

## Multiresidue Determination of 156 Pesticides in Watermelon by Dispersive Solid Phase Extraction and Gas Chromatography/Mass Spectrometry

Thanh Dong Nguyen,<sup>†,‡</sup> Myoung Hee Lee,<sup>§</sup> and Gae Ho Lee<sup>†,\*</sup>

<sup>†</sup>*Department of Chemistry, Chungnam National University, Daejeon 305-764, Korea. \*E-mail: ghlee@cnu.ac.kr*

<sup>‡</sup>*Institute of Environmental Technology, Vietnamese Academy of Science and Technology, Hanoi, Vietnam*

<sup>§</sup>*Department of Cosmetic Science, Daejeon Health Sciences College, Daejeon, Korea*

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A rapid multiresidue method was developed for the simultaneous determination of 156 pesticides in commercial watermelon. The method involves a liquid-liquid extraction using acetonitrile coupled with dispersive solid phase extraction cleanup. The extracted elution of pesticides was determined by gas chromatography with electron impact mass spectrometric detection in the selected ion monitoring mode (GC-MS-SIM). Standards were prepared spiking blank watermelon samples to counteract the observed matrix effect. The method was validated by fortified at the level 0.020-0.120 mg/kg in watermelon. The average recoveries of all analytes were between 70% and 121%, and standard deviations were below 16%. The limit of quantitation (LOQ) for most compounds was below 0.005 mg/kg, which were lower than the maximum residue levels established by Korean legislations. The proposed method has been applied to the analysis of the 156 pesticide residues in commercial watermelon samples.

**Key Words :** Dispersive solid phase extraction, Watermelon, Pesticide residues, GC-MS-SIM

### Introduction

Watermelon (*Citrulus Lanatus*), a member of the Cucurbitaceae family, is related to the cantaloupe, squash and pumpkin, other plants that also grow on vines on the ground. The annual production of watermelon in Korea is about 320000 tons. Plant watermelon diseases caused by fungi, bacteria, nematodes and viruses are one of the main limiting factors in obtaining higher yields. One of the solutions is to apply pesticides at many steps of the cultivation process. Even when applied in accordance with Good Agricultural Practices (GPA), they can leave residues, which can be detrimental to watermelon safety. The presence of pesticide residues in fruit in general and in watermelon in particular is one important concern for consumers, due to their possible long adverse health effects, especially for children as they consume a higher proportion of fruits in relation to their body weight and are more susceptible to chemicals since they are in early development stages. In order to protect consumers' health, many countries including Korea have restricted the use of pesticides by establishing legal directives on maximum residue levels (MRLs) to control their presence in food.<sup>1</sup>

The low detection levels required by regulatory bodies, the variable of the polarity, volatility and solubility of the pesticides lead the difficulty in the development of effective methods for pesticides multiresidue analysis. Based on the physio-chemical properties of pesticides, their determinations are usually accomplished by gas chromatography (GC) using specific detectors such as electron capture detection (ECD),<sup>2</sup> nitrogen phosphorus detection (NPD)<sup>3</sup> and flame photometric detection (FPD).<sup>4</sup> However, the above mentioned detection methods cover a limited range of pesti-

cide 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. The currently worldwide most used pesticide residues extraction methods are based on Luke method<sup>5</sup> or miniaturized Luke method<sup>6</sup> followed with cleanup procedures such as solid-phase extraction (SPE)<sup>7,8</sup> and gel permeation chromatography (GPL)<sup>9</sup> seem to be complicated, consume a large volume of solvent and take much of time. Therefore, new methods in sample preparation and measurement should be studied and developed.

There is continued interest in the development of alternative procedures of sample preparation, because of the need to reduce time, expense and solvents as well as to increase sample throughput and reduce labor. One of the most promising and recent sample preparation techniques is the Quick Easy Cheap Effective Rugged and Safe (QuEChERS) method,<sup>10,11</sup> which offers many advantages over the traditional techniques, such as high recoveries for wide polarity and volatility range of pesticides, high sample throughput, the use of smaller amounts of organic solvent and no chlorinated solvents are used, very little lab ware is used and there is increased the safety for lab workers.

The aim of this study was to develop a multiresidue method for the determination of 156 pesticide residues commonly used in fruit grove in Korea. Sample extraction was carried by liquid-liquid extraction using acetonitrile. Gas chromatography with mass selective detection afforded the determination of the pesticides at concentrations below their maximum allowed level. The proposed method was selected as the more suitable method for routine analysis of pesticide traces in watermelon with the advantage of low cost, easy to carry out and nonspecific instrumentation demands.

## Experimental

**Materials and reagents.** Pesticide analytical standards 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-d<sub>8</sub>, Acenaphthene-d<sub>10</sub>, Phenanthrene-d<sub>10</sub>, Fluoranthene-d<sub>10</sub> and Triphenyl phosphate) were purchased from C/D/N Isotopes INC. (Quebec, Canada) and Chemservice (West Chester, PA, USA). Glacial acetic acid and solvents of pesticide analytical grade were obtained from J.T. Baker (Philipsburg, NJ, USA). The purified water was 18M $\Omega$  (Ultra-pure water, Sinhan science tech, Daejeon, Korea). Anhydrous MgSO<sub>4</sub> and NaCl were purchased from Wako (Osaka, Japan). Primary secondary amine (PSA) sorbent was purchased from Varian (Varian, Harbor City, CA). Graphite carbon black (GCB) was purchased from Supelco (Bellefonte, PA, USA).

Watermelon samples were collected from markets and supermarkets located in central part of Korea.

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

### Apparatus.

**GC analysis:** GC-MS analyses were run on 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.

Analytes were separated in a fused silica capillary column (J&W DB 5MS), 5% phenyl polysiloxane as nonpolar stationary phase (30 m  $\times$  0.25 mm i.d.) and 0.25  $\mu$ m film thickness, supplied by Agilent (Palo Alto, CA, USA). 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 220 °C and a 1  $\mu$ L volume was injected in splitless mode.

**Mass spectrometric parameters:** Electron impact mass spectra was obtained at 70 eV of electron energy, ion source temperature was 200 °C, MS transfer temperature was 280 °C. Scan mode was performed from m/z 50 to 550 at 0.5 s per scan. Solvent delay time was 5.0 min.

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

An Ecospin 3180C (Biotron, Daejeon, Korea) vacuum concentrator was used for concentration works.

### Analytical method.

**Determination procedure:** 15 g homogenized watermelon sample was put to a 50 mL Teflon centrifuge tube; mixture of internal standards and 10 mL of acetonitrile (HAc 0.5%) were added and shake the sample vigorously for 1 min using

a vortex mixer; sample tube was then put into refrigerator for 30 min; add 5 g MgSO<sub>4</sub> and 1.2 g NaCl and vortex immediately for 1 min; centrifuge the extract for 5 min at 4000 rpm in 4 °C; transfer 2 mL aliquot of the upper layer into a 5 mL micro-centrifuge vial containing 50 mg primary secondary amine (PSA), 300 mg MgSO<sub>4</sub> and 20 mg graphite carbon black (GCB); vortex for 1 min and centrifuge the extracts for 5 min at 4000 rpm in 4 °C; transfer 1.2 mL of the upper layer into an 1.8 mL Effendox vial and put to vacuum concentrator to concentrate to dryness; add 0.4 mL of acetonitrile that contain 0.1 mg/L of triphenyl phosphate (TPP) to dissolve the residue and transfer to auto sampler vial. The sample is now ready for GC-MS analysis.

**Recovery study:** For recovery studies, 15 g of homogenized watermelon sample with no pesticides detected previously were spiked prior to determination procedure by addition of mixture of standard pesticides solution to give the 0.020, 0.080 and 0.120 mg/kg of each compound. They were then prepared according to the determination procedure described as above.

**Matrix matched calibration:** The calibration standards were prepared in matrix-matched solution in which standards and internal standards were added to the blank extracts. Matrix matched calibration standards were used for all quantitations, although the influence of the watermelon matrix on recoveries was periodically assessed by injecting standards in acetonitrile. The calibration concentrations were 0.010, 0.020, 0.040, 0.080, 0.120 and 0.160 mg/kg (For bromacil, cycloprothrin, cypermethrin, cyproconazole, endosulfan, flucythrinate, fludioxonil, fluralinate, phosmet, propanil, pyrazophos, sanmarton and tralomethrine the standard concentrations were 0.020, 0.040, 0.080, 0.160, 0.240 and 0.320 mg/kg).

## Results and Discussion

**Quantitation.** One target and two qualifier ions were used in SIM mode to quantitative analysis of pesticides. Pesticides were identified according to the retention times, the target and qualifier ions. The quantitation was based on the peak area ratio of the target ion divided by the internal standards. Table 1 summaries some pesticides studied with their target and qualifier ions used in SIM mode to analyze pesticides in watermelon. For identification of pesticides, the retention time and three ions (one for target and two for qualifier) with the assistance of the NIST's pesticides library were used.

**Linearity.** Six-level calibration using multi-internal standards was used for quantitation. The linearity for all pesticides was satisfied with  $R^2 \geq 0.99$  from 0.010 mg/kg to 0.160 mg/kg. The four internal standards were employed at beginning of the sample preparation stage help to control the significant losses of the analytes during extraction. Adding TPP at last stage of sample preparation was used to control the amount of sample injection in GC.

**Sensitivity.** In order to increase the sensitivity for high number of pesticides, the 156 pesticides were divided into

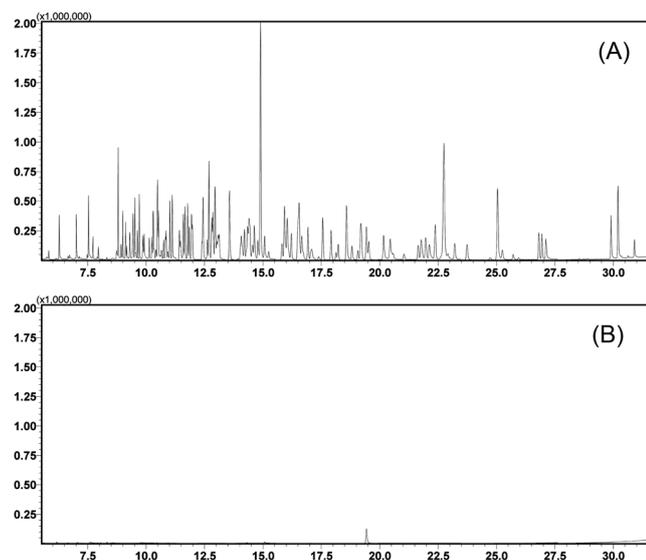
**Table 1.** Some pesticides studied with their target and qualifier ions

Name	Observed ion (m/z)	Name	Observed ion (m/z)
Acetochlor	223 146 162	Fensulfthion	293 308 156
Amitraz	121 162 293	Flufenoxuron	305 126 98
Benalaxyl	148 206 325	Hexaconazole	83 214 231
Bifenthrin	181 166 422	Indoxacarb	235 203 122
Bromacil	207 205 233	Iprobenfos	91 204 288
Cadusafos	159 213 127	Isoprothiolane	118 204 290
Chinomethionat	234 206 116	Kresoxim-methyl	116 131 206
Chlorpropham	127 213 154	Lufenuron	353 203 355
Chlorpyrifos	197 199 314	Methidathion	145 85 302
Cyfluthrine 1	163 206 226	Myclobutanil	179 288 150
Dichlorobenil	171 173 136	Omethoate	156 110 126
Dichlovos	109 220 185	Oxadiazone	175 258 244
Dicofol	139 251 250	Pachlobutrazol	236 125 238
Diethofencarb	267 225 196	Parathion-methyl	263 125 109
Disulfoton	88 274 186	Penthoate	274 320 246
Diuron	187 124 159	Pirimicarb	166 72 238
Edifenphos	109 173 310	Procymidone	96 283 285
Ethafluralin	316 276 333	Propargite	135 150 350
Ethion	231 384 153	Quintozene	295 237 265
Fenoxycarb	186 116 255	Terbufos	231 288 153
Fenpropathrin	97 181 349	Tolyfluanid	238 137 181

the groups due to their polarities and volatilities. No large interference peak in the GC chromatogram in Figure 1 demonstrated that the cleanup procedure used in this study was accepted.

**Vacuum concentrator.** Previous study showed that the using of vacuum concentrator was not affected to the recovery yield thus vacuum concentrator was used in this study with concentration factor of 3.<sup>11</sup>

**Effect of acetic acid on recovery of some problematic pesticides.** captan, chlorothalonil, dicofol, dichlofluanid,

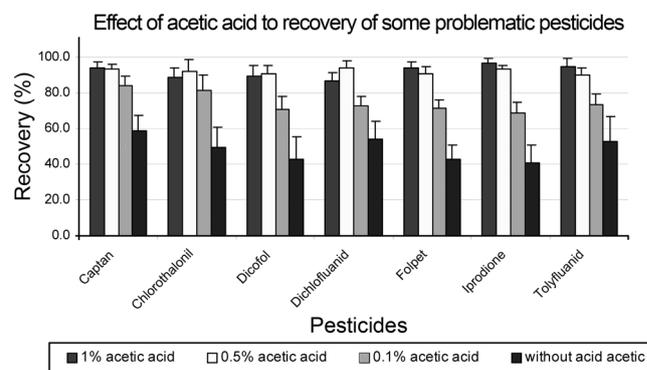


**Figure 1.** Chromatogram obtained for (A) Spiked watermelon sample (0.080 mg/kg). (B) Control watermelon sample.

folpet, iprodione and tolyfluanid are problematic pesticides that are difficult in multiresidue analysis. In sample matrix environments, captan, folpet, dichlofluanid, tolyfluanid, dicofol, iprodione and chlorothalonil easily degrade to tetrahydrophthalimide, phthalimide, *N,N*-dimethyl-*N*-phenylsulphamide, dimethylamino-sulfotoluidide, dichlorobenzophenone, 3,5-dichloroaniline and 4-hydroxy-2,5,6-trichloroisophthalonitrile, respectively. The root problems for these problematic pesticides are diverse and hard to control. For example, the losses of chlorothalonil caused by not only during sample preparation steps but also during the GC analysis due to its thermally stable and susceptible to adverse effects in the GC injection port, column, and MS ion source. Among control parameters that can factor into the rate of degradation of these pesticides include pH, type of solvent, light intensity, matrix components, temperature and analyte concentration, two factors (pH and temperature) were selected in this study because most of these pesticides are base-sensitive, can easily be controlled and previous study<sup>11</sup> showed good results achieved when control these two factors. Results from experimental analysis showed that adding acetic acid helped to improve the recovery of these problematic pesticides above 80% (Fig. 2). The addition of acetic acid did not negative affect the stability of the other studied pesticides and no deterioration of the GC system performance was observed after the long-term injection of acetonitrile containing 0.5% acetic acid. The guard column was used and regularly replaced after 500 injections in order to keep the column lifetime.

**Recovery.** The recoveries of all analytes between 70% and 121% with RSDs < 16% were obtained from watermelon spiked ( $n = 5$ ) at 0.020, 0.080 and 0.120 mg/kg (except for bromacil, cycloprothrin, cypermethrin, cyproconazole, endosulfan, flucythrinate, fludioxonil, fluralinate, phosmet, propanil, pyrazophos, sanmarton and tralomethrine where the standard concentrations were 0.040 to 0.240 mg/kg), as shown by the data in Table 2.

**Limits of quantitation.** The LOQs were calculated by considering a value 10 times that background noise. For most of the compounds, the LOQs are below 0.005 mg/kg.



**Figure 2.** Effect of acetic acid to recovery of some problematic pesticides.

**Table 2.** LOQs, retention time and mean percent recovery  $\pm$  RSD of 156 pesticides in watermelon samples

Name	LOQs (mg/kg)	Retention time (min)	Recovery <sup>a</sup>			Name	LOQs (mg/kg)	Retention time (min)	Recovery <sup>a</sup>		
			0.020	0.080	0.120				0.020	0.080	0.120
Acetochlor	0.003	11.598	85 $\pm$ 5	91 $\pm$ 6	103 $\pm$ 4	Ethoprophos	0.003	9	86 $\pm$ 5	83 $\pm$ 5	96 $\pm$ 6
Alachlor	0.002	11.847	85 $\pm$ 5	90 $\pm$ 7	102 $\pm$ 4	Etiozazole	0.004	22.748	72 $\pm$ 5	93 $\pm$ 8	106 $\pm$ 4
Aldrin	0.003	12.8	88 $\pm$ 6	84 $\pm$ 9	89 $\pm$ 5	Fenamidon	0.003	22.728	72 $\pm$ 4	95 $\pm$ 7	106 $\pm$ 4
Amitraz	0.007	24.742	81 $\pm$ 6	80 $\pm$ 10	108 $\pm$ 16	Fenarimol	0.004	25.053	115 $\pm$ 4	93 $\pm$ 6	104 $\pm$ 4
Benalaxyl	0.002	19.189	83 $\pm$ 3	91 $\pm$ 6	101 $\pm$ 3	Fenazaquin	0.004	22.759	79 $\pm$ 3	98 $\pm$ 6	110 $\pm$ 4
BHC-alpha	0.002	9.63	92 $\pm$ 2	84 $\pm$ 5	93 $\pm$ 7	Fenitrothion	0.007	12.402	87 $\pm$ 4	89 $\pm$ 8	96 $\pm$ 8
BHC-beta	0.002	10.136	77 $\pm$ 3	74 $\pm$ 7	90 $\pm$ 8	Fenobucarb	0.002	8.801	94 $\pm$ 5	87 $\pm$ 4	100 $\pm$ 6
BHC-delta	0.002	10.75	82 $\pm$ 7	87 $\pm$ 7	97 $\pm$ 3	Fenoxycarb	0.003	22.13	81 $\pm$ 6	91 $\pm$ 6	106 $\pm$ 5
BHC-gamma	0.002	10.249	80 $\pm$ 3	75 $\pm$ 7	90 $\pm$ 7	Fenpropathrin	0.004	22.632	79 $\pm$ 3	82 $\pm$ 7	96 $\pm$ 5
Bifenoxy	0.02	22.927	84 $\pm$ 4	82 $\pm$ 12	83 $\pm$ 11	Fenthion	0.002	12.943	79 $\pm$ 5	88 $\pm$ 7	100 $\pm$ 4
Bifenthrin	0.002	22.381	75 $\pm$ 5	87 $\pm$ 6	94 $\pm$ 3	Fipronil	0.004	14.425	95 $\pm$ 5	83 $\pm$ 7	90 $\pm$ 3
Bromacil	0.015	12.462	75 $\pm$ 5	86 $\pm$ 9	99 $\pm$ 6	Flucythrinate	0.015	28.935	116 $\pm$ 12	105 $\pm$ 6	90 $\pm$ 8
Bromopropylate	0.008	21.969	91 $\pm$ 5	82 $\pm$ 6	88 $\pm$ 3	Fludioxonil	0.015	16.567	71 $\pm$ 5	98 $\pm$ 7	107 $\pm$ 10
Buprofezin	0.002	16.665	88 $\pm$ 4	98 $\pm$ 6	108 $\pm$ 3	Flufenacet	0.004	13.129	82 $\pm$ 5	91 $\pm$ 8	104 $\pm$ 7
Cadusafos	0.004	9.439	87 $\pm$ 3	83 $\pm$ 6	96 $\pm$ 6	Flufenoxuron	0.003	10.939	83 $\pm$ 10	79 $\pm$ 12	85 $\pm$ 12
Captafol	0.004	20.172	107 $\pm$ 4	85 $\pm$ 7	98 $\pm$ 4	Fluquinconazole	0.004	27.12	78 $\pm$ 5	84 $\pm$ 6	105 $\pm$ 5
Captan	0.02	14.298	81 $\pm$ 8	86 $\pm$ 11	85 $\pm$ 8	Flusilazole	0.002	16.714	87 $\pm$ 8	82 $\pm$ 6	99 $\pm$ 5
Carboxin	0.004	16.517	75 $\pm$ 5	86 $\pm$ 6	95 $\pm$ 2	Flutolanil	0.005	15.982	75 $\pm$ 5	87 $\pm$ 6	98 $\pm$ 4
Chinomethionat	0.008	14.786	85 $\pm$ 2	82 $\pm$ 7	90 $\pm$ 1	Fluvalinate	0.015	30.236	114 $\pm$ 5	104 $\pm$ 6	91 $\pm$ 6
Chlofennapyl	0.002	17.386	79 $\pm$ 5	84 $\pm$ 7	91 $\pm$ 2	Folpet	0.07	14.531	87 $\pm$ 6	73 $\pm$ 11	80 $\pm$ 3
Chlofentezine	0.002	5.753	83 $\pm$ 9	85 $\pm$ 3	84 $\pm$ 14	Fosthiazate	0.004	13.611	94 $\pm$ 8	100 $\pm$ 10	95 $\pm$ 13
Chlorfenvinphos	0.008	14.344	77 $\pm$ 5	89 $\pm$ 8	105 $\pm$ 8	Furathiocarb	0.003	23.729	85 $\pm$ 8	78 $\pm$ 6	112 $\pm$ 8
Chlorobenzilate	0.002	17.665	80 $\pm$ 5	86 $\pm$ 6	92 $\pm$ 1	Heptachlor	0.002	11.897	82 $\pm$ 9	92 $\pm$ 14	98 $\pm$ 6
Chlorothalonil	0.03	10.857	75 $\pm$ 8	74 $\pm$ 10	81 $\pm$ 3	Hexaconazole	0.002	15.818	101 $\pm$ 5	86 $\pm$ 6	96 $\pm$ 4
Chlorpropham	0.005	9.121	88 $\pm$ 4	81 $\pm$ 6	96 $\pm$ 7	Hexaflumuron	0.005	7.479	79 $\pm$ 8	86 $\pm$ 6	92 $\pm$ 9
Chlorpyrifos	0.002	12.998	78 $\pm$ 10	84 $\pm$ 8	95 $\pm$ 4	Imazalil	0.008	15.932	75 $\pm$ 5	87 $\pm$ 6	98 $\pm$ 4
Chlorpyrifos-methyl	0.002	11.643	97 $\pm$ 5	92 $\pm$ 7	112 $\pm$ 5	Indoxacarb	0.004	7.139	88 $\pm$ 13	88 $\pm$ 6	99 $\pm$ 10
Cycloprothrin	0.015	9.559	85 $\pm$ 11	83 $\pm$ 4	98 $\pm$ 11	Iprobenfos	0.004	11.016	77 $\pm$ 6	100 $\pm$ 8	121 $\pm$ 8
Cyfluthrin	0.005	28.05	105 $\pm$ 13	75 $\pm$ 7	87 $\pm$ 7	Isodione	0.01	21.654	72 $\pm$ 5	83 $\pm$ 7	92 $\pm$ 4
Cyhalothrin	0.004	25.258	94 $\pm$ 5	84 $\pm$ 9	84 $\pm$ 5	Isazophos	0.005	10.826	81 $\pm$ 5	89 $\pm$ 7	101 $\pm$ 4
Cypermethrin	0.015	28.555	75 $\pm$ 3	95 $\pm$ 8	87 $\pm$ 7	Isophenphos	0.003	14.352	110 $\pm$ 5	86 $\pm$ 8	100 $\pm$ 6
Cyproconazole	0.01	17.086	79 $\pm$ 4	82 $\pm$ 7	100 $\pm$ 5	Isoprothiolane	0.007	16.095	79 $\pm$ 5	88 $\pm$ 7	95 $\pm$ 3
Deltamethrin	0.04	30.91	78 $\pm$ 4	98 $\pm$ 6	88 $\pm$ 4	Kresoxim-methyl	0.003	16.932	79 $\pm$ 10	86 $\pm$ 7	94 $\pm$ 2
Diazinon	0.002	10.53	86 $\pm$ 3	84 $\pm$ 5	100 $\pm$ 8	Lufenuron	0.004	7.409	86 $\pm$ 6	82 $\pm$ 15	83 $\pm$ 8
Dichlofluanid	0.005	12.62	88 $\pm$ 4	84 $\pm$ 7	97 $\pm$ 4	Malathion	0.005	12.69	106 $\pm$ 5	85 $\pm$ 8	99 $\pm$ 6
Dichlorobenil	0.002	7.015	94 $\pm$ 8	85 $\pm$ 3	88 $\pm$ 7	Mecarbam	0.005	14.398	82 $\pm$ 4	85 $\pm$ 9	99 $\pm$ 6
Dichlovos	0.002	6.28	89 $\pm$ 4	91 $\pm$ 5	95 $\pm$ 5	Mepronil	0.005	18.584	74 $\pm$ 5	87 $\pm$ 7	102 $\pm$ 4
Diclofop-methyl	0.004	20.458	79 $\pm$ 5	86 $\pm$ 7	92 $\pm$ 2	Metalaxyl	0.002	11.981	91 $\pm$ 6	92 $\pm$ 8	103 $\pm$ 5
Dicloran	0.004	9.86	79 $\pm$ 7	77 $\pm$ 7	89 $\pm$ 7	Metconazole	0.004	22.697	117 $\pm$ 11	79 $\pm$ 7	103 $\pm$ 6
Dicofol	0.003	13.071	76 $\pm$ 5	86 $\pm$ 8	103 $\pm$ 4	Methidathion	0.003	14.901	75 $\pm$ 5	88 $\pm$ 6	95 $\pm$ 2
Dieldrin	0.002	16.211	86 $\pm$ 4	82 $\pm$ 7	82 $\pm$ 1	Metobromuron	0.004	11.173	81 $\pm$ 7	76 $\pm$ 16	119 $\pm$ 12
Diethofencarb	0.004	12.816	88 $\pm$ 5	90 $\pm$ 7	104 $\pm$ 5	Metolachlor	0.004	12.863	89 $\pm$ 5	92 $\pm$ 7	103 $\pm$ 5
Dimethoate	0.008	9.899	82 $\pm$ 4	83 $\pm$ 6	95 $\pm$ 7	Metribuzin	0.004	11.477	106 $\pm$ 5	82 $\pm$ 7	103 $\pm$ 7
Dimethylvinphos	0.004	12.96	85 $\pm$ 5	87 $\pm$ 8	99 $\pm$ 7	Mevinphos	0.007	7.532	88 $\pm$ 3	83 $\pm$ 4	94 $\pm$ 5
Diphenamid	0.004	13.576	88 $\pm$ 5	91 $\pm$ 7	103 $\pm$ 5	Myclobutanil	0.002	16.597	117 $\pm$ 4	88 $\pm$ 6	102 $\pm$ 4
Diphenylamine	0.005	8.933	94 $\pm$ 2	84 $\pm$ 5	94 $\pm$ 7	Nitrapyrin	0.005	7.721	76 $\pm$ 6	80 $\pm$ 4	89 $\pm$ 4
Disulfoton	0.002	10.657	74 $\pm$ 7	85 $\pm$ 6	99 $\pm$ 4	Nuarimol	0.008	20.074	72 $\pm$ 7	90 $\pm$ 7	104 $\pm$ 3
Diuron	0.008	6.732	86 $\pm$ 11	84 $\pm$ 5	93 $\pm$ 8	Omethoate	0.005	8.737	84 $\pm$ 6	87 $\pm$ 8	109 $\pm$ 10
Edifenphos	0.004	19.229	77 $\pm$ 3	80 $\pm$ 7	93 $\pm$ 7	op-DDD	0.002	16.543	80 $\pm$ 5	89 $\pm$ 6	94 $\pm$ 2
Endosulfan-alpha	0.015	15.248	86 $\pm$ 3	86 $\pm$ 8	88 $\pm$ 2	op-DDT	0.002	17.993	72 $\pm$ 3	82 $\pm$ 11	87 $\pm$ 5
Endosulfan-beta	0.015	17.447	84 $\pm$ 2	86 $\pm$ 9	88 $\pm$ 1	Oxadiazone	0.002	16.483	84 $\pm$ 1	86 $\pm$ 7	91 $\pm$ 1
Endrine	0.003	17.041	71 $\pm$ 7	85 $\pm$ 9	91 $\pm$ 3	Oxadixyl	0.005	18.136	74 $\pm$ 6	91 $\pm$ 5	107 $\pm$ 4
EPN	0.008	22	74 $\pm$ 5	83 $\pm$ 8	79 $\pm$ 12	Oxyfluorfen	0.008	16.732	93 $\pm$ 2	83 $\pm$ 7	81 $\pm$ 7
Ethafluralin	0.003	9.171	87 $\pm$ 3	89 $\pm$ 5	92 $\pm$ 9	Pachlobutrazol	0.002	15.075	79 $\pm$ 6	89 $\pm$ 6	102 $\pm$ 7
Ethion	0.003	18.225	98 $\pm$ 5	76 $\pm$ 7	90 $\pm$ 4	Parathion	0.005	13.031	90 $\pm$ 4	89 $\pm$ 9	95 $\pm$ 8

<sup>a</sup>Mean percent recovery  $\pm$  RSD of pesticides in watermelon samples at 0.020, 0.080 and 0.120 mg/kg fortification levels ( $n = 5$ )

Table 2. Continued

Name	LOQs	Retention	Recovery <sup>a</sup>			Name	LOQs	Retention	Recovery <sup>a</sup>		
	(mg/kg)	time (min)	0.020	0.080	0.120		(mg/kg)	time (min)	0.020	0.080	0.120
Parathion-methyl	0.005	11.664	88 ± 4	87 ± 8	94 ± 10	Pyridaphenthion	0.003	21.807	75 ± 6	77 ± 6	107 ± 7
Penconazole	0.002	14.077	112 ± 5	84 ± 8	104 ± 7	Pyrimethanil	0.003	10.487	86 ± 3	81 ± 5	98 ± 8
Pendimethalin	0.003	14.036	102 ± 4	89 ± 8	95 ± 8	Quintozene	0.01	10.349	79 ± 5	85 ± 14	95 ± 6
Penthoate	0.003	14.454	70 ± 2	86 ± 7	93 ± 1	Sanmarton	0.02	30.205	112 ± 4	76 ± 6	94 ± 5
Permethrine	0.003	26.82	103 ± 2	84 ± 6	97 ± 4	Simazine	0.01	9.921	82 ± 2	81 ± 5	101 ± 7
Phorate	0.005	9.519	74 ± 2	81 ± 4	97 ± 6	Tebuconazole	0.004	20.126	94 ± 9	101 ± 6	103 ± 6
Phosalone	0.008	23.754	111 ± 3	75 ± 8	92 ± 5	Tebufenpyrad	0.004	22.769	79 ± 3	92 ± 6	103 ± 5
Phosmet	0.012	21.773	116 ± 3	75 ± 8	93 ± 6	Teflubenzuron	0.005	6.337	84 ± 11	82 ± 10	86 ± 13
Phosphamidone	0.004	11.432	70 ± 7	87 ± 8	116 ± 12	Terbufos	0.003	10.311	78 ± 3	83 ± 6	99 ± 7
Pirimicarb	0.002	11.119	94 ± 7	94 ± 7	109 ± 7	Terbuthylazine	0.005	10.298	89 ± 2	84 ± 6	102 ± 8
Pirimiphos-ethyl	0.002	13.711	71 ± 4	87 ± 6	103 ± 6	Tetradifon	0.002	23.216	84 ± 5	88 ± 7	93 ± 2
Pirimiphos-methyl	0.002	12.438	78 ± 4	90 ± 7	104 ± 5	Thiobencarb	0.002	12.671	84 ± 5	90 ± 7	102 ± 4
pp'-DDD	0.002	17.823	75 ± 2	85 ± 7	92 ± 1	Thiometon	0.004	9.71	87 ± 3	81 ± 6	92 ± 5
pp'-DDE	0.002	16.221	86 ± 2	85 ± 6	89 ± 1	Tolclofos-methyl	0.002	11.779	85 ± 6	90 ± 7	100 ± 3
pp'-DDT	0.002	19.537	84 ± 3	74 ± 8	87 ± 2	Tolyfluamid	0.004	14.212	92 ± 4	82 ± 9	94 ± 6
Procymidone	0.002	14.636	90 ± 5	89 ± 7	92 ± 1	Tralomethrine	0.015	17.567	79 ± 5	86 ± 6	92 ± 1
Profenofos	0.008	16.108	76 ± 3	78 ± 7	97 ± 4	Triadimefon	0.002	13.099	71 ± 5	83 ± 8	96 ± 5
Prometryn	0.01	11.946	83 ± 5	90 ± 7	104 ± 6	Triadimenol	0.002	14.687	79 ± 4	86 ± 6	101 ± 7
Propanil	0.015	11.428	74 ± 6	85 ± 8	113 ± 5	Triazophos	0.008	18.819	78 ± 4	82 ± 7	99 ± 5
Propargite	0.004	20.561	83 ± 5	98 ± 6	115 ± 5	Tricyclazole	0.01	16.049	97 ± 5	80 ± 8	95 ± 5
Pyrazophos	0.015	25.112	80 ± 4	91 ± 7	103 ± 4	Triflumizole	0.004	14.795	85 ± 10	84 ± 6	83 ± 9
Pyridaben	0.002	26.953	115 ± 3	76 ± 7	97 ± 6	Zoxamide	0.010	14.569	88 ± 5	82 ± 7	81 ± 2

### Conclusions

About 156 different pesticides residues in watermelon were determined simultaneously. Acetonitrile was used for extraction and dispersive solid phase extraction for cleanup. The GC-MS-SIM analysis showed a high sensitivity and confirmatory power necessary for the determination of pesticide residues at the levels lower than Korea' MRLs required for watermelon. The proposed method allowed the simultaneous determination and confirmation of a large number of pesticides with good reproducibility and low detection limits.

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