos | 4 | 19.894 | 91 \pm 8 | 89 \pm 4 | 97 \pm 6 |
| endosulfan | 5 | 15.715 | 84 \pm 5 | 95 \pm 4 | 94 \pm 7 |
| endrine | 4 | 17.565 | 92 \pm 7 | 97 \pm 5 | 97 \pm 7 |
| EPN | 4 | 22.613 | 90 \pm 4 | 87 \pm 5 | 98 \pm 9 |
| ethion | 4 | 18.771 | 89 \pm 4 | 94 \pm 4 | 97 \pm 8 |
| fenarimol | 4 | 25.872 | 93 \pm 5 | 98 \pm 7 | 104 \pm 10 |
| fenitrothion | 3 | 12.729 | 92 \pm 6 | 86 \pm 6 | 97 \pm 6 |
| fenpropathrin | 4 | 23.229 | 85 \pm 5 | 89 \pm 4 | 90 \pm 8 |
| fensulfothion | 5 | 18.273 | 88 \pm 5 | 86 \pm 7 | 94 \pm 6 |
| fenthion | 2 | 13.308 | 88 \pm 5 | 88 \pm 5 | 86 \pm 5 |
| flucythrinate | 5 | 29.567 | 95 \pm 10 | 82 \pm 9 | 90 \pm 12 |
| flufenoxuron | 4 | 11.199 | 102 \pm 4 | 97 \pm 13 | 106 \pm 6 |
| flusilazole | 2 | 17.202 | 91 \pm 6 | 99 \pm 5 | 104 \pm 7 |
| fluvalinate | 5 | 30.535 | 81 \pm 7 | 81 \pm 6 | 92 \pm 11 |
| folpet | 20 | 14.950 | 81 \pm 9 | 90 \pm 9 | 86 \pm 10 |
| heptachlor | 2 | 12.283 | 92 \pm 5 | 100 \pm 7 | 108 \pm 8 |
| hexaconazole | 2 | 16.387 | 95 \pm 10 | 94 \pm 4 | 98 \pm 6 |
| imazalil | 5 | 16.289 | 94 \pm 12 | 98 \pm 5 | 98 \pm 7 |
| iprobefos | 4 | 11.301 | 105 \pm 4 | 100 \pm 4 | 100 \pm 7 |
| iprodione | 5 | 22.229 | 82 \pm 8 | 88 \pm 5 | 90 \pm 8 |
| isoprothiolane | 4 | 16.521 | 91 \pm 4 | 96 \pm 4 | 99 \pm 7 |
| malathion | 4 | 13.041 | 95 \pm 4 | 91 \pm 4 | 94 \pm 6 |
| metalaxyl | 2 | 12.369 | 82 \pm 5 | 112 \pm 4 | 102 \pm 6 |
| methidathion | 4 | 15.346 | 111 \pm 4 | 91 \pm 3 | 93 \pm 8 |
| metribuzin | 4 | 12.460 | 97 \pm 5 | 99 \pm 4 | 105 \pm 7 |
| myclobutanil | 2 | 17.133 | 94 \pm 5 | 100 \pm 5 | 103 \pm 7 |
| op-DDD | 1 | 17.105 | 97 \pm 3 | 99 \pm 5 | 102 \pm 6 |
| oxadiazone | 2 | 16.877 | 92 \pm 8 | 93 \pm 9 | 98 \pm 8 |
| oxyfluorfen | 5 | 17.235 | 98 \pm 6 | 92 \pm 4 | 106 \pm 5 |
| pachlobutrazol | 2 | 15.528 | 105 \pm 10 | 92 \pm 6 | 91 \pm 6 |
| parathion | 5 | 13.399 | 88 \pm 5 | 85 \pm 5 | 105 \pm 8 |

Table 4. Continued

| name | LOQs ($\mu\text{g}/\text{kg}$) | retention time (min) | recovery ^a | | |
|-------------------|----------------------------------|----------------------|----------------------------|----------------------------|-----------------------------|
| | | | 10 $\mu\text{g}/\text{kg}$ | 40 $\mu\text{g}/\text{kg}$ | 120 $\mu\text{g}/\text{kg}$ |
| GC-MS-SIM | | | | | |
| penconazole | 2 | 14.481 | 107 \pm 7 | 100 \pm 5 | 105 \pm 7 |
| pendimethalin | 4 | 14.440 | 108 \pm 5 | 90 \pm 5 | 103 \pm 6 |
| penthoate | 4 | 14.881 | 106 \pm 5 | 95 \pm 4 | 98 \pm 6 |
| permethrine | 4 | 27.296 | 88 \pm 4 | 98 \pm 6 | 101 \pm 9 |
| phorate | 2 | 9.719 | 106 \pm 5 | 100 \pm 5 | 101 \pm 7 |
| phosalone | 4 | 24.381 | 84 \pm 6 | 91 \pm 10 | 93 \pm 11 |
| phosmet | 5 | 22.368 | 96 \pm 7 | 92 \pm 5 | 94 \pm 6 |
| pirimicarb | 2 | 11.397 | 94 \pm 5 | 95 \pm 3 | 96 \pm 6 |
| pirimiphos-ethyl | 2 | 14.108 | 103 \pm 6 | 101 \pm 6 | 105 \pm 7 |
| pirimiphos-methyl | 2 | 12.775 | 96 \pm 5 | 97 \pm 4 | 102 \pm 5 |
| pp'-DDD | 1 | 18.451 | 96 \pm 4 | 96 \pm 4 | 97 \pm 6 |
| pp'-DDE | 1 | 16.796 | 90 \pm 4 | 96 \pm 4 | 99 \pm 6 |
| pp'-DDT | 1 | 20.107 | 92 \pm 8 | 96 \pm 9 | 96 \pm 8 |
| procymidone | 2 | 15.067 | 87 \pm 5 | 83 \pm 4 | 82 \pm 5 |
| profenofos | 4 | 16.580 | 87 \pm 6 | 88 \pm 2 | 89 \pm 7 |
| propanil | 5 | 11.691 | 92 \pm 9 | 91 \pm 5 | 94 \pm 8 |
| propargite | 5 | 21.159 | 98 \pm 5 | 102 \pm 5 | 102 \pm 5 |
| prothiofos | 4 | 16.195 | 92 \pm 5 | 91 \pm 4 | 94 \pm 5 |
| pyrazophos | 5 | 26.246 | 93 \pm 4 | 85 \pm 7 | 88 \pm 6 |
| pyridaben | 2 | 27.404 | 91 \pm 5 | 94 \pm 8 | 103 \pm 11 |
| quintozene | 4 | 10.608 | 88 \pm 6 | 94 \pm 7 | 91 \pm 7 |
| sanmarton | 15 | 30.224 | 101 \pm 7 | 103 \pm 10 | 114 \pm 12 |
| simazine | 4 | 10.122 | 102 \pm 3 | 99 \pm 4 | 100 \pm 7 |
| tebuconazole | 4 | 20.746 | 95 \pm 7 | 101 \pm 7 | 109 \pm 7 |
| terbufos | 4 | 10.553 | 94 \pm 5 | 101 \pm 3 | 102 \pm 7 |
| tetradifon | 2 | 23.842 | 99 \pm 4 | 97 \pm 5 | 98 \pm 9 |
| thiobencarb | 2 | 13.091 | 98 \pm 4 | 98 \pm 4 | 98 \pm 6 |
| tolclofos-methyl | 2 | 12.093 | 89 \pm 4 | 98 \pm 4 | 101 \pm 7 |
| tralomethrine | 5 | 18.085 | 92 \pm 4 | 97 \pm 4 | 99 \pm 5 |
| triadimefon | 2 | 13.571 | 98 \pm 5 | 97 \pm 4 | 100 \pm 7 |
| triadimenol | 2 | 15.116 | 102 \pm 5 | 93 \pm 4 | 95 \pm 6 |
| triazophos | 5 | 19.354 | 95 \pm 6 | 96 \pm 4 | 98 \pm 7 |
| triflumizole | 4 | 15.217 | 97 \pm 6 | 100 \pm 6 | 105 \pm 6 |
| LC/ESI-MS/MS | | | | | |
| acetamiprid | 0.1 | 6.383 | 90 \pm 5 | 92 \pm 2 | 96 \pm 4 |
| azoxystrobin | 0.2 | 14.124 | 105 \pm 4 | 100 \pm 3 | 99 \pm 1 |
| boscalid | 0.1 | 14.491 | 94 \pm 4 | 93 \pm 4 | 93 \pm 1 |
| clothianidin | 0.4 | 5.259 | 81 \pm 3 | 88 \pm 3 | 92 \pm 3 |
| cyazofamid | 5.0 | 18.312 | 96 \pm 4 | 92 \pm 3 | 95 \pm 3 |
| diethofencarb | 0.2 | 13.397 | 99 \pm 3 | 94 \pm 3 | 97 \pm 2 |
| dimethomorph | 0.1 | 12.242 | 108 \pm 6 | 99 \pm 2 | 98 \pm 2 |
| fenobucarb | 0.1 | 12.933 | 86 \pm 3 | 102 \pm 3 | 106 \pm 3 |
| fluquinconazole | 2.2 | 14.655 | 87 \pm 3 | 96 \pm 4 | 99 \pm 3 |
| imidacloprid | 3.0 | 5.735 | 95 \pm 6 | 95 \pm 2 | 96 \pm 2 |
| isoprocarb | 0.2 | 11.429 | 88 \pm 3 | 105 \pm 2 | 104 \pm 3 |
| methomyl | 0.2 | 3.202 | 87 \pm 4 | 90 \pm 3 | 97 \pm 4 |
| pencycuron | 0.2 | 21.581 | 100 \pm 4 | 102 \pm 3 | 102 \pm 1 |
| pyrimethanil | 0.3 | 9.527 | 77 \pm 1 | 80 \pm 5 | 82 \pm 7 |
| tebufenozide | 0.1 | 17.617 | 98 \pm 2 | 96 \pm 3 | 98 \pm 3 |
| tebupirimfos | 0.1 | 26.959 | 86 \pm 5 | 90 \pm 3 | 94 \pm 3 |
| tetraconazole | 0.2 | 14.678 | 88 \pm 4 | 92 \pm 3 | 96 \pm 3 |
| thiacloprid | 0.1 | 7.690 | 90 \pm 3 | 92 \pm 2 | 94 \pm 3 |
| thiamethoxam | 0.2 | 4.229 | 102 \pm 4 | 96 \pm 3 | 95 \pm 3 |
| tricyclazole | 0.5 | 6.562 | 84 \pm 4 | 84 \pm 4 | 86 \pm 4 |
| trifloxystrobin | 0.2 | 24.486 | 93 \pm 3 | 97 \pm 3 | 97 \pm 2 |

^a Mean percent recovery \pm RSD of pesticides in vegetable samples at 120, 40, and 10 $\mu\text{g}/\text{kg}$ fortification levels ($n = 5$).

method used, which allowed the determination and identification of trace pesticide present in the sample.

Comparison of GC-ECD and GC-MS-SIM in the Analysis of pp'-DDE in Real Sample. The pp'-DDE (p-p'-dichlorodiphenyldichloroethylene) belongs to a chlorinated

pesticide group. Until now, GC-ECD has been the most popular method used for the analysis of pp'-DDE because GC-ECD is well-known as a sensitivity technique for the analysis of chlorinated pesticides. GC-ECD chromatogram of pp'-DDE (**Figure 1**) showed an interference peak near the elute time of pp'-DDE, thus

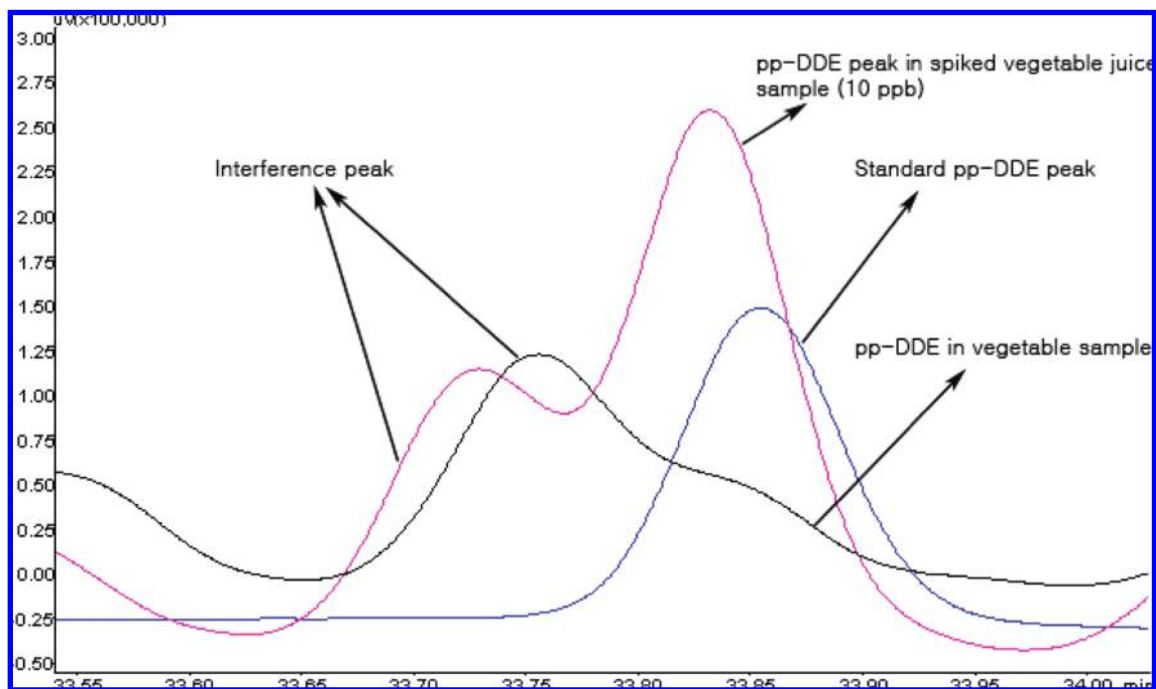


Figure 1. Extracted pp'-DDE from real sample by GC-ECD.

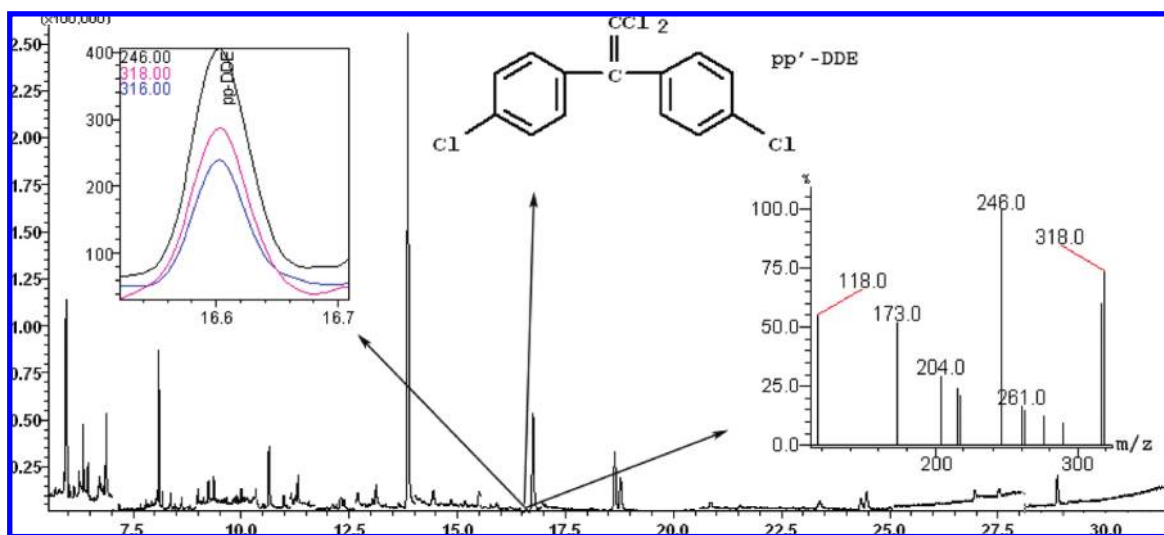


Figure 2. Extracted pp'-DDE from real sample by GC-MS-SIM.

leading to difficulty in qualitative and quantitative determinations of pp'-DDE by GC-ECD. The GC-MS-SIM chromatogram of pp'-DDE (Figure 2) showed that the pp'-DDE was well-extracted from the interference peak by the GC-MS-SIM mode. This example emphasizes the indispensability of using GC-MS as a replacement technique for GC-ECD in the analysis of chlorinated pesticides in food samples in general and in vegetable juice in particular.

Although regulations on MRLs in the area of vegetable juice products are currently not available, the analyses and the quickly received results of pesticide residue levels in vegetable juice samples have helped manufacturers adjust their input materials, so as to guarantee the quality of their products as well as good health for consumers.

Conclusions. A simple, sensitive, accurate, and rapid method was developed to determine 118 different physicochemical properties of pesticide residues in vegetable juice. The proposed method not only allowed the simultaneous determination and

confirmation of a large number of pesticides with good reproducibility and low detection limits but also showed usefulness in routine analysis due to its fast and easy implementation. The pp'-DDE case pressed the needed of using GC-MS in the application of pesticide residue analysis. This work may also be helpful for the authorities in Korea to make their decision regarding MRLs for vegetable juice.

LITERATURE CITED

- (1) Ismail, S. M. M.; Ali, H. M.; Habiba, R. A. GC-ECD and GC-MS analyses of propenofos residues and its biochemical effects in tomatoes and tomato products. *J. Agric. Food Chem.* **1993**, *41*, 610–615.
- (2) Albero, B.; Snchez-Brunete, C.; Tadeo, J. L. Determination of organophosphorus pesticides in fruit juices by matrix solid phase dispersion and gas chromatography. *J. Agric. Food Chem.* **2003**, *51*, 6915–6921.
- (3) Bolles, H. G.; Dixon-White, H. E.; Peterson, J. R.; Tomerlin, J. R.; Day, E. W.; Oliver, G. R. U.S. Market basket study to determine

- residues of insecticide Chlopyrifos. *J. Agric. Food Chem.* **1999**, *47*, 1817–1822.
- (4) Štajnbaher, D.; Zupančič-Kralj, L. Multiresidue method for determination of 90 pesticides in fresh fruits and vegetables using solid-phase extraction and gas chromatography-mass spectrometry. *J. Chromatogr. A* **2003**, *1015*, 185–198.
- (5) Obana, H.; Okihashi, M.; Akutsu, K.; Kitagawa, Y.; Hori, S. Determination of acetamiprid, imidacloprid, and nitenpyram residues in vegetables and fruits by high-performance liquid chromatography with diode-array detection. *J. Agric. Food Chem.* **2002**, *50*, 4464–4467.
- (6) Obana, H.; Okihashi, M.; Akutsu, K.; Kitagawa, Y.; Hori, S. Determination of neonicotinoid pesticide residues in vegetables and fruits with solid phase extraction and liquid chromatography mass spectrometry. *J. Agric. Food Chem.* **2003**, *51*, 2501–2505.
- (7) Albero, B.; Sánchez-Brunete, C.; Tadeo, J. L. Multiresidue determination of pesticides in juice by solid-phase extraction and gas chromatography-mass spectrometry. *Talanta* **2005**, *66*, 917–924.
- (8) Gelsomino, A.; Petrovičová, B.; Tiburtini, S.; Magnani, E.; Felici, M. Multiresidue analysis of pesticides in fruits and vegetables by gel permeation chromatography followed by gas chromatography with electron-capture and mass spectrometric detection. *J. Chromatogr. A* **1997**, *782*, 105–122.
- (9) Motohashi, N.; Nagashima, H.; Parkanyi, C. Supercritical fluid extraction for the analysis of pesticide residues in miscellaneous samples. *J. Biochem. Biophys. Methods* **2000**, *43*, 313–328.
- (10) Bandoniene, D.; Gfrerer, M.; Lankmayr, E. P. Comparative study of turbulent solid-liquid extraction methods for the determination of organochlorine pesticides. *J. Biochem. Biophys. Methods* **2004**, *61*, 143–153.
- (11) Hernando, M. D.; Agüera, A.; Fernández-Alba, A. R.; Piedra, L.; Contreras, M. Gas chromatographic determination of pesticides in vegetable samples by sequential positive and negative chemical ionization and tandem mass spectrometric fragmentation using an ion trap analyzer. *Analyst* **2001**, *126*, 46–51.
- (12) Anastassiades, M.; Lehotay, S. J.; Štajnbaher, D.; Schenck, F. J. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid phase extraction” for the determination of pesticide residues in procedure. *J. AOAC Int.* **2003**, *86*, 412–431.
- (13) Lehotay, S. J.; de Kok, A.; Hiemstra, M.; van Bodegraven, P. Validation of a fast and easy method for the determination of residues from 229 pesticides in fruits and vegetables using gas and liquid chromatography and mass spectrometric detection. *J. AOAC Int.* **2005**, *88*, 595–614.
- (14) Nguyen, T. D.; Lee, B. S.; Lee, B. R.; Lee, D. M.; Lee, G. H. A multiresidue method for the determination of 109 pesticides in rice using Quick Easy Cheap Effective Rugged and Safe (QuEChERS) sample preparation method and gas chromatography/mass spectrometry with temperature control and vacuum concentration. *Rapid Commun. Mass Spectrom.* **2007**, *18*, 3115–3122.
- (15) Nguyen, T. D.; Yu, J. E.; Lee, D. M.; Lee, G. H. A multiresidue method for the determination of 107 pesticides in cabbage and radish using QuEChERS sample preparation method and gas chromatography mass spectrometry. *Food Chem.* **2008**, *110*, 207–213.

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