

Applicability of Using GC-PDD (Pulsed Discharge Detector) for Multiresidual Pesticides Analysis

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Abstract The electron-capture detector (ECD) of gas chromatographs (GC) has been used widely in pesticide analysis. However, as ECD relies on radioactive material, it is troublesome to purchase and maintain. Therefore, potent replacements for ECD were investigated. A Pulsed-discharge detector (PDD) for ECD was tested and the analytical results of PDD (ECD mode), μ ECD, and nitrogen-phosphorus detector (NPD) were compared for 107 pesticides including organochlorine, organophosphorus, pyrethroids etc. The number of pesticides identified at the lowest limit of detection (LOD) was 36, 29, and 2 for PDD, μ ECD, and NPD, respectively. The remaining pesticides showed same response to PDD and μ ECD. The GC-PDD analysis of pesticides spiked into representative agricultural products (brown rice, spinach, and mandarin oranges) also showed good and/or equivalent recoveries using GC- μ ECD.

Keywords: pesticides, gas chromatograph (GC), pulsed-discharge detector (PDD), electron-capture detector (ECD), nitrogen phosphorus detector (NPD)

Introduction

Gas chromatograph (GC) and high performance liquid chromatograph (HPLC) are the most common analytical instruments for pesticides in foods and in the environment (1-3). There are a variety of detectors developed for GC and the electron capture detector (ECD) is one of the most sensitive detectors used for identification of electro-negative compounds like organochlorine pesticides (4-9). The ECD uses a radioactive Beta emitter (electrons) to ionize some of the carrier gas and produce a current between a pair of biased electrodes (10). The radioisotope, ^{63}Ni , included in the ECD cell is strictly regulated. Therefore, the procedure for purchasing, installing, reporting, using, maintaining, and retiring ECDs are quite complicated. The radioactive material is under the application of the laws such Article 65-75, Chapter 7, "Radioactive compounds and radiation producers" and Clause 3, Article 76-90, Chapter 8, "Waste management and transport" of the law for atomic energy. Further, the usage report and the use permission of the radiation generated by radioactive materials are under the control of the Ministry of Science and Technology, Korea Institute of Nuclear Safety, Korea Radioisotope Association (11).

On the other hand, the Pulsed Discharge Detector (PDD) in helium mode utilizes a stable, low powered, pulsed DC discharge in helium as an ionization source. The eluate from the column, flowing counter to the flow of helium from the discharge zone, are ionized by photons from the helium discharge. The bias electrode(s) focus the resulting electrons toward the collector electrode, where they cause changes in the standing current which is quantified as the detector output. In the electron capture mode, the PDD has selectivity for monitoring high electron affinity compounds such as freons, chlorinated

pesticides, and other halogen compounds (11, 12). PDDs from vendors such as Valco Instruments Co., Inc. (Houston, TX, USA) could replace flame ionization detectors (FID) in helium mode and would also be able to function as a specific photoionization detector for selective determination of aliphatics, aromatics, amines, as well as other species depending on which noble gas (argon, krypton, or xenon) depending on the desired cut-off point) would dope the helium discharge gas. For the ECD mode of PDD, the dopant gas (xenon or CH_4 in helium) is first ionized by the photons from the discharge. Resulting electrons, in the absence of any electron-capturing compounds, constitute the detector standing current. The electron capture process occurs when electron capturing compounds enter the detector, resulting in a decrease in the detector standing current which give rise to the PDD response (13).

A total of 107 pesticides were tested to determine the viability of different GC detectors from PDD to ECD and nitrogen phosphorus detectors (NPD) (14). The pesticides included in this study are among the target pesticides of the official multi-residual pesticides analysis method (MRM) No. 83 on Korea Food Code, which is the major pesticide analysis method used by the actual official spots of Korea Food & Drug Administration (KFDA) (15). After the determination of limit of detection (LOD) for each pesticide on each of the three detectors, a field test was performed to confirm the applicability of PDD for the pesticides with sample matrices. The actual sample matrices, brown rice, spinach, and mandarin oranges were spiked with selected pesticides among the 107 pesticides tested in this research. The spiked samples were then analyzed by GC-PDD after the preparation by the modified Korea Food Code MRM No. 83.

Materials and Methods

Reagents and apparatus The 107 pesticide standards above the purity 95% were purchased from ChemService,

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Inc. (West Chester, PA, USA), Dr. Ehrenstorfer (Augsburg, Germany) and Wako Pure Chemical Industries (Osaka, Japan). Each pesticide standard was dissolved in acetone as a stock solution with the concentration of 1,000 mg/L and preserved under the -4°C within three months. The working solution for each pesticide was prepared in acetone at a concentration range of 0.1 to 50 mg/L single or mixture solution. They were prepared every two weeks as needed. Pesticide analysis grade acetonitrile, acetone, and hexane were obtained from Burdick & Jackson (Muskegon, MI, USA). And all other chemicals were obtained from Junsei Chemical Co. (Tokyo, Japan). The 107 pesticides were divided into 6 groups in which all peaks belong to each group were non-overlapping on a non-polar GC capillary column. The blank sample, mandarin, spinach, and brown rice for background testing were purchased in the organic vegetable corner of the department store located in Suwon, Korea. The sample was homogenized using a Diaz900 homogenizer (Heidolph, Numburg, Germany). And the excess solvent was evaporated using an Eyela N-1000 vacuum evaporator (Tokyo, Japan). The residual pesticides were extracted using a Supelco SPE vacuum manifold (Bellefonte, PA, USA) and Waters florisil cartridge (1 g, 5 mL) (Milford, MA, USA).

Instrument conditions A DB-5 capillary column (30 m \times 0.32 mm i.d., Agilent J&W Scientific, Folsom, CA, USA) with a film thickness of 0.25 μm , was utilized for all GC analysis. For GC- μECD and NPD analysis, an Agilent 6890 Gas Chromatograph (Agilent, Palo Alto, CA, USA) was used. GC-PDD analysis was performed with an ACME 6000 Gas Chromatograph (Younglin, Anyang, Korea) equipped with D-4-1-HP58-220 PDD (Valco Instrument Co. Inc., Houston, TX, USA). The nitrogen carrier gas with 2 mL/min flow rate was adapted for GC- μECD and NPD analysis with constant flow mode. However, helium at a flow rate of 1 mL/min was used for GC-PDD. The oven temperature condition for all three GC analyses was same as held constant at 80°C for 2 min, increasing to 280°C at $10^{\circ}\text{C}/\text{min}$ and remained at 280°C for 15 min. Each 1 μL of sample was injected with split mode (split ratio, 50:1) at 260°C except GC-NPD in which splitless mode was adapted due to the low sensitivity comparing μECD and PDD. The detector temperature was fixed at 280°C for all three detectors. To operate PDD in the electron capture mode, 3 mL/min of helium with 3.05% Xenon was introduced as a dopant gas which was just upstream from the column exit. The make up gas for PDD, μECD , and NPD was 30 mL/min helium, 60 mL/min nitrogen and 1 mL/min nitrogen, respectively. The hydrogen gas flow for NPD was 3 mL/min. The sample was injected automatically on to the column.

Sample preparation The modified official MRM No. 83 on Korea Food Code was applied to brown rice, spinach, and mandarin oranges spiked with 18, 17, and 11 different pesticides, respectively. The spiked pesticide mixtures were prepared in acetone (12.5 $\mu\text{g}/\text{mL}$). The pesticide mixture (12.5 μg of each pesticide) was added to the sample (20 g) and homogenized for 3 min after adding 50 mL of acetonitrile. In the case of brown rice, the sample

was pre-soaked for 4 hr in the 30 mL of distilled water before homogenization. The homogenized sample was filtered under vacuum and the filtrate was kept at 4°C for 30 min after salting out with 10 g of sodium chloride. Only 20 mL of the upper layer was taken for evaporation to dryness and followed by dissolution with 2 mL of acetone in hexane (20/80, v/v). It was loaded onto the activated Florisil SPE cartridge and was eluted by 5 mL of acetone in hexane (20/80, v/v). The eluate was evaporated under a gentle stream of nitrogen gas in a 30°C water bath and analyzed by GC after making up to final volume 2 mL with acetone in hexane (20/80, v/v).

Instrumental analysis All injections were repeated three times and the lowest limit of peak identification for the LOD was three times of the noise level in height. For the determination of peak identity, relative retention time (RRT) compared to the retention time of myclobutanil peak was used. To check out LOD of each pesticide, each group of pesticide with the concentration of 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, and 1 was prepared. The final pesticide concentration for LOD could be converted to the concentration in the sample with considering dilution factor 4. For instance, if the LOD 1 $\mu\text{g}/\text{mL}$ was acquired from the pesticide standard, it could be converted to 0.25 $\mu\text{g}/\text{mL}$ after considering the dilution factor 4 which was originally from the sample amount of 20 g and the final solution volume of 2 mL. However, all LOD mentioned in this study was the concentration of the pesticide standard solution without any conversion.

Results and Discussion

Comparison of LOD on three different GC detectors A total of 85 and 74 pesticides were included in the LOD range from 0.001 to 0.005 mg/mL for PDD and μECD , respectively. The rest showed LODs in the range of 0.01 to 0.1 mg/mL (Table 1). Only 62 of the 107 pesticides detected using GC-PDD and μECD were detected by GC-NPD. Most of the pesticides detected by the NPD had an LOD from 0.01 to 1 $\mu\text{g}/\text{mL}$ except 13 pesticides had an LOD of 0.005 $\mu\text{g}/\text{mL}$. The number of pesticides having the lowest LOD range for PDD, μECD , and NPD was 36, 29, and 2 pesticides, respectively. The rest of the pesticides demonstrated a similar LOD when using PDD and μECD . Among them, 13 pesticides for PDD and 22 pesticides for μECD had LODs in the 0.001 $\mu\text{g}/\text{mL}$ range. Seventeen and 5 pesticides were detectable at an LOD of 0.005 $\mu\text{g}/\text{mL}$, by PDD and μECD , respectively. Myclobutanil (LOD 0.005 $\mu\text{g}/\text{mL}$) and mefenacet (LOD 0.01 $\mu\text{g}/\text{mL}$) were the only 2 pesticides that showed the lowest LOD on NPD rather than PDD and μECD . The LOD of mefenacet (0.05 $\mu\text{g}/\text{mL}$) using PDD and μECD might be not enough to satisfy the Maximum Residue Limit (MRL) 0.01 ppm of brown rice even after converting the result with a dilution factor of 4. Therefore, NPD is the best choice for the analysis of mefenacet in the brown rice among the three detectors tested.

The class of pesticides showing the lowest LODs using PDD was organochlorine pesticides including 7 pesticides such as $\gamma\text{-BHC}$. The 6 pyrethroid pesticides like cypermethrine had the second lowest LODs. The organophos-

Table 1. Relative retention time and LOD of each pesticide on GC-PDD, μ -ECD, and NPD

No.	Pesticide	Chemical class	RRT ¹⁾	LOD (mg/L)		
				PDD	μ -ECD	NPD
1	Acetochlor	Chloroacetamide	0.86	0.005	0.005	-
2	Acrinathrin	Pyrethroid	1.18	0.005	0.005	0.05
3	Alachlor	Chloroacetamide	0.87	0.005	0.005	0.01
4	Aldrin	Organochlorine	0.91	0.001	0.001	-
5	Anilofos	Organophosphorus	1.13	0.005	0.005	0.005
6	Benfluralin	Dinitroaniline	0.75	0.005	0.001	0.01
7	α -BHC	Organochlorine	0.77	0.001	0.001	-
8	β -BHC	Organochlorine	0.79	0.001	0.005	-
9	γ -BHC	Organochlorine	0.8	0.001	0.005	-
10	δ -BHC	Organochlorine	0.82	0.001	0.001	-
11	Bifenox	Diphenyl ether	1.13	0.005	0.001	-
12	Bifenthrin	Pyrethroid	1.11	0.005	0.001	-
13	Bromacil	Uracil	0.89	0.001	0.005	0.05
14	Bromopropylate	Benzilate	1.12	0.001	0.001	-
15	Butachlor	Chloroacetamide	0.97	0.001	0.005	0.05
16	Captafol	Phthalimide	1.09	0.05	0.1	-
17	Captan	Phthalimide	0.95	0.01	0.001	0.01
18	Chinomethionat	Quinoxaline	0.97	0.001	0.005	0.05
19	Chlomethoxyfen	Diphenyl ether	1.1	0.005	0.01	0.5
20	Chlonitrofen	Diphenyl ether	1.06	0.005	0.01	0.5
21	Chlorfenapyr	Pyrazole	1.02	0.005	0.005	0.1
22	Chlorobenzilate	Chlorinated hydrocarbon	1.02	0.01	0.005	-
23	Chlorothalonil	Arylnitrile	0.83	0.005	0.01	0.05
24	Chlorpyrifos	Organophosphorus	0.91	0.005	0.001	0.005
25	Cyfluthrin	Pyrethroid	1.28	0.005	0.01	0.5
			1.3			
26	Cyfluthrin-beta	Pyrethroid	1.3	0.005	0.005	0.1
27	Cyhalothrin	Pyrethroid	1.22	0.05	0.05	-
28	Cyhalothrin-lambda	Pyrethroid	1.17	0.001	0.005	-
29	Cypermethrin	Pyrethroid	1.32	0.005	0.01	0.1
			1.33			
30	Cypermethrin-alpha	Pyrethroid	1.31	0.005	0.005	0.05
			1.33			
31	Cypermethrin-zeta	Pyrethroid	1.32	0.005	0.1	1
			1.33			
32	DDD-p,p	Organochlorine	1.04	0.001	0.005	-
33	DDE-p,p	Organochlorine	1	0.001	0.001	-
34	DDT(pp' & op)	Organochlorine	0.93	0.001	0.001	-
			0.98			
35	Deltamethrin	Pyrethroid	1.54	0.005	0.005	0.1
36	Dichlobenil	Benzonitrile	0.55	0.005	0.001	0.005
37	Dichlofluanid	Sulphamide	0.9	0.005	0.01	0.05

Table 1. (continued)

No.	Pesticide	Chemical class	RRT ¹⁾	LOD (mg/L)		
				PDD	μ-ECD	NPD
38	Diclofop-methyl	Aryloxyphenoxypropionate	1.08	0.005	0.005	-
39	Diclomezine	Unknown	1.08	0.05	0.01	-
40	Dicloran	Chlorophenyl	0.78	0.001	0.005	-
41	Dicofol	Organochlorine	0.91	0.005	0.01	-
42	Dieldrin	Organochlorine	1	0.001	0.001	-
43	Difenoconazole	Triazole	1.48	0.01	0.05	1
			1.49			
44	Dimethenamid	Chloroacetamide	0.85	0.01	0.01	0.01
45	Dinocap	Dinitrophenol derivative	1.08	0.05	0.1	1
			1.09			
			1.1			
			1.12			
46	Disulfoton	Organophosphorus	0.82	0.05	0.05	-
47	Dithiopyr	Pyridine	0.88	0.005	0.001	0.05
48	Endosulfan-alpha	Organochlorine	0.98	0.005	0.001	-
49	Endosulfan-beta	Organochlorine	1.03	0.005	0.001	-
50	Endosulfan-sulfate	Organochlorine	1.07	0.001	0.001	-
51	Endrin	Organochlorine	1.03	0.001	0.005	-
52	Esfenvalerate	Pyrethroid	1.42	0.005	0.005	0.05
			1.45			
53	Ethalfuralin	Dinitroaniline	0.73	0.005	0.001	0.01
54	Etridiazole	Aromatic hydrocarbon	0.62	0.005	0.05	0.5
55	Fenarimol	Pyrimidine	1.19	0.001	0.001	0.005
56	Fenclorim	Pyrimidine	0.76	0.005	0.005	0.05
57	Fenitrothion	Organophosphorus	0.89	0.005	0.001	0.005
58	Fenpropathrin	Pyrethroid	1.12	0.005	0.005	0.1
59	Fenvalerate	Pyrethroid	1.42	0.005	0.005	0.05
			1.45			
60	Fipronil	Phenylpyrazole	0.94	0.005	0.001	0.005
61	Flucythrinate	Pyrethroid	1.33	0.005	0.005	0.05
			1.35			
62	Flusulfamid	Unknown	1.15	0.05	0.005	-
63	Fluvalinate-tau	Pyrethroid	1.45	0.005	0.01	-
			1.46			
64	Folpet	Phthalimide	0.96	0.05	0.005	0.5
65	Halfenprox	Pyrethroid	1.32	0.05	0.05	-
66	Heptachlor	Organochlorine	0.87	0.001	0.005	-
67	Heptachlor-epoxide	Organochlorine	0.95	0.005	0.01	-
68	Imazalil	Imidazole	0.99	0.01	0.05	-
69	Imibenconazole	Triazole	1.7	0.005	0.01	0.1
70	Indanofan	Unknown	1.13	0.005	0.005	-
71	Isoprothiolane	Phosphorothiolate	0.99	0.001	0.001	-
72	Linuron	Urea	0.89	0.05	0.005	-

Table 1. (continued)

No.	Pesticide	Chemical class	RRT ¹⁾	LOD (ml/L)		
				PDD	μ-ECD	NPD
73	Mefenacet	Oxyacetamide	1.35	0.05	0.05	0.01
74	Methoxychlor	Unknown	1.12	0.01	0.005	-
75	Metobromuron	Urea	0.84	0.005	0.05	0.05
76	Metolachlor	Chloroacetamide	0.9	0.005	0.005	0.01
77	Metribuzin	Triazinone	0.85	0.005	0.001	0.005
78	Myclobutanil ¹⁾	Triazole	1	0.01	0.01	0.005
79	Nitrapyrin	Unknown	0.62	0.001	0.05	-
80	Nonachlor	Unknown	0.99	0.005	0.001	-
81	Nuarimol	Pyrimidine	1.08	0.005	0.001	0.005
82	Oxadiazon	Oxadiazole	1	0.005	0.001	0.005
83	Oxyfluorfen	Diphenyl ether	1	0.001	0.001	0.05
84	Parathion-methyl	Organophosphorus	0.86	0.001	0.005	0.005
85	Pentachloroaniline	Unknown	0.85	0.01	0.001	-
86	Permethrin	Pyrethroid	1.23	0.01	0.01	-
			1.24			
87	Phenthoate	Organophosphorus	0.95	0.005	0.001	0.01
88	Phosmet	Organophosphorus	1.11	0.05	0.01	0.1
89	Pretilachlor	Chloroacetamide	0.99	0.005	0.005	0.01
90	Prochloraz	Imidazole	1.26	0.005	0.005	0.005
91	Procymidone	Dicarboximide	0.95	0.005	0.005	0.05
92	Prodiamine	Dinitroaniline	0.88	0.001	0.01	0.05
93	Profenofos	Organophosphorus	0.99	0.005	0.005	0.05
94	Propanil	Anilide	0.85	0.005	0.01	0.05
95	Prothiofos	Organophosphorus	0.99	0.01	0.001	0.5
96	Pyrazoxyfen	Pyrazole	-	0.005	0.05	0.5
97	Pyributicarb	Thiocarbamate	1.1	0.005	0.005	0.1
98	Quintozene	Chlorophenyl	0.8	0.001	0.001	-
99	Tebupirimfos	Organophosphorus	0.78	0.01	0.05	-
100	Tefluthrin	Pyrethroid	0.82	0.005	0.001	-
101	Tetradifon	Organosulfur	1.15	0.005	0.01	-
102	Thiazopyr	Pyridine	0.9	0.001	0.001	-
103	Tolyfluanid	Sulphamide	0.94	0.005	0.005	0.05
104	Tralomethrin	Pyrethroid	1.54	0.005	0.01	0.1
105	Triadimefon	Triazole	0.91	0.001	0.001	0.05
106	Trifluralin	Dinitroaniline	0.74	0.005	0.001	0.005
107	Vinclozolin	Dicarboximide	0.86	0.005	0.001	0.05

¹⁾Myclobutanil was the standard for relative retention time (RRT).

phorus pesticides, diphenyl ether and triazole pesticides showed also the lowest LOD on PDD. On the other hand, organophosphorus pesticides like chlorpyrifos were the major pesticide class showing the lowest LOD on μECD. Three dinitroaniline pesticides such as trifluralin and each 2 pesticides belong to three classes such as organochlorine, phthalimide, and pyrethroides were also among the most

sensitively detected pesticides by μECD among the three detectors.

Among the pesticides having an LOD of 0.05 μg/mL, phosmet, cyhalothrin, and captafol may be not detected by PDD at the MRL concentration 0.02 ppm specified for green peas, potato, and taro, respectively. The converted LOD of 0.0125 μg/mL might not satisfy the MRL due to

the matrix effect of the sample. In the case of captafol, LOD of μ ECD was two times higher than PDD. Therefore, a more sensitive detection method should be developed for the analysis of captafol in taro for MRL enforcement purposes in Korea.

Field sample analysis by GC-PDD In performing analyses of complex food samples, various problems can be encountered, which are caused by the matrix unavoidably present in the sample injected into the GC system. Such problems may occur both at the detector and the injector site (16). Therefore, analyses of the pesticides with various

sample matrices are necessary. To test the applicability of GC-PDD for the analysis of pesticides in agricultural products, brown rice, spinach, and mandarin oranges were selected as the representatives for cereals, vegetables, and fruits, respectively. The chromatograms of the recovered pesticides from the three sample matrices were shown in Fig. 1-3. In the case of brown rice, 18 spiked pesticides were recovered at 83-138% except prochloraz (Table 2). The recovery rate of prochloraz as low as 38% might be originated from the loss during extraction with polar solvent system (4). Prochloraz may be recovered better by stronger non-polar solvents like hexane/acetone (90:10, v/

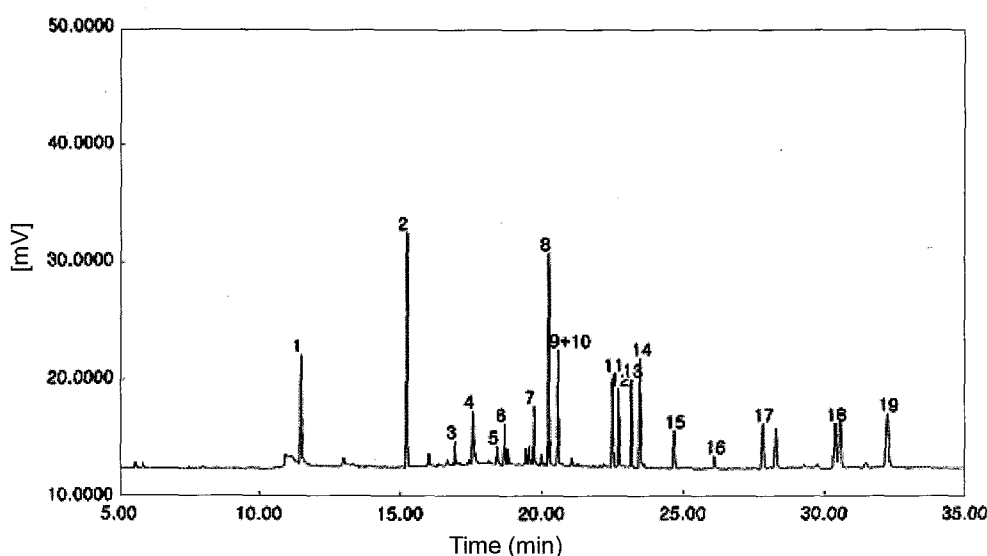


Fig. 1. Gas chromatogram of residual pesticides recovered from brown rice analyzed by GC-PDD (12.5 μ g of each pesticide was spiked into 20 g of the sample). Peak identity: 1) Dichlobenil, 2) Ethalfluralin, 3) Disulfoton, 4) Propanil, 5) Linuron, 6) Metolachlor, 7) Procymidone, 8) α -Endosulfan, 9) imazalil, 10) Captafol, 11) Pyributicarb, 12) Methoxychlor, 13) Anilofos, 14) Pyrazophos, 15) Prochloraz, 16) Flucythrinate, 17) Fluvalinate, 18) Deltamethrin.

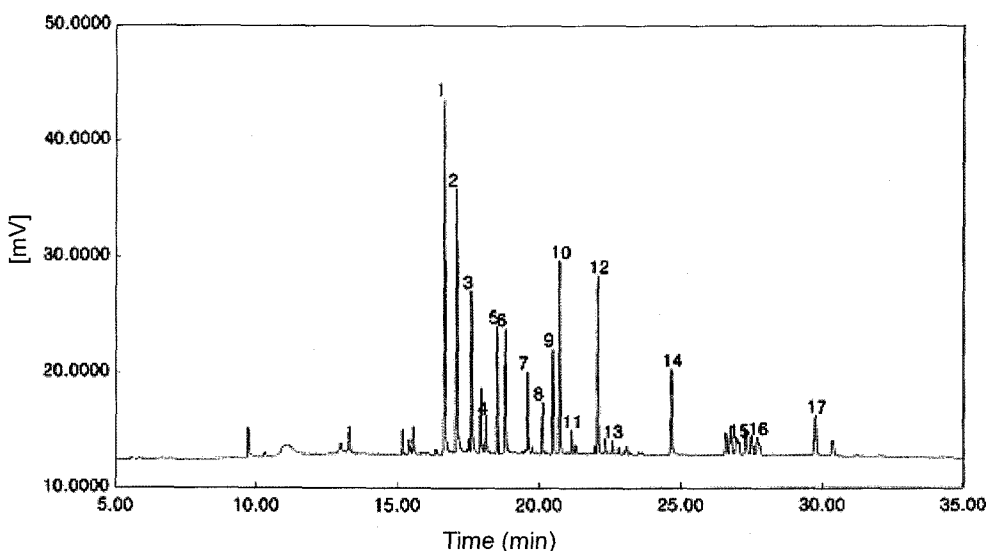


Fig. 2. Gas chromatogram of residual pesticides recovered from spinach analyzed by GC-PDD (12.5 μ g of each pesticide was spiked into 20 g of the sample). Peak identity: 1) Quintozene, 2) Chlorothalonil, 3) Metribuzin, 4) Alachlor, 5) Dichlofluanid, 6) Triadimefon, 7) Penthoate, 8) Butachlor, 9) Profenofos, 10) Dieldrin, 11) Chlorbenzilate, 12) Endosulfan-sulfate, 13) Dinocap, 14) Fenarimol, 15) Cyfluthrin, 16) Cypermethrin, 17) Fenvalerate.

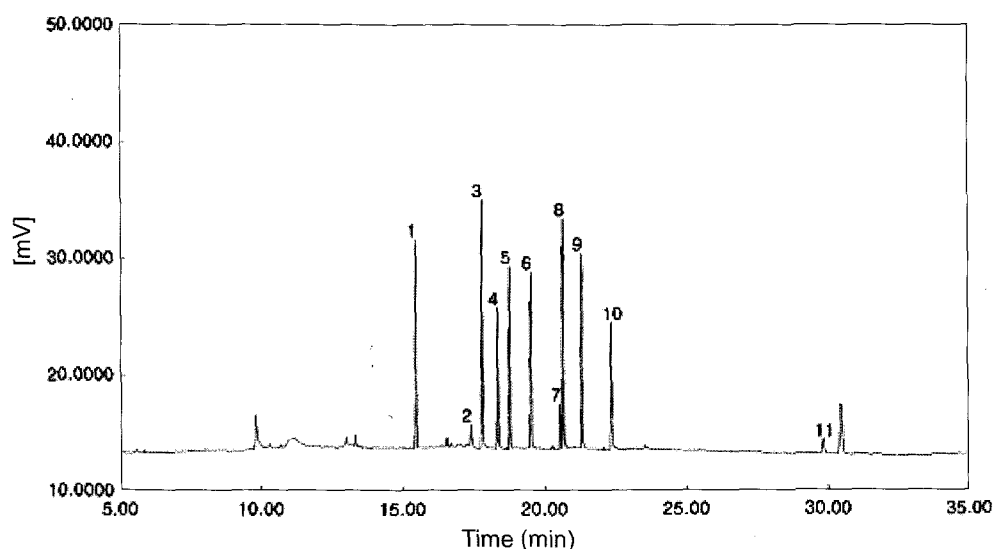


Fig. 3. Gas chromatogram of residual pesticides recovered from mandarin analyzed by GC-PDD (12.5 µg of each pesticide was spiked into 20 g of the sample). Peak identity: 1) Benfluralin, 2) Metobromuron, 3) Vinclozolin, 4) Fenitrothion, 5) Chlorpyrifos, 6) Tolyfluanid, 7) Pretilachlor, 8) Oxyfluorfen, 9) β-Endosulfan, 10) Nuarimol, 11) Esfenvalerate.

v) considering its solubility (17, 18). The spinach spiked with 17 pesticides including quitozene, which was the most frequently detected fungicide in root vegetables, was also analyzed by GC-PDD and showed recovery levels between 55 to 112% (Table 2). The pesticides recovered at levels less than 70% by GC-PDD, metribuzin, endosulfan sulfate, dieldrin, and chlorbenzilate also showed similar recovery levels by GC-µECD after preparation of samples

using the same protocol. Therefore, the low recovery levels are likely not due to the low response of the compounds in the detector. In the mandarin orange sample spiked with 11 pesticides such as nuarimol, all pesticides were recovered over the 70% (Table 2). Nuarimol was the pesticide recovered at 14.4 and 6.5% from apple and pear, respectively, by the sample preparation method of Park (4). However, it was recovered at a level of 71% using the

Table 2. Recovery data of the spiked pesticides on brown rice, spinach, and mandarin oranges by GC-PDD after preparation by modified pesticide MRM No. 83 of the Korea Food Code

Pesticides	Recovery in brown rice (%)	Pesticides	Recovery in spinach (%)	Pesticides	Recovery in mandarin (%)
Dichlobenil	98	Quitozene	103	Benfluralin	102
Ethalfuralin	95	Chlorothalonil	79	Metobromuron	84
Disulfoton	89	Metribuzin	55	Vinclozolin	92
Propanil	83	Alachlor	112	Fenitrothion	89
Linuron	90	Dichlofluanid	83	Chlorpyrifos	93
Metolachlor	98	Triadimefon	70	Tolyfluanid	95
Procymidone	109	Phenthoate	78	Pretilachlor	108
α-Endosulfan	90	Butachlor	71	Oxyfluorfen	97
Imazalil	84	Profenofos	98	Endosulfan-beta	77
Captafol	138	Dieldrin	63	Nuarimol	71
Pyributicarb	85	Chlorobenzilate	64	Esfenvalerate	87
Methoxychlor	95	Endosulfan-sulfate	60		
Anilofos	85	Dinocap	105		
Pyrazophos	122	Fenarimol	72		
Prochloraz	38	Cyfluthrin	88		
Flucythrinate	87	Cypermethrin	85		
Fluvalinate-tau	91	Fenvalerate	88		
Deltamethrin	93				

Food Code No. 83 sample preparation method followed by GC-PDD analysis. The six MRLs of nuarimol have been established for the 5 fruits such as melon and apple, and for vegetables such as, welsh onion in Korea.

In conclusion, GC-PDD showed almost equivalent or better performance than GC- μ ECD as there was a greater number of pesticides (36) that showed the lowest LOD which was greater than 29 (of 107 total pesticides) achieved using μ ECD. A total of 97 pesticides showed an LOD between 0.001 to 0.01 μ g/mL by GC-PDD which is similar to the 93 pesticides detected at the same LOD range by GC- μ ECD. The GC-PDD analysis of the spiked pesticides from the representative agricultural products, brown rice, spinach, and mandarin oranges also showed similar recoveries using GC- μ ECD. Therefore, GC-PDD (ECD mode) might suitably replace GC- μ ECD for the analysis of the residual pesticides from agricultural products.

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