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토양 침투수중 MCPP의 유도체화 및 잔류분석

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Derivatization and Residual Determination of MCPP in Soil Leachate

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Abstract

Analytical methods for the determination of the derivatives of the herbicide (±)-2-(4-chloro-2-methylphenoxy)propionic acid (MCPP) by capillary column gas chromatography with mass spectrometer (GC-MS) and electron-capture detection (GC-ECD) were studied. A successful procedure was introduced for the ester preparation using H_2SO_4 as the catalyst and the alcohol 2,2,2-trichloroethanol (TCE) or 2,2,2-trifluoroethanol (TFE). The identificaiton and elucidation of MCPP by GC-MS spectrometry following the esterification with diazomethane, BF_3/methanol, H_2SO_4/methanol, TCE, TFE, or pentafluorobenzyl bromide (PFB) were carried out. A comparison of the response-sensitivities among those MCPP esters was made with GC-ECD. Although the methylation product of MCPP was confirmed by GC-MS, its low sensitivity to the ECD limited the detection of MCPP. TCE, TFE, and PFB derivatization methods resulted in a high rate of MCPP esterifications and very sensitive ECD molecular responses. Based on efficiency, convenience, worker safety, and least sample contamination, TFE esterificaiton was considered as the superior method for MCPP analysis to the other methods of derivatization. An accurate method is described for quantifying MCPP in soil leachates by GC-ECD at very low concentrations without the requirement of a complicated clean-up process. As a result, MCPP residues at concentrations of less than 0.1μg in 100 ml soil leachate were detected.

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Introduction

(±)-2-(4-chloro-2-methylphenoxy) propionic acid (MCPP), a phenoxy acid herbicide, is extensively used for maintenance of home lawns and golf courses. This is due to its selective weed-control efficiency and low mammalian toxicity. Either high polarity or low volatility of MCPP makes it ineffective to be analyzed by gas chromatography (GC) without generating a more volatile derivative. Serveral methods for the preparation of derivatives of herbicides, to facilitate GC analysis, have been reviewed by Cochrane[1]. A few methods for esterifying MCPP have been studied. Most of them involve methylation with diazomethane[2-5], BF_3/methanol mixture[6,7], and fuming sulfuric acid/ethanol[8]. The formation of methyl-MCPP using diazomethane was confirmed by GC-mass selective detection (MS) in this study. The U.S. Environmental protection Agency (EPA) method for MCPP determination[4] uses diazomethane methylation for GC-ECD analysis. This method is considered dangerous by many university safety officers and methyl-MCPP results in a low response when analyzed by GC-ECD. When the fate of pesticides is determined in the environment, it is of great importance to use methods that are very sensitive and accurate.

MCPP derivatives, prepared to improve the sensitivity and selectivity of subsequent detection by GC-ECD, include the formation of 2-chloroethyl-MCPP[9], 2,2,2-trichloroethyl (TCE)-MCPP[10] and pentafluorobenzyl (PFB)-MCPP[11]. Unfortunately, these procedures have complicated cleanup procedures which eliminate their utility when large numbers of samples are processed. A recent study[12] using BF_3 as the catalyst, indicated that BF_3/2,2,2-trifluoroethanol (BF_3/TFE) failed to react with MCPP and dicamba (3,6-dichloro-2-methoxybenzoic acid), which elicited our attempt to apply H_2SO_4/TFE for formation of TFE-MCPP.

This communication reports the development of a simple and practicable method for derivatizing MCPP with TFE, while using H_2SO_4 as the catalyst. The formation of the resulting ester was confirmed by GC-MS. The sensitivity of the TFE ester was compared with other esters by GC-ECD. The method was evaluated further with MCPP residue extracted from a soil leachate.

Experiment

Reagents

Pesticide-grade hexane, methanol, diethyl ether, acetone, and analytical grade sulfuric acid were purchased from T.J. Baker (Phillipsburg, NJ). TFE, TCE, PFB_{Br}, BF_3/methanol mixture (14% w/v), and diethylene glycol monoethyl ether were obtained from Sigma Chemical Co. (St. Louis, MO). Diazald, anhydrous sodium sulfate, sodium chloride, and potassium carbonate were obtained from Aldrich Chemical Co. (Milwaukee, WIS). Pure MCPP, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and dicamba were purchased from Chem Service (West Chester, PA, 100%). Diazomethane was made according to the method described in Technical Information Bulletin No. AL-113 (Aldrich Chemical Co. Milwaukee, WIS).

The stock solution of MCPP was prepared by dissolving 0.1g in 100 ml acetone in a 100 ml volumetric flask and the calibration standards were developed by diluting and derivatizing the stock solution to concentrations over a range of 0.005 to 1.0mg L^{-1} MCPP in hexane.

Diazomethane methylation

One milliliter of the stock solution of MCPP was placed in a 10 ml teflon-capped vial and dried slowly under N_2. Diazomethane solution (2 ml) was added to the vial, the vial was swirled gently for 1 min, and allowed to react at room temperature (ca. 23°C) for 30 min. The remaining diazomethane was evaporated under a gentle N_2 stream, and two drops of methanol were added to the solution which was completely dried with N_2. Two milliliters of hexane were added to the vial followed by ca. 5 ml of buffer solution (0.1 M NaOH + 0.005 M $NaHCO_3$) (pH-10) and the mixture was vigorously shaken. The two phases were allowed to separate and a 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.

Methylation-reaction temperatures were controlled in an adjustable water bath (Blue M Co. Blue Island, IL). This same method was used for preparing the methyl esters of 2,4,5-T and dicamba.

BF_3/methanol methylation

One milliliter of the MCPP stock solution was transferred to a 10 ml teflon-capped vial and dried slowly under N_2. Two milliliters of the BF_3 /methanol mixture were added to the vial and the vial was capped tightly, thoroughly mixed, and allowed to react at 23, 60, 80 and 100°C for 30 min. After the reaction, the remaining BF_3 was evaporated under N_2 for 30 sec. Five milliliters of buffer solution (pH-10) and 2 ml hexane were added to the methanol solution, vigorously mixed, and allowed to partition. One milliliter of the hexane layer was pipetted into a volumetric flask and the solution was diluted to volume with hexane.

H_2SO_4/methanol methylation

This procedure was similar to the BF_3/methanol method except that 0.5 ml of H_2SO_4 and 1 ml of methanol were used as reagents.

H_2SO_4/TFE esterification

One milliliter of the MCPP stock solution was dried in a teflon-capped vial under N_2 and 0.5 ml H_2SO_4 and 1.0 ml TFE were added to the vial. The vial was capped tightly, the mixture was gently swirled and the reaction was allowed to occur at room temperature for 30 min. Following the reaction, 1 ml saturated aqueous NaCl solution, 4 ml deionized water, and 2 ml hexane were added to the vial and the vial was shaken vigorously. The two liquid phases were allowed to separate and 1 ml of the hexane layer was transferred to a volumetric flask and diluted to volume with hexane.

Reaction times of 30, 60, 120, 240, and 480 min were tested to maximize the efficiency of esterificaiton.

H_2SO_4/TCE esterification

This procedure was similar to the procedure used for the formation of MCPP-TFE ester with the addition of a 16 hr period to the time of reaction experiment and the use of TCE for derivatization of MCPP. The temperature was increased to 60°C for 30, 60 and 120 min to confirm the completion of the reaction.

PFB esterification

A modification of the method presented by Chau and Agemian[11] was used. One milliliter of the MCPP stock, 0.2 ml PFB_{Br} (1% v/v), and 2 drops of aqueous potassium carbonate (30% w/v) solutions were added to a 10 ml vial. The capped vial was vigorously shaken for 1 min and allowed to complete the reaction at room temperature for 30 min. Following the reaction, 2 ml hexane, 1 ml saturated aqueous NaCl solution, and 4 ml deionized water were added to the vial. The solution was shaken vigorously for 1 min and 1 ml of the hexane layer was transferred to a volumetric flask and diluted to volume with hexane.

Several reaction periods were tested to determine the most efficient conditions for forming the PFB derivative.

Extraction of fortified soil leachate samples

The soil leachate was obtained from lysimeters constructed in the greenhouse[13] and filled with a rooting mix of sand: sphagnum peat moss (85 : 15). The lysimeters subtended growth boxes that contained 'Tifdwarf' bermudagrass [*Cynodon dactylon* (L) Pers. × *C. transvaalensis* Burtt-Davy〉. Soil leachate was fortified using the stock solution of MCPP to give a final concentration of 5μg L^{-1}. The thoroughly mixed solution was filtered using Whatman (Hillsboro, OR) filter paper (GF/A) and homogenized for 30 min before extraction.

A 100 ml aliquot of the fortified leachate was acidified with 2 ml of conc. H_2SO_4 to pH 1~2. The 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 combined ether extracts were dehydrated over anhydrous Na_2SO_4 and concentrated to approximately 3 ml using a Kuderna-Danish (K-D) apparatus (SUPELCO Inc. Bellefonte, PA) in a 60°C water bath. The K-D tube and three-ball Snyder column were rinsed three times with 2 ml diethyl ether and the rinsate is dried under a stream of N_2. The extracted MCPP was esterified according to the methods previously described.

Apparatus

The Hewlett Packard Model 5890 gas chromatograph (Hewlett Packard Inc. Sunnyvale, CA) series II was linked to an HP 3365 series II ChemStation and was equipped with an electron captecter (ECD). The Rtx-1 (RESTEK Inc. Bellefonte, PA) capillary column, 30 m × 0.53 mm id, had a coating thickness of 1 micron and a 5 m guard column connected to the entrance end. The column was connected to the ECD. Injection port and detector temperatures were 250 and 300°C, respectively. Helium was used to carry analytes at a rate of 13−15 ml min^{-1}. The make-up gas was 5% argon in methane. Two microliters of each sample were injected and each sample-injection was repeated. Oven conditions were adjusted for each herbicide ester.

The oven temperature conditions for the esters were: (a) TFE esters-initial 130°C (6 min-hold), programming rate 30°C min^{-1}, final 250°C (5 min-hold); (b) methyl esters-initial 150°C (5 min-hold), programming rate 30°C min^{-1}, final 250°C (5 min-hold); (c) TCE esters-initial 180°C (8 min-hold), programming rate 30°C min^{-1}, final 250°C (5 min-hold); (d) PFB esters-initial 190°C (7 min-hold), programming rate 20°C min^{-1}, final 250°C (3 min-hold).

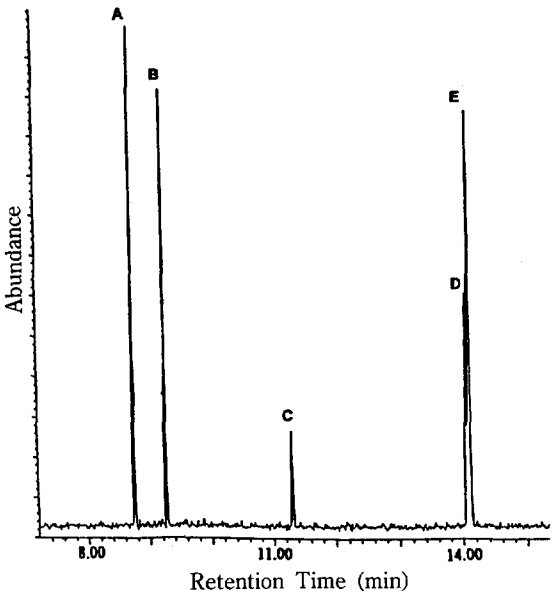

Fig. 1. Total ion chromatograms of (A) TFE-MCPP, 2mg L^{-1}; (B) Methyl-MCPP, 2mg L^{-1}; (C) Methyl-2,4,5-T, 1mg L^{-1}; (D) TCE-MCPP, 2mg L^{-1}; (E) PFB-MCPP, 2mg L^{-1}.

The mass selective detector (MSD) was a Hewlett Packard 5890 GC equipped with a 5971A MSD controlled by an HP G1034B 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 temperatures were 230°C and 280°C, respectively. The oven temperature was controlled with an initial temperature of 80°C (3 min-hold), a program rate of 20°C min^{-1} to a temperature of 200°C (4 min-hold), and proceeded to 250°C (3 min-hold). The carrier gas was helium, and set at a head pressure of 90 kpa. Two microliters of each sample were injected using an automatic sample injector (HP 7673). Each sample injection was repeated. Samples were injected in a sequence program using an intermittent solvent injection following sets of three samples.

Results and Discussion

The methylation of MCPP with BF_3/methanol[6], diazomethane[5], and H_2SO_4/methanol was carried out. There has been no report on the methylation of MCPP with H_2SO_4/methanol. However, the relative response (RR) value, peak area of analyte per peak area of internal standard, for the product from the H_2SO_4/methanol method was comparable to methyl-MCPP formed according to the BF_3/methanol method. During preparation, the same reaction time (30 min) but different reaction temperatures were used to determine the optimum reaction temperature for each method. The synthesized esters and a certain concentration of methyl-2,4,5-T, the internal standard, were injected into the GC-MS to verify the product and quantify the efficiency of the esterification method. The product was identified by comparison of the mass spectra with the respective spectra in a reference library (G1034C MS ChemStation, Hewlett Packard). The data from the total ion

Table 1. Comparison of the methylation methods of MCPP.

Temp./ Reagent	RR*		
	BF_3/methanol	Diazomethane	H_2SO_4/methanol
23	3.23 (±0.19)	4.74 (±0.07)	4.59 (±0.09)
60	4.73 (±0.07)	4.72 (±0.04)	4.27 (±0.11)
80	4.65 (±0.02)	4.77 (±0.08)	4.21 (±0.12)
100	4.68 (±0.08)	4.48 (±0.10)	4.10 (±0.18)

* RR (from the TIC)=peak area of analyte/peak area of methyl-2,4,5-T (internal standard). RR values represent the average of four experiments and standard deviations in parenthesis.

chromatogram (TIC) of MSD are presented in Table 1. The RR value is an analytical parameter determined from the ratio of the peak areas of methyl-MCPP to those of methyl-2,4,5 T. The data indicate that the methylation of MCPP by diazomethane and H_2SO_4/methanol reached an optimum at room temperature (Table 1). Increasing the temperature from room temperature to 60°C during methylation by the BF_3/methanol method improved the methylation efficiency. Further increases in temperature did not influence efficiency of this method and increasing the temperature above room temperature did not improve the efficiency of esterification by the diazomethane or H_2SO_4/methanol methods. The higher temperatures resulted in the formation of side-products for the H_2SO_4/methanol method. Increasing the temperature above room temperature for the diazomethane method resulted in crystallization in the solution which could produce an explosion[14]. According to the results shown in Table 1, it was concluded that the three methods can be applied for the methylation of MCPP.

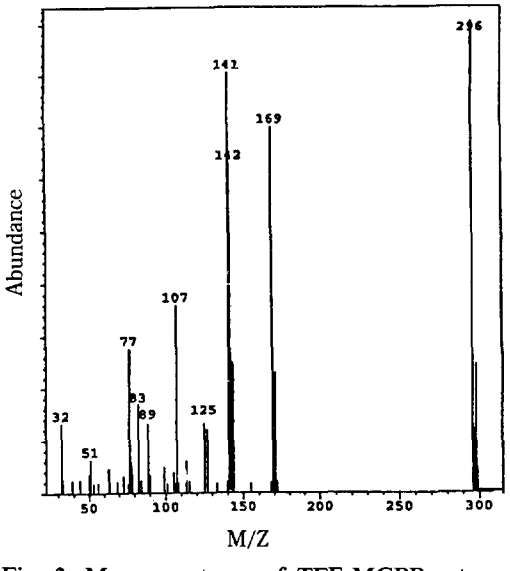

Fig. 2. Mass spectrum of TFE-MCPP ester.

Table 2. Molecular peak and base peak of herbicide esters in mass spectra.

Ester	Molecular peak(M/Z)	Major peaks(M/Z)
Methyl-MCPP	228	169*, 142, 107
TFE-MCPP	296	169, 141*, 107
TCE-MCPP	346	169*, 142, 107
PFB-MCPP	394	181, 169*, 142

* Indicates the base peak in the spectrum.

Table 3. Comparison of the esterification methods of MCPP

Time/ Reagent	RR*		
	TCE	TFE	PFB
30min	0.42 (± 0.02)	3.36 (± 0.04)	3.55 (± 0.31)
60min	1.55 (± 0.02)	5.61 (± 0.10)	7.10 (± 0.12)
120min	2.16 (± 0.04)	7.06 (± 0.16)	9.01 (± 0.11)
240min	3.60 (± 0.21)	6.94 (± 0.23)	9.70 (± 0.30)
480min	5.31 (± 0.11)	7.07 (± 0.20)	9.60 (± 0.19)
960min	5.57 (± 0.05)		

* RR(from the TIC)=peak area of analyte/peak area of methyl-2,4,5-T(internal standard).
RR values represent the average of three expe-riments and standard deviations in parenthesis.

Although the methylation of MCPP could be accomplished, the responses of the respective MCPP derivatives to ECD measurement were not sensitive enough for residue analysis. Figure 2 represents the mass spectrum of TFE-MCPP. This spectrum has not been previously published. The major ions on the spectrum are: m/z 296 (molecular ion), m/z 169 (TFE-MCPP less TFE-carboxylic ion), m/z 141 and 142 (TFE-MCPP less ethyl TFE-carboxylic ion), m/z 107 (m/z 142 less Cl ion), m/z 125 and 83 (TFE ion fragmentation), m/z 77 (MCPP ion fragmentation). According to the above description, the

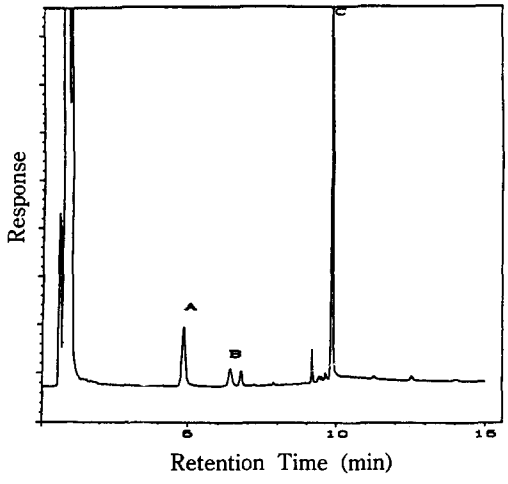

Fig. 3. Gas chromatogram of MCPP derivatives (A) 100μg L^{-1} TFE ester; (B) 500μg L^{-1} methyl ester; (C) 25μg L^{-1} TCE & PFB esters.

TFE-MCPP can be identified and confirmed. The esterification could be complete simply without using sophisticated equipments.

Different reaction times were tried during the preparation to determine an optimum reaction period. Table 3 lists the relative response of TCE-MCPP, TFE-MCPP, PFB-MCPP using methyl-2,4,5-T as the internal standard for determination of the RR values. The TFE-MCPP esterification reaction reached maximum in 2 hr. The PFB-MCPP required about 4 hr to reach a reaction maximum and TCE-MCPP reaction requires more than 8 hr to reach a maximum. The saturated state was confirmed by increasing reaction temperature to 60 °C during the TCE-MCPP preparation.

The sensitivity of MCPP esters to GC-ECD detection was investigated (Fig. 3). The temperature program described in Experiment section (a) was used for this mixture. The separation and retention time of the products were acceptable except that between TCE-MCPP and PFB-MCPP (Fig. 3-C) and these analyses were conducted individually.

Table 4. The sensitivity of MCPP derivatives measured with GC-ECD.

Ester	Peak area integration	Peak height integration
Methyl-MCPP	1	1
TFE-MCPP	80	140
TCE-MCPP	660	700
PFB-MCPP	1130	1240

Estimated minimum detection : 1.0 ppb × 2 μL injection for TFE derivatives. Data obtained from the comparison of 100 ppb sample's responses.

The relative detection limits were obtained by the measurement of each MCPP derivative (100 μg L^{-1}) with GC-ECD. The results given in Table 4 were compared by setting the response of methyl-MCPP as 1. As expected, PFB and TCE derivatives resulted in higher detector responses compared to the other esters. TFE-MCPP was not so sensitive as the PFB and TCE derivatives of MCPP. However, it resulted in ca. 100 times greater response than methyl-MCPP. The estimated limit of detection for TFE-MCPP was 2 pg (2 μL injection of 1 μg L^{-1} sample).

These results indicate that the three methods of esterification of MCPP (TFE, TCE, and PFB) are superior to diazomethane methylation. We tested these methods for determining MCPP in a soil leachate and for forming products that will interfere during GC-ECD analyses. Concentration response curves were developed for TFE-MCPP, TCE-MCPP, and PFB-MCPP using methyl-dicamba as the internal standard for TFE-MCPP and methyl-2,4,5-T as it for TCE-MCPP and PFB-MCPP. The different internal standards used were for the convenience of measurement. The

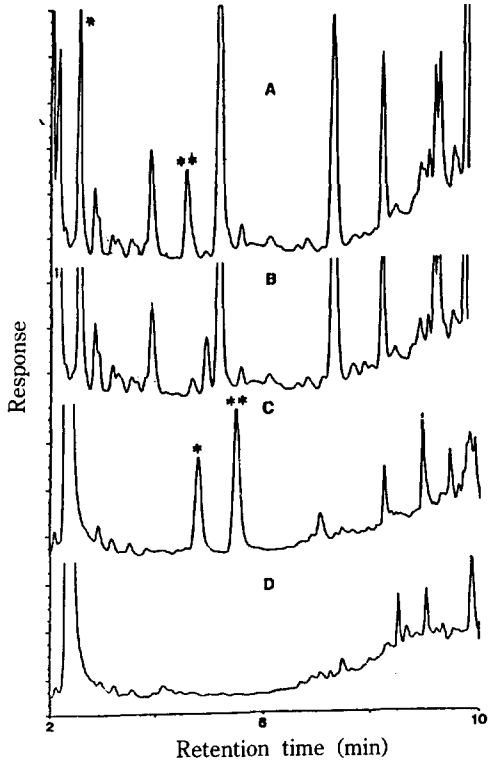

Fig. 4. Gas chromatograms of soil leachate samples (A) 100μg L^{-1} methyl-2,4,5-T, retention time 2.50min(*) ; 250μg L^{-1} PFB-MCPP, retention time 4.65min (**) ; (B) leachate with PFB only ; (C) 250μg L^{-1} TFE-MCPP, retention time 4.81min(*) ; 100μg L^{-1} methyl-dicamba, retention time 5.52min(**) ; (D) leachate with TFE only.

temperature program conditions during chromatography were selected to obtain product peaks without interference. The RR was linear over the concentration range of 5.0 to 250 μg L^{-1} (R^2>0.99) for all concentration response curves (curves not included). Fortified (5 μg L^{-1}) soil leachate was used for testing the derivatizing methods. Different reaction times were used to ensure reaction optimization. TFE-MCPP and TCE-MCPP esters were developed at a temperature of 60°C for 2 hrs. PFB-MCPP ester was reacted for 8 hrs at room temperature. Figure 4 shows the extraction results of 100 ml spiked (Fig. 4A and 4C) and nonspiked-blank (Fig. 4B and 4D) soil leachates. The scale in Fig. 4A and 4B is 10 times smaller than their real values. PFB-MCPP (Fig. 4A) gave a very strong response (ca. 120% recovery) to ECD. However, it was noted that this method resulted in numerous foreign peaks on the chromatogram. This was also seen in Fig. 4B, which would require a cleanup procedure before it could be reliably used. The TCE-MCPP method gave similar results (data not shown). Figure 4C shows the result of TFE-MCPP method for derivitization of MCPP in soil leachate. The chromatogram indicates a good peak separation with no interference from peaks of foreign substances in the leachate. The average recovery was above 90 % from soil leachate. Compared to the TCE and PFB methods for esterifying MCPP, the TFE method resulted in slightly less molecular response, in the ECD, but resulted in a much cleaner chromatogram.

According to the preparation procedure and residue esterification results described above, a method has been developed for analyzing MCPP in soil leachate. The TFE method is simple, safe, economical, and has a low detection limit (≤2 pg by GC-ECD analysis).

요 약

토양 침투수중에 잔류하는 제초제 MCPP를 추출, 유도체를 합성하여 GC-MS로 확인하고 capillary GC-ECD로 잔류분석하였다. Diazomethane과 BF_3/MeOH 등을 이용하여 합성한 MCPP의 methyl 유도체, 황산을 촉매로 이용하여 합성한 MCPP의 2,2,

2-trifluoroethyl(TFE) 및 2,2,2-trichloroethyl(TCE) 유도체, 그리고 MCPP의 pentafluorobenzyl(PFB) 유도체간의 잔류분석법을 비교한 결과 이 연구에서 개발된 MCPP-TFE 유도체화가 간편하고 신속, 안전한 유도체화 기술로서 GC-ECD에서 비교적 감도가 우수한 편이었다. MCPP의 methyl 유도체는 GC-ECD에서 그 감도가 너무 낮아 시료가 소량인 경우 ppb 수준의 잔류분석이 불가능하였고 MCPP-TCE 및 MCPP-PFB 유도체는 그 감도는 우수하였으나 크로마토그람상의 방해물질이 많아 액액분리에 의한 정제만으로는 잔류분석이 곤란하였다. MCPP-TFE 유도체화에 의하면 토양침투수 100 ml 중 0.1μg 미만의 농도를 가진 MCPP의 잔류분석이 액액분리에 의한 정제만으로 가능하였다.

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