Korean J. Environ. Agric.
Vol. 14, No. 1, April 1995

새로운 유도체 합성법에 의한 토양침투수중 2,4-D, dicamba 및 mecoprop의 동시 분석법에 관한 연구

홍무기 · 이희덕 · 박건상

New Esterification Method for the Simulataneous Analysis of 2,4-D, Dicamba and Mecoprop in Soil Leachates by GC/MS and GC/ECD

Moo-Ki Hong, Hee-Duck Lee, Kun-Sang Park

Abstract

Capillary gas chromatography using electron capture(EC) and mass selective(MS) detectors was used for the simultaneous quantitation of 2,4-dichlorophenoxy acetic acid(2,4-D), 3,6-dichloro-2-methoxybenzoic acid(Dicamba), and (±)2-(4-chloro-2-methylphenoxy) propionic acid(mecoprop) extracted from soil leachates. The 2,2,2-trifluoroethanol(TFE) esters of the acid analytes were synthesized using H_2SO_4 as the catalyst. Efficiency of derivatization and instrumental molecular-response were compared with herbicides methylated with BF_3-methanol(14% W/V), H_2SO_4-methanol(33% V/V), and diazomethane. The molecular integrity of TFE-2,4-D, TFE-dicamba, and TFE-mecoprop, in the mixture, was confirmed by the GC/MSD method. The TFE-Esterification efficiency was maximized by adjusting the volume of H_2SO_4 the reaction time, and temperature. Optimal efficiency for the herbicide mixture was obtained by adding 1 ml of H_2SO_4 and 1 ml of TFE to the dried sample and allowing the reaction to proceed at 22°C for 8 hr or using 0.5 ml H_2SO_4 and 1 ml of TFE at 60°C. For 120 min increasing the temperature and decreasing the reaction time were required for maximum esterification efficiency. The sensitivity of the GC/ECD to the TFE esters was about 2~20 times greater than that to the methyl ester derivatives. The herbicides were extracted and esterified to TFE derivatives simultaneously from soil leachates previously spiked with the analytes. Herbicide recovery, peak resolution, and detector sensitivity were excellent without using column cleanup procedures.

Division of food chemistry, department of hygiene, national institute of health

INTRODUCTION

Gas chromatography(GC) is one of the most sensitive, effective, and rapid analytical methods used for the investigation of pesticide residues. It is the method used most commonly for the quantitative determination of large number of samples for pesticide residues at μg L^{-1} concentrations. Although there are methods for the GC determination of most organic compounds, there is a continual search for methods that allow increased resolution in the determination of smaller quantities of analytes without intensive sample processing.

Herbicide formulation, containing mixtures of 2, 4-dichlorophenoxy acetic acid(2,4-D), 3,6-dichloro-2-methoxybenzoic acid(dicamba) and (±)2-(4-chloro-2-methylphenoxy)propionic acid(mecoprop), is commonly used for the control of broadleaf weeds in turf. To obtain the necessary information on herbicide residues remaining in the environment, it is important to develop a dependable and sensitive method for the simultaneous analysis of these three herbicides. The most common method used for the analyses of 2,4-D and dicamba is the determination of their methyl esters by GC/ECD.[1,2,3,4,5,6]

However, it is not possible to simultaneously determine the methyl esters of 2,4-D, dicamba, and mecoprop by GC/ECD, due to the low response of the ECD to methyl-mecoprop. A publication[1] reported the simultaneous determination of the three herbicides. However, this method included steps for chemical separation and esterification which are not easily followed. A more sensitive method using pentafluorobenzyl bromide(PFBBr) to esterify 2,4-D, dicamba and several other herbicides for analyses of the PFB esters by GC /ECD has been reported.[7,8] However, no study has been reported for the sequential determination of mecoprop in the presence of 2,4-D and dicamba.

Recently, a new method was developed, using TFE(2,2,2-trifluoroethanol) esterification to increase the sensitivity of mecoprop for GC/ECD analysis.[9] Based on the results for TFE-mecoprop esters, we developed a one-step esterification method for the simultaneous quantitation of 2,4-D, dicamba and mecoprop residues in soil leachates. The method is simple, rapid and safe and the herbicide esters were confirmed by mass selective detector(MSD) and analyzed by total ion chromatography(TIC) and GC/ECD.

EXPERIMENTAL PROCEDURES

Reagent. Pesticide-grade hexane, methanol, diethyl ether and acetone and analytical grade sulfuric acid were obtained from J.T. Baker(Phillipsburg, NJ). TFE, BF_3-methanol(14% W/V) and diethylene glycol monoethyl ether were purchased from Sigma Chemical Co.(St. Louis, MO). Diazald, anhydrous sodium sulfate and sodium chloride were obtained from Aldrich Chemical Co.(Milwaukee, WIS.) Mecoprop, 2,4-D, dicamba and 2,4, 5-trichlorophenoxy acetic acid(2,4,5-T) were purchased from Chem Service(West Chester,PA). All solvents and chemicals were used without further purification.

Diazomethane was synthesized from Diazald™ according to the method described in Technical Information Bulletin NO. AL-113(Aldrich Chemical Co. Milwaukee, WIS.) and stored in a freezer. The stock solution of the analytes was prepared by dissolving 100 mg pure compound in 100 ml acetone.

Diazomethane methylation. One milliliter of each analyte and 2,4,5-T(included as an internal standard) stock solution were transferred to a 10 ml vial and dried slowly under nitrogen gas. Two milliliters of diazomethane solution were added to the vial and the vial was teflon capped. The solution was gently swirled, and allowed to react at 22, 60, 80, or 100°C for 30 min. Following reaction, diazomethane was removed by nitrogen gas, two drops of methanol were added to the mixture and the solution was slowly dried under nitrogen gas. Two milliliters of hexane were added to the vial followed by 5 ml of buffer solution(0.1 M NaOH + 0.05 M $NaHCO_3$, pH 10) and the mixture was vigorously shaken. The two phases were allowed to separate and 1 ml aliquot of the hexane layer(top layer) was transferred to a volumetric flask and diluted with hexane to the final volume. All procedures involving diazomethane or BF_3 were conducted under the hood with sufficient air flow. An adjustable water bath(Blue M Co. Blue Island, IL) was used to determine the influence of temperature on derivatization efficiency.

BF_3 / Methanol Methylation. A modification of the method presented by Cessna[5] was used for analyte methylation. One milliliter of the analyte stock solution was dried slowly in a 10 ml vial under nitrogen gas. Two milliliters of the BF_3-methanol mixture were added to the herbicide solution, thoroughly mixed and allowed to react at 22, 60, 80 or 100°C for 30 min. After the reaction, the remaining BF_3 was evaporated under nitrogen gas. Five milliliters of buffer solution(pH 10) and 2 ml hexane were added to the mixture, the mixture was shaken vigorously, and two layers were allowed to separate. One milliliter of the hexane layer was pipetted into a volumetric flask and the solution was diluted to volume with hexane. The influence of temperature on reaction efficiency was determined.

H_2SO_4 / Methanol Methylation. This procedure was similar to the publication[10] and the BF_3 /methanol procedure except that 0.5 ml of H_2SO_4 and 1 ml of methanol were used as reagents.

H_2SO_4 / TFE Esterification. A mixture containing 1 ml of each analyte stock solution was dried under nitrogen gas in a vial. One milliliter of TFE and the experimental volume of H_2SO_4 were added to the vial, the vial was teflon capped, the mixture was gently swirled, and the reaction was allowed to occur at experimental times and temperatures. Following the reaction, 5 ml deionized water and 2 ml hexane were added to the vial. The vial was teflon-capped and the mixture was shaken vigorously. The remaining TFE and H_2SO_4 were easily removed in the water phase. The two liquid phases were allowed to separate and 1ml aliquot of the hexane phase was transferred to a volumetric flask and diluted to volume with hexane.

Optimization of TFE Esterification. The efficiency for the TFE-analyte formation was tested by adjusting the quantity of H_2SO_4, the reaction time, and the reaction temperature. During derivatization, the volume of H_2SO_4 was tested over a range of 0.1 ml to 2 ml; reaction time was observed from 30 min to 14 hr; reaction temperature was increased from 22°C to 100°C.

The final derivatized analyte(10mg L^{-1}) was combined with an aliquot of methyl-dicamba(internal standard) and the mixture was analyzed by GC-MS. The relative response(RR)(sample peak area/internal standard peak area) of each analyte was calculated from the results of TIC. The best

condition to make TFE derivatives was interpreted from the comparison of RR values.

Analyte Standard Concentration Curves. The standard concentration curves for the analytes were prepared from a mixture of the herbicide stock solutions according to the conditions previously determined to yield maximum efficiency. The analyte stock solution was diluted to concentrations over the range between 10 and 1000 μg L^{-1} and mixed with methyl-dicamba(100 μg L^{-1}) before the analyses by GC-ECD.

Extraction of Fortified Soil Leachate Samples. Soil leachate was obtained from lysimeters located in the greenhouse filled with a rooting mix of sand : sphagnum peat moss(85 : 15). The lysimeters subtended growth boxes that contained 'Tifdwarf' bermudagrass [Cynodan dactlon(L), transvaal ensis Burtt-Davy]. The leachates were fortified with 1 mL mecoprop, 0.2 mL 2,4-D, and 0.1 ml dicamba of the diluted stock solutions(10 ppm) to give final concentrations of 10, 2 and 1 ppb, respectively. The thoroughly mixed solution was acidified with H_2SO_4 to pH 1 in preparation for extraction. A 100 mL aliquot of the fortified leachate was uniformly stirred, transferred to a 250 mL separatory funnel, and extracted three times with 50 mL aliquots of diethyl ether while saving the diethyl ether extracts.

The ethereal extracts were dehydrated over Na_2SO_4 and concentrated to 3 mL using a Kuderna-Danish(K-D) apparatus(SUPELCO Inc, Bellefonate, PA) in a 65°C water bath. The concentrated extract was transferred to a 10 mL vial. The K-D tube and three-ball Snyder column were rinsed three times with 2 mL diethyl ether while adding the rinsate to the vial and the combined solution was dried under a gentle stream of N_2. The dry extracts were esterified using the method conditions resulting in optimum esterification efficiency for the analytes. One mL of TFE and 0.5 mL H_2SO_4 were added to the vial and reacted in a 60°C water bath for 2 hr. Methyl-dicamba was used as an internal standard because of its GC retention time not coinciding with the retention times for the TFE ester of the extracted analytes.

Apparatus. The Hewlett Packard Model 5890 gas chromatograph series II was linked to HP 3396 series II integrator and equipped with ECD. RTx-(RESTEK Inc. Bellefonate, PA) capillary column(30 m × 0.53 mm) had a coating thickness of 1 micron and a 5 m guard column connected to the entrance end. Injection port and detector temperatures were set at 250 and 300°C, respectively. Helium was used to carry analytes at a rate of 13~415ml/ min and the make up gas was 5% argon in methane. Two microliters of each sample were injected and each sample-injection was repeated. The oven temperature conditions were programmed as follows ; initial temperature, 130°C(8 min-hold) ; temperature ramp rate, 30° C/min ; final temperature, 250°C(3 min-hold) ; preinjection equilibration time, 3 min-hold.

All mass analyses were made using a Hewlett Packard 5890 GC equipped with a 5970 MSD controlled by an HP Unix MS Chemstation. We used an HP-5 fused silica capillary column(30 m × 0.25 mm id) with a film thickness of 0.25 micron and a splitless injection. The injection port and interface temperature were 230°C and 280°C, respectively. The oven temperature was controlled with an initial temperature of 80°C(3 min-hold), a programmed ramp rate, 20°C/min, to a temperature of 200°C(4 min-hold), and proceeded to 250°C(3 min-hold). The carrier gas was helium controlled at a head pressure of 90 kPa. During

the experiment, an automatic sample injector(HP model 7673) was used to inject samples(2 microliter) and each sample injection was repeated. Samples were injected in a sequence program using an intermittent solvent injection following a set of 3 samples.

RESULTS AND DISCUSSION

Esterification methods utilizing diazomethane, BF_3/methanol, and H_2SO_4/methanol have been used in the analyses of residues of phenoxyalkanoic acid herbicides. We used these methods to esterify 2,4-D, dicamba and mecoprop when analyzed by GC/MS. Diazomethane effectively methylated the three analytes(Table 1) and dicamba was not effectively esterified by the BF_3/methanol or the H_2SO_4/methanol methods because of the apparent steric hindrance to esterification for the 2,6-di-substituted benzoic acid. However, results of additional experiments indicated that increasing the concentration ratio of H_2SO_4 to methanol from 1 : 2 to a ratio of 3 : 2 increased the methylation of dicamba to an efficiency comparable to methylation of dicamba with diazomethane (data not included). Changing temperature and time of the methylation reaction did not increase the reaction efficiency(data not included). Esterification efficiency of 2,4-D and mecoprop with BF_3 /methanol responded to temperature increases up to 60°C(Table 1). When using H_2SO_4 as the catalyst, the highest esterification efficiency for these analytes occurred at 22°C and decreased at higher temperatures. These results indicate that diazomethane is the superior reagent for converting the three analytes to methyl esters and this method is effective when conducted at room temperature(ca. 22°C).

Table 1. Results of different methylation procedures for herbicides mecoprop, 2, 4-D and dicamba.

Temp./ Method	BF_3/methanol	diazomethane	H_2SO_4/methanol
(°C)	.....	RR ratio	.....
		mecoprop	
22	3.22 ± 0.19	4.74 ± 0.07	4.59 ± 0.08
60	4.73 ± 0.07	4.72 ± 0.04	4.27 ± 0.10
80	4.69 ± 0.02	4.77 ± 0.08	4.20 ± 0.12
100	4.75 ± 0.08	4.48 ± 0.10	4.10 ± 0.12
		2,4-D	
22	2.81 ± 0.07	4.46 ± 0.11	3.69 ± 0.03
60	3.81 ± 0.11	4.30 ± 0.03	3.54 ± 0.02
80	3.79 ± 0.13	4.14 ± 0.02	3.45 ± 0.04
100	3.62 ± 0.19	4.11 ± 0.03	3.54 ± 0.06
		dicamba	
22	–	5.49 ± 0.07	–
60	–	5.23 ± 0.05	–
80	–	5.08 ± 0.04	–
100	–	5.12 ± 0.11	–

RR value=peak area of analyte/peak area of 2,4, 5-T of the TIC peak.
Methyl-2,4,5-T was used as an internal standard.

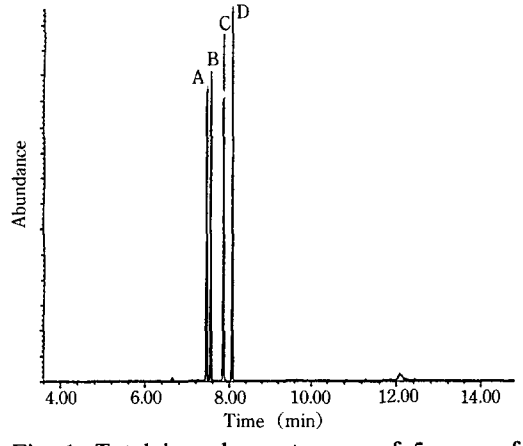

Fig. 1. Total ion chromatogram of 5 ppm of (A) TFE-dicamba, (B) TFE-mecoprop, (C) Methyl-dicamba & (D) TFE-2,4-D esters.

However, the GC/ECD response to methyl-mecoprop is not so sensitive as the responses to 2,4-D and dicamba.[9] Therefore, simultaneous analysis of the three analytes, as methyl esters, at low concentrations is not easily accomplished. To increase the response of ECD to derivatized mecoprop, the TFE/H_2SO_4 method was utilized for esterification. The previous work indicated that the TFE-mecoprop had several times higher relative responses to the GC/ECD than the methyl-mecoprop.[9] Therefore, formation of TFE esters of the analytes could result in the simultaneous quantitation of 2,4-D, dicamba and mecoprop. Following formation of the TFE ester, the derivatives were analyzed by GC/MS as a fundamental proof of molecular structure.[12] Figure 1 shows the TIC chromatogram of a sample containing 5 mg/L of the analytes as TFE ester and methyl-dicamba ester(Fig. 1-C). The products of TFE esterification are readily separated under the chromatography conditions and resulted in well defined peaks of : (A) TFE-dicamba(at 7.45 min), (B) TFE-mecoprop(at 7.57 min), (C) methyl-dicamba(at 7.85 min) and (D) TFE-2,4-D(at 8.09 min) esters. There were no apparent side products or decomposed analyte components. The TFE analyte esters were confirmed by mass spectroscopy. The mass spectra of TFE-dicamba, TFE-mecoprop and TFE-2,4-D esters are presented in Fig. 2-A, 2-B and 2-C, respectively. In the data obtained from the spectral analysis of TFE-dicmaba(Fig. 2-A), The m/z 302 corresponds to the molecular ion of TFE-dicamba ester ; m/z 203 corresponds to the molecular ion with the loss of OCH_2CF_3. The other major peak at m/z 188 and 175 corresponded to losses of OCH3 and CO2 from dicamba molecular ion. In the spectral analyses for TFE-mecoprop(Fig. 2-B), the molecular ion is at m/z

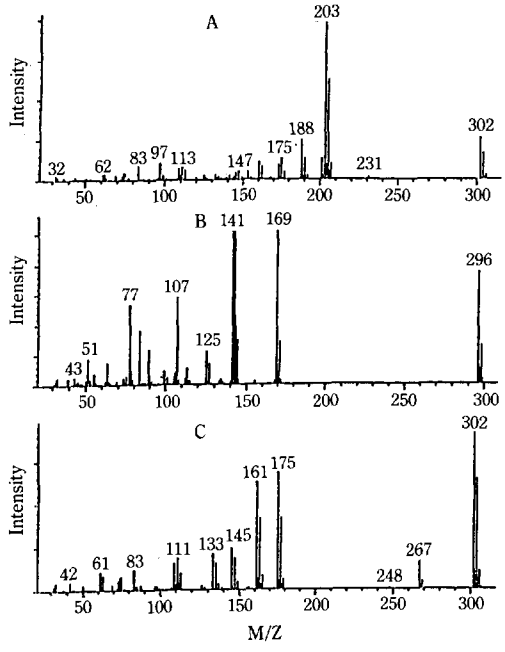

Fig. 2. Mass spectra.
(A) TFE-dicamba,
(B) TFE-mecoprop,
(C) TFE-204,D esters

296 and the major peak at m/z 169 and 141 represent the fragments with the loss of $CO_2CH_3CF_3$ and $CHCH_3CO_2CH_2CF_3$ from the molecular ion, respectively. The spectral analyses of TFE-2,4-D include the molecular ion m/z 302. The base peak at m/z 175 results from the loss of $CO_2CH_3CF_3$ from the molecular ion and the major peak at m /z 161 corresponds to the loss of CH_2 from m/z 175 fragment. These data identify the TFE esters of the analytes which have not been previously reported.

Generally, chemical derivatization for simultaneous analyses rarely results in maximum yield for all components. Therefore, we conducted experiments for determining the conditions for optimizing the derivatization of each of the analytes and ultimately describing the optimum condition

Table 2. RR* ratio of TFE esters of mecoprop, 2,4-D and dicamba formed at 3 volumes of H_2SO_4 and 6 reaction times at 22°C.

Herbicides	H_2SO_4	30min	60min	120min	240min	480min	840min
				RR ratio×10^2			
mecoprop	0.5mL	70.43± 0.07	96.40± 0.40	108.93± 1.29	120.44± 0.69	119.70± 0.38	114.09± 0.71
	1.0mL	40.54± 0.02	61.19± 1.30	85.09± 0.07	102.89± 1.41	102.61± 0.09	102.07± 2.48
	1.5mL	30.43± 0.23	44.30± 0.43	61.79± 1.21	82.04± 1.14	71.47± 1.82	67030± 1.46
2,4-D	0.5mL	91.79± 0.24	100.99± 0.73	102.90± 3.37	104.38± 0.56	102.72± 0.15	96.17± 0.97
	1.0mL	74.47± 0.23	86.83± 0.22	95.34± 2.97	95.41± 0.72	96.74± 0.99	94.06± 0.52
	1.5mL	59.72± 0.06	77.98± 0.86	88.12± 0.16	88.59± 0.85	91.72± 1.52	92.84± 0.14
dicamba	0.5mL	2.49± 0.03	3.50± 0.29	6.13± 0.29	12.76± 0.11	25.01± 0.01	38.34± 0.91
	1.0mL	39.46± 0.14	53.86± 0.07	73.86± 0.17	88.05± 0.71	96.43± 0.49	100.10± 0.80
	1.5mL	78.21± 0.85	102.05± 0.07	105.32± 1.33	105.26± 0.38	105.93± 0.56	106.80± 0.13

* RR ratio=peak area of analyte/peak area of methyl-dicamba(internal stnadard).

Table 3. RR* ratio of TFE esters of mecoprop, 2,4-D and dicamba formed at 3 volumes of H_2SO_4 and 4 reaction times at 60°C.

Herbicides	H_2SO_4	30min	60min	120min	240min
			RR ratio×10^2		
mecorop	0.5mL	95.43± 3.64	112.09± 0.84	115.52± 0.93	116.52± 0.13
	1.0mL	115.31± 0.91	89.79± 0.32	78.89± 0.36	62.97± 0.47
	1.5mL	50.71± 1.26	43.10± 1.71	22.94± 0.78	4.20± 0.41
2,4-D	0.5mL	96.16± 1.71	98.11± 0.30	99.56± 0.63	101.95± 1.24
	1.0mL	98.78± 1.22	91.36± 0.76	91.43± 1.35	91.13± 0.16
	1.5mL	91.01± 0.40	91.50± 0.86	86.59± 2.07	82.75± 1.34
dicamba	0.5mL	93.18± 1.64	94.31± 1.65	98.09± 1.54	99.03± 0.40
	1.0mL	85.11± 2.00	91.91± 1.70	89.20± 1.61	82.99± 0.13
	1.5mL	96.74± 2.38	97.84± 0.83	89.61± 0.27	67.80± 0.87

* RR ratio=peak area of analyte/peak area of methyl-dicamba(internal stnadard).

for the simultaneous analyses of the three analytes.

When conducting the esterification at 22°C, increasing the H_2SO_4 content increased reaction efficiency only for dicamba(Table 2) This response is similar to that of dicamba methylation to increased concentration of H_2SO_4. Additionally, most reaction efficiencies for the three analytes tended to increase with the increase in reaction time. A maximum reaction efficiency occurs, for the three analytes, at a H_2SO_4 amount up to 1.0 mL and the amounts larger than 1.5 mL would result in a decay of the product over times. Generally, maximum reaction efficiency was obtained in the reaction for 480 min and increasing time of reaction above 480 min increased the reaction efficiency only for dicamba when reacted with 1.0 mL of H_2SO_4.

Increasing the reaction temperature to 60°C (Table 3) changed the efficiency of the reaction compared with the reaction conducted at 22°C. Generally, maximum reaction efficiency occurs, for the three analytes, when using 0.5 mL of H_2SO_4 with the sufficient reaction time. The reaction efficiency for analytes in 1.0 and 1.5 mL H_2SO_4 decreased with the increase of time at 60°C(Table 3). These data indicate that maximum efficiency for forming TFE esters of the three analytes occurs after 120 min reaction time when catalyzed with 0.5 mL of H_2SO_4 and reacted at 60°C. Therefore, increasing the reaction temperature from 22 to 60°C, the reaction time for maximum efficiency is reduced from 480 to 120 min when using 0.5 mL of H_2SO_4. Additionally, the reaction time can be reduced to 30 min at a reaction temperature of 60°C when increasing the H_2SO_4 content from 0.5 mL to 1.0 mL to obtain maximum reaction efficiency for mecoprop and 2,4-D. The RR for dicamba obtained at a reaction time of 30 min, a reaction temperature of 60°C, and H_2SO_4 volume of 1.0 mL is slightly lower than other values.This can not be explained. The data indicate that several combinations of catalyst volume and reaction time and temperture can be used to obtain a high reaction efficiency. We chose to conduct the reactions using 1 mL of TFE and 0.5 mL of H_2SO_4 at 60°C for 2 hr. The relative responses of the GC/ECD to the derivatized analytes are presented in Table 4. Both peak area and height were computed and listed. The relative detector responses were estimated on the basis of the detector response to methyl-mecoprop which was designated as 1 and the relative response of the detector to the other derivatized analytes is calculated according to this base. The responses of all TFE esters are much better than the methyl esters of respective analytes in the GC/ECD. TFE-mecoprop resulted in an increase in detector response of 20 times greater than the response to methyl-mecoprop. When comparing the methyl esters of the analytes, the detector responses to TFE-2,4-D and TFE-dicamba are 34

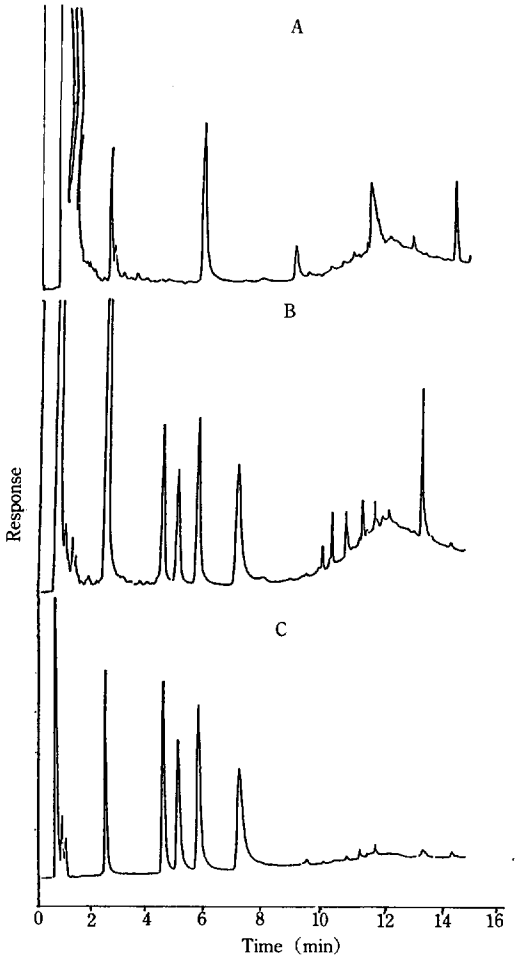

Fig. 3. Typical gas chromatograms of the extract of (A) soil leachate containing methyl-dicamba without other analytes (B) soil leachate containing analytes and methyl-dicamba and (C) soil leachate containing the same concentration of analytes methyl-dicamba.

Table 4. Relative detector response for analyte esters(methyl-mecoprop=1).

Herbicides	Peak Area		Peak Area	
	Methylation	TFE esterification	Methylation	TFE esterification
mecoprop	1	20	1	20
2,4-D	34	114	31	67
dicamba	96	157	92	194

The methylation was made by diazomethane method.
The results were obtained by comparing $0.1 ngL^{-1}$ of each ester.

and 96 times greater than the response to methyl-mecoprop, respectively. Whereas, the same comparisons with the respective TFE esters yield factors of differences of 6 and 8, respectively. The increased sensitivities of the analytes, when using TFE esters, compared with the methyl esters and the reduced differences in derivatized analyte responses in the ECD allow the potential of simultaneous analyses of analytes at very low concentrations in soil water. The residues of 2,4-D, dicamba and mecoprop in soil leachate, following fortification to a concentration of 1 μg/L, were extracted and esterified. The esters were analyzed by GC/ECD and typical chromatograms of these analyses are presented in Fig. 3. Fig. 3A is the chromatogram of methyl-dicamba(internal standard) added to soil leachate void of additional analytes. The retention time for methyl-dicamba is 5.5 min. The chromatogram has a clean baseline from retention times of 4 to 8 min, which are the range of retention times for the TFE esters of the three analytes. The chromatograms of the analytes extracted from the soil leachate and derivatized with TFE along with the internal standard(methyl-dicamba) are shown in Fig. 3B. The retention times for TFE-dicamba, TFE-mecoprop and TFE-2,4-D are 4.2, 4.8 and 6.9 min, respectively. The chromatogram in Fig. 3C is the results of the esterified standard solution of the three analytes with TFE and methyl-dicamba analyzed by GC/ECD. The peak at retention times of 4.2, 4.8, 5.5 and 6.9 represent TFE-dicamba, TFE-mecoprop, methyl-dicamba and TFE-2,4-D, respectively. These data indicate good separation of the peaks resulting from derivatized analytes with TFE and a good fit for using methyl-dicamba for the internal standard.

Standard concentration curves were developed for the TFE-analytes to determine the recovery from leachate extraction. All curves had an R2 greater than 0.99. The average recovery for the extraction of the spiked leachates was 80, 90 and 98% for mecoprop, dicamba and 2,4-D, respectively. The lower recovery for mecoprop can not be explained, nevertheless, 80% recovery is considered adequate. Data included in this manuscript indicate that TFE derivatization of 2,4-D, mecoprop and dicamba is an effective method for the simultaneous analyses of these three analytes in soil water. The method of extraction and analyses is simple, effective and reproducible for the three analytes.

LITERATURE CITED

1. Khan, S. U. (1975) ; Electron Capture Gas-Liquid Chromatographic Method for the Simultaneous Analysis of 2,4-D, Dicamba and

Mecoprop Residues in Soil, Wheat and Barley, *J. Assoc. Off. Anal. Chem.* **58**, 1027~1031

2. Siltanen, H., Mutanen, R. (1985) ; Formation of Derivatives of Chlorophenoxy Acids and Some Other Herbicides. *Chromatographia,* **20**, 685~688
3. Cessna, A. J., Grover, R., Kerr, L. A., Aldred, M. L. (1985) ; A Multiresidue Method for the Analysis and Verification of Several Herbicides in Water, *J. Agric. Food Chem.* **33**, 504~507
4. Gurka, D. F., Shore, F. L., Pan, s., Amick, E. N. (1986) ; Single-Laboratory Validation of EPA Method 8150 for Determination of Chlorinated Herbicides in Harardous Wast, *J. Assoc. Off. Anal. Chem.*, **69**, 970~975.
5. Cessna, A. J. (1990) ; The Determination of Residue of 2,4-D in Post-emergence-Treated Triticale, Pestic. Sci. **30**, 141~147
6. Ngan, F., Ikesaki, T. (1991) ; Determination of Nine Acidic Herbicides in Water and Soil by Gas Chromatography Using an Electron-Capture Detector, *J. Chromatogr.* **537**, 385~395
7. Chau, A. S. Y., Terry, K. (1976) ; Analysis of Pesticides by Chemical Derivatization III. Gas Chromatographic Characteristics and Condition for the Formation of Pentafluorobenzyl Derivatives of Ten Herbicidal Acids, J. Assoc. Off. Anal. Chem. **59**, 633~636
8. Lee, H. B., Stokker, Y. D., Chau, A. S. Y. (1986) ; Chemical Derivatization Analysis of Pesticide Residues, X. Analysis of Ten Acid Herbicides in Natural Water, J. Assoc. Off. Anal. Chem. **69**, 557~560
9. Lee, A. S., Hong, M. K., Smith, A. (1994) ; Improved Esterification of MCPP for Sensitive Detection on Capillary GC/MS and GC/ECD, *J. Assoc. off, Anal. Chem. International* **77**(5) 1077~1083
10. Hong, M. K. (1994) ; Studies on the Analytical Methods and Quantity of Residual 2,4-D in Imported Fruits, *J. Fd. Hyg.* **9**(2), 89~94
11. Cairn, T. Regulatory Mass Spectrometry for Pesticide Residues Analysis (1992) ; Past, Present, and Future, *J. Assoc. Off. Anal. Chem. International,* **75**, 591~593.