Method for the Determination of Glyphosate and (Aminomethyl)phosphonic Acid in Soil Using Electron Capture Gas Chromatography

Philip L. Eberbach*,† and Lyle A. Douglas

School of Agriculture and Forestry, University of Melbourne, Parkville, Victoria 3052, Australia

A procedure for extraction of the phosphonic acid herbicide glyphosate and its metabolite (aminomethyl)-phosphonic acid from soils and for analysis of these two compounds by electron capture gas chromatography is described. Both compounds were extracted from the soil with aqueous triethylamine, cleaned up with anion- and cation-exchange resins, and derivatized in a single-step procedure with trifluoroacetic anhydride and trifluoroethanol. Where extraction of soil immediately followed fortification, recovery of glyphosate ranged from 88% to 104%. However, where extraction was delayed 13 h after fortification, the recovery of glyphosate varied from 48% to 67%. This low recovery of glyphosate was thought to be due to adsorption of some of the herbicide to soil particles during the period prior to extraction. This suggested that triethylamine was able to extract soluble glyphosate and weakly adsorbed glyphosate but not glyphosate that was strongly adsorbed during a pre-extraction period.

INTRODUCTION

Much of the current information regarding degradation of glyphosate (GLYPH) in soil has relied on the use of ^{14}C-labeled GLYPH, where the degradative behavior of the herbicide has been inferred from measurements of $^{14}CO_2$ evolution from treated soil. While commonly used to measure pesticide degradation, this technique cannot measure availability of the soluble substrate or the rate of substrate catabolism to intermediates. Hence, measuring the rate of evolution of the end product of degradation allows only inferences to be made regarding the kinetics of substrate decomposition.

The literature relating to GLYPH and (aminomethyl)-phosphonic acid (AMPA) analysis of soil and plant tissue has been comprehensively reviewed by Bardalaye et al. (1985). Chromatographic methods are the most commonly used techniques for analysis of these compounds in biological and soil samples, and procedures are available for laboratories possessing thin-layer chromatography (TLC), gas–liquid chromatography (GLC), and high-performance liquid chromatography (HPLC) facilities. TLC methods are considered to be semiquantitative (Moye et al., 1983), and many laboratories do not have the facilities to adopt the published HPLC methods. Hence, GLC methods, particularly where combined with electron capture detection, are appropriate for the needs of many users.

Only the GLC methods as listed in the *Pesticide Analytical Manual* (1977) (PAM) and that of Roy and Konar (1989) have been used for the quantitative analysis of residues of GLYPH in soils. Although the PAM (1977) procedure has been recommended by the U.S. Environmental Protection Agency, it is relatively time-consuming and involves a dual-step derivatization procedure using potentially hazardous diazomethane. It has also been reported that several workers have experienced low and irreproducible recoveries of GLYPH residues in soils when using this procedure (Miles and Moye, 1988). In the procedure described by Roy and Konar (1989), GLYPH and AMPA were extracted with phosphoric acid and derivatized according to the procedure of Deyrup et al. (1985). While results were reported to be reproducible, the recoveries of both GLYPH and AMPA from fortified soils were low.

Some of the difficulties associated with the analysis of soils for residues of GLYPH may be related to the sorption of the chemical to clay minerals and organic matter (Sprankle et al., 1975b). Additionally, results of Miles and Moye (1988) showed that GLYPH sorption by clay minerals was not correlated to the cation-exchange capacity or the surface area of the sorbent, indicating specific rather that general sorption, and also was affected by the pH of the surrounding medium. In this paper, we report the results of an investigation in which extraction of GLYPH from fortified soils using triethylamine is quantified by using electron capture GLC. GLYPH and AMPA were extracted from four soil types at two different time intervals after fortification and derivatized with trifluoroacetic anhydride (TFAA) and trifluoroethanol (TFE) in a single-step procedure prior to GLC analysis.

EXPERIMENTAL PROCEDURES

Instrumentation. A Packard 439 gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD) was used for all measurements. A 2.2. m × 4 mm i.d. silanized glass column was packed with 1.5% OV-17 + 1.95% QF1 Chromosorb WHP 80/100 mesh (S.G.E., Ringwood, Victoria, Australia). A carrier gas purifier and oxygen trap was installed in front of the column to prevent deterioration of the column and oxidation of the ^{63}Ni foil. Carrier gas flow (N_2) was maintained at 15 mL min^{-1} while the makeup gas flow rate was held at 30 mL min^{-1}. Column temperature was 160 °C while the injector port and detector were maintained at 260 and 280 °C, respectively. The fluorine derivatives of GLYPH and AMPA that were produced in this procedure did not decompose at these temperatures.

Glassware and Reagents. Derivatization reactions were carried out in 15 mm × 125 mm unsilanized borosilicate glass culture tubes fitted with Teflon-lined screw caps. GLYPH (analytical grade) was obtained from Monsanto Chemical Co. Anion-exchange resin (Ag 1-X8, 100–200 mesh, Cl^- form) and cation-exchange resin (Ag 50W-X8, 100–200 mesh, H^+ form) were

* Author to whom correspondence should be addressed.
† Present address: Centre of Conservation Farming, School of Agriculture, Charles Sturt University—Riverina, P.O. Box 588, Wagga Wagga, NSW 2650, Australia.

0021-8561/91/1439-1776$02.50/0

Table I. Some Soil Chemical Properties

soil	pH (1:5H_2O)	silt, g kg^{-1}	clay, g kg^{-1}	organic carbon	CEC,[a] mequiv 100 g^{-1}
Walpeup sandy loam	7.26	11	64	6.7	4.5
Wimmera clay	8.35	145	466	11.3	29.8
Culgoa silty clay loam	8.36	26	168	15.6	15.7
Rutherglen loam	5.35	118	214	13.1	5.9

[a] CEC, cation-exchange capacity.

obtained from Bio-Rad Laboratories Pty. Ltd., Australia. TFE, TFAA, and AMPA were obtained from Sigma Chemical Co. Triethylamine (laboratory grade) was obtained from Unilab Chemicals and was glass distilled in this laboratory prior to use. Dimethyldichlorosilane (2% v/v in dichloroethane) was obtained from Ajax Chemicals. All other chemicals used were obtained from Mallinckrodt Chemicals and were of pesticide grade quality or better. All glassware was washed prior to use in chromic acid (80 °C) followed by deionized water, methyl alcohol, hexane, and acetone. All plastics and glassware (except for derivatization tubes) were silanized by coating with a solution of dimethyldichlorosilane for 10 min, allowed to dry, and rinsed with deionized water before use. Silanization of derivatization tubes had no effect on either efficiency or rate of derivatization and was therefore considered to be unnecessary.

Soils. Four soils typical of those commonly found in cropping regions of Victoria were used in the development of this method. Some properties of these soils are given in Table I.

Preparation of Exchange Resins. Anion-exchange resin was pretreated with 0.5 M HCl and washed with deionized water until the pH of the washings was stable at approximately 5.5. After use, the anion-exchange resin was discarded as it was not able to be regenerated. Prior to use, the cation-exchange resin was pretreated with 2.0 M NaOH and washed in deionized water until the pH of the washings was stable (pH ~5.5). The resin was then washed with 0.5 M HCl to convert it into the H^+ form, and this was followed by washings with deionized water until the pH was stable (~5.5). After use, the cation-exchange resin was regenerated by using the same process except that the resin was initially heated, with stirring, in 2.0 M NaOH. After heating, the cleared supernatant was discarded and the resin heated a further three times in 2.0 M NaOH until the ammoniacal odor disappeared and the supernatant cleared. The above washing procedure using 0.5 M HCl was then repeated until a stable pH of 5.5 was achieved.

Extraction and Ion Exchange. The procedure for extraction and cleanup of GLYPH and AMPA residues from soil is based on a procedure previously described by Lundgren (1986) and has the following modifications. The amended soil sample (3.5 g) was extracted by shaking mechanically for 15 min in 30 mL of aqueous 0.1 M triethylamine. The suspension was then centrifuged for 10 min (2300*g*) and the supernatant filtered through cotton wool into a 100-mL Erlyenmeyer flask containing 5 mL of cation-exchange resin. The soil sediment was resuspended in 10 mL of water, shaken by hand, and then centrifuged for 10 min. The supernatant was filtered through cotton wool into the Erlenmeyer flask containing the original soil extract. This flask was shaken for 5 min, and after the exchange resin had settled, the supernatant was decanted into a 150-mL Erlenmeyer flask containing 9 mL of anion-exchange resin. The flask containing the anion-exchange resin was shaken for 10 min and the solution decanted and added to a column made from a 30-mL disposable plastic syringe that had a cotton wool pad inserted at the base. The resin was then washed with deionized water as reported by Lundgren (1986), and the phosphonic acids were eluted by shaking for 3 × 10 min with 0.1 M HCl (3 × 10 mL). After each wash, the acid elutant was added to the column and collected in a 250-mL evaporation flask. The resin, along with the last 10 mL of elutant, was added to the column, and the excess elutant was flushed from the exchange resin in the syringe with the syringe plunger. The elutant was evaporated to dryness at 32 °C under reduced pressure. The sample was resuspended in deionized water (1 mL) and the evaporation step repeated. After evaporation, the residue was resuspended in deionized water (1 mL) prior to derivatization.

Derivatization. The derivatization procedure was as described by Deyrup et al. (1985) but with the following modifications. After excess water was evaporated from the derivatization tube and the tube had cooled to room temperature, 120 μL of TFAA and 60 μL of TFE were added. It should be noted that prior to the addition of TFAA to the derivatization tubes containing the GLYPH residues, all liquid was evaporated completely. This was necessary as TFAA reacts violently with water, forming trifluoroacetic acid (Bretherick and Muir, 1981). The tube was then capped and heated at 100 °C for 1 h.

Excess reagents were removed by flushing with dry N_2 for 5 min at room temperature, and the GLYPH and AMPA derivatives were dissolved in 200 μL of redistilled nanograde ethyl acetate; 0.5-μL samples of this solution were injected into the gas chromatograph.

Gas Chromatograph Calibration. The gas chromatographic response was calibrated by injecting a range of derivatized GLYPH and AMPA standards into the instrument and integrating the corresponding peak areas. A linear regression of GLYPH or AMPA concentration (micrograms per milliliter) of the standards (X) vs corresponding peak areas (Y) was calculated, enabling concentrations of GLYPH and AMPA in unknown samples to be determined.

Fortification of Soils. A 10-μg sample of GLYPH in 1.0 mL of water (4 °C) was added to 3.5 g of air-dried soil (4 °C) in a silanized glass incubation bottle. The soil sample was extracted 30 s after fortification according to the procedure previously described or capped and refrigerated (4 °C) overnight and then extracted.

RESULTS AND DISCUSSION

Chromatography. Deyrup et al. (1985) reported that trifluoro derivatives of GLYPH and AMPA were adequately separated on a 1.8 m × 2 mm silanized glass Ultra-Bond 20 SE 80/100 mesh support column at 150 °C. The retention times recorded were approximately 1.8 min for the AMPA and 2.5 min for the GLYPH derivative, but both peaks appeared to be resolved in the tail of the solvent peak when analyzed by electron capture detection. To improve peak resolution with electron capture detection, a column packed with 1.5% OV-17 and 1.95% QF-1 on a Chromosorb WHP 80/100 mesh support was used. Retention times when this column was used corresponded to 2.85 min for the AMPA derivative and 4.57 min for the GLYPH derivative. As final resolution of the solvent peak was approximately 1.25 min after sample injection, the derivatives of GLYPH and AMPA were chromatographed well clear of any influence of the solvent peak (Figure 1).

Recovery from the Extract and Elutant. The single-step procedure for the derivatization of GLYPH and AMPA as described by Deyrup et al. (1985) was conducted with samples where no soil was used. This procedure also showed applicability for the derivatization of GLYPH dissolved in other solvents. Percent recoveries of GLYPH from fortified triethylamine and from fortified HCl were 100.7 ± 5% and 101 ± 3%, respectively (n = 3). This indicated that GLYPH was stable in both the extract and elutant and was recovered after reduced pressure evaporation from both reagents and that no interference to the derivatization reaction by residues of either reagents was apparent.

Ion Exchange Cleanup Chromatography. From the early stages of method development it became apparent that the use of an anion-exchange resin only for the cleanup of soil extracts was inadequate to clean the samples prior to quantification by electron capture detection as too much detector interference was encountered. The inclusion of a cation-exchange cleanup step markedly reduced background interference (Figure 2).

Preparation of Exchange Resin. The recovery of GLYPH from the cation-exchange resin (H^+ form) com-

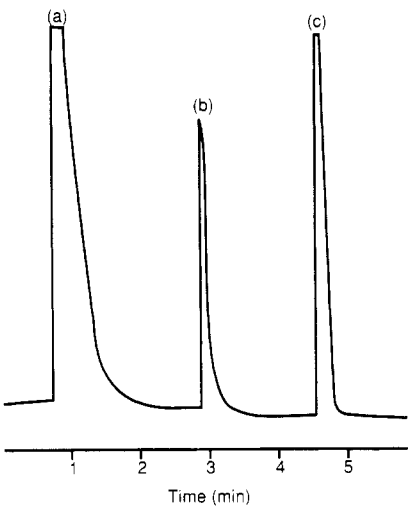

Figure 1. Chromatograms of derivatized standards of GLYPH and AMPA: (a) solvent (Rt = 0.90 min); (b) AMPA derivative (2 ng injected, Rt = 2.87 min); (c) GLYPH derivative (160 ng injected, Rt = 4.57 min).

pared well with the amount of GLYPH initially added. Low recoveries of GLYPH were noted when this resin was used in the Na^+ form (Table II), and this was thought to be due to adsorption of GLYPH by the resin in the Na^+ form or by partial inhibition of the derivatization reaction by Na ions. The results support findings of Parish and Stock (1965) which have shown that the acylation step for derivatization of carboxylic acids may be impeded by the formation of sodium trifluoroacetate.

The recovery of GLYPH from new anion-exchange resin was comparable with the amount of GLYPH initially added (Table III). A variety of attempts were made to regenerate the resin after use, but all were unsuccessful. We concluded that the problems associated with the rejuvenation of this resin were insurmountable and therefore opted for using new resin for each assay. Similar observations have been reported by Brønstad and Friedstád (1976).

Determination of Elutant Volume. Increasing the volume of elutant increased the recovery of GLYPH from the anion-exchange resin. Percent recoveries of GLYPH from the exchange resin following elution with two or three aliquots of 0.1 M HCl (10 mL), each with a shake period of 10 min, were 81.3% and 103.2%, respectively. Lundgren (1986) reported a recovery of only 51% of applied GLYPH from this resin where less elutant and a shorter shaking period were used. Similarly, Brønstad and Friedstád (1976) reported a consistent recovery of 58% of applied GLYPH from this resin in a column with 40 mL of elutant. However, they suggested that more GLYPH could be recovered by increasing the volume of elutant.

Recovery from Fortified Soil. The recovery of GLYPH from soils extracted 30 s after addition of the herbicide compared well for each of the soils examined (Table IV). Recoveries ranged from 85% for the Wimmera clay to 104% for the Walpeup sandy loam and suggested that the triethylamine extractant was adequate to extract soluble and weakly bound GLYPH. However, when extraction was delayed for 13 h, the recovery of GLYPH was considerably lower. In this instance, recoveries ranged from 48% for the Walpeup sandy loam to 67% for the Culgoa silty clay loam. These data, and others to be reported later, suggest that even though there were considerable differences between the clay and organic matter contents of the soils used (Table I), all soils contained sufficient quantities of GLYPH-sorbent components to strongly sorb sufficient quantities of the applied GLYPH which was not able to be extracted by triethylamine. Roy and Konar (1989) reported similar recoveries for GLYPH from soil by extraction with phosphoric acid 24 h after addition of the herbicide. Although traces of AMPA were present in the soils extracted 13 h after the addition of the herbicide, the amount of the metabolite recovered from each soil was insufficient to account for the apparent loss of GLYPH from each soil. Hence, while decomposition could account for some loss of the herbicide, it was not considered to be the principal phenomenon that resulted in the observed loss of extractable GLYPH. Conversely, GLYPH has previously been shown to be readily and rapidly adsorbed to soil particles (Sprankle et al., 1975a), and it was thought that adsorption of the

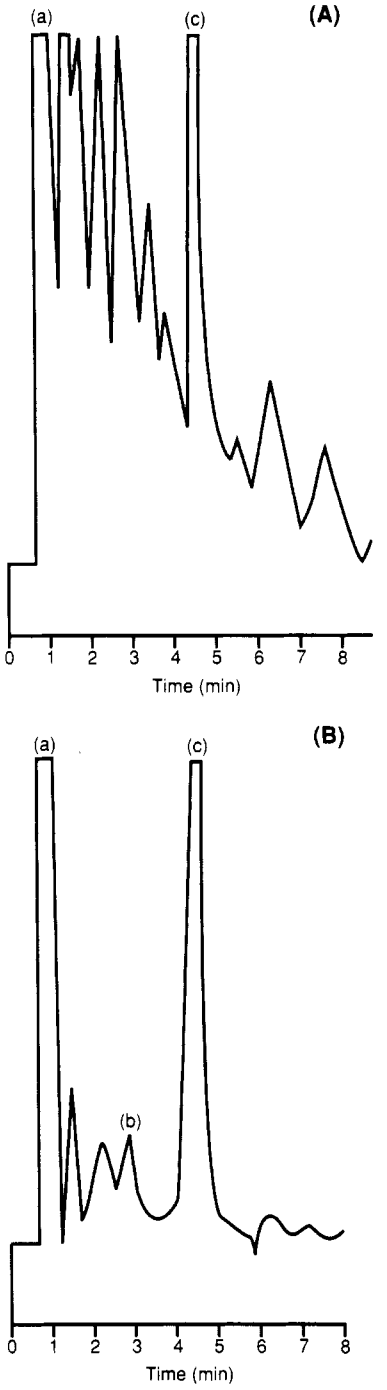

Figure 2. Chromatograms for GLYPH and AMPA extracted from fortified Wimmera soil: (A) where anion exchange was the only form of cleanup; (B) where cation exchange preceded anion-exchange cleanup. (a) Solvent; (b) AMPA; (c) GLYPH.

Table II. Effect of Various Cation-Exchange Washing Procedures on the Recoveries of GLYPH from Fortified Extractant

resin washing procedure	glyphosate added,[a] μg	glyphosate recovd, μg	SE
fortified extractant only	10.00	10.07[b]	0.51
new resin washed with 2 M NaOH (100 °C) and 0.5 M HCl[c]	10.0	9.51	0.26
used resin washed with 2 M NaOH (100 °C) and 0.5 M HCl	10.00	9.83	0.62
used resin washed with 2 M NaOH (100 °C)	10.00	-[d]	-

[a] Triethylamine fortified with GLYPH, cleaned up with cation-exchange resin, evaporated under vacuum, and derivatized. [b] Mean of three replicates. [c] Followed by washing with deionized water until neutral. [d] Irreproducible.

Table III. Effect of Various Anion-Exchange Washing Procedures on the Recoveries of GLYPH from Fortified Extractant

resin washing procedure	glyphosate added,[a] μg	glyphosate recovd, μg	SE
fortified extractant only	10.00[b]	10.07	0.51
new resin washed in 0.5 M HCl at 20 °C[c]	10.00	9.21	0.77
used resin washed in 0.5 M HCl at 20 °C	10.00	1.44	1.01
used resin washed in 0.5 M HCl at 100 °C	10.00	2.81	0.51

[a] Triethylamine fortified with GLYPH, cleaned up with anion-exchange resin, evaporated under vacuum, and derivatized. [b] Mean of three replicates. [c] Followed by washing with deionized water until neutral.

Table IV. Recovery of Glyphosate from Four Fortified Soil Samples

soil type	time lag[a]	glyphosate added,[b] μg (g of soil)$^{-1}$	glyphosate recovd, μg (g of soil)$^{-1}$	SE[c]	AMPA recovd, ng (g of soil)$^{-1}$	SE[d]
Walpeup sandy loam	30 s	2.86	2.98[e]	0.31	BDL[f]	
	13 h	2.86	1.36	0.05	11.8	2.4
Wimmera clay	30 s	2.86	2.42	0.29	BDL	
	13 h	2.86	1.78	0.16	12.7	4.1
Culgoa silty clay loam	30 s	2.86	2.78	0.37	BDL	
	13 h	2.86	1.91	0.06	20.9	4.2
Rutherglen loam	30 s	2.86	2.53	0.31	BDL	
	13 h	2.86	1.48	0.13	33.3	3.0

[a] Time lag between addition of GLYPH and extraction. [b] Soils (3.5 g of soil) fortified with 10 μg of GLYPH in 1 mL of deionized water. [c] Standard error of recovery of GLYPH. [d] Standard error of recovery of AMPA. [e] Mean of three replicates. [f] BDL, below minimum detectable limit.

herbicide may account for the low recoveries observed when extraction was delayed for 13 h.

In this study we fortified each of the soils with 10 μg of GLYPH per 3.5 g of soil (2.87 ppm), and at these rates GLYPH was very easily recovered and detected. From subsequent investigations, the results of which shall be reported later, we have satisfactorily extracted GLYPH from fortified soils and AMPA at concentrations as low as 83 and 6 ng (g of soil)$^{-1}$, respectively. Using the method reported here, it is possible to be able to detect lower concentrations of both compounds in several ways including dissolving the GLYPH and AMPA derivatives in smaller volumes of ethyl acetate, increasing the injection volume into the GLC, or further amplifying the signal from the detector. However, the latter two options are likely to result in an increase in the signal to noise ratio.

Several different mechanisms of adsorption of GLYPH by soils have been postulated; these include hydrogen bonding at low soil pH (Miles and Moye, 1988), complex formation with aluminum or ferric–ferrous ions at low pH (Hensley et al., 1978), binding in the interlayer space of montmorillonite where surface pH is low (Shoval and Yariv, 1979), and bonding to clay particles (Glass, 1987; McConnell and Hossner, 1985) possibly via the phosphonic acid moiety (Hance, 1976; Sprankle et al., 1975b). As a number of these mechanisms would be operative in a soil at one time, the probability of finding an extractant that can effectively desorb GLYPH satisfactorily from all soils under all circumstances is quite unlikely. Miles and Moye (1988), who tested a number of extractants for their ability to desorb GLYPH from soils, reported that desorption of GLYPH increased with increasing extractant pH. Satisfactory recovery of GLYPH residues using triplicate extraction with KOH from two silty loam soils, both with high organic matter content, was achieved (86–119% recovery). Nomura and Hilton (1977) reported that extraction of the more strongly adsorbed fraction of [^{14}C]-GLYPH was achieved by adopting increasingly severe methods of extraction using alkaline extractants. In their paper, the last remaining adsorbed fraction of GLYPH could only be liberated from the soil by ignition of the sample. While Miles and Moye (1988) showed that KOH was suitable as an extractant for GLYPH residues in silty loam soil when the analysis of the FMOCCl derivative was by HPLC, we found that KOH was an unsuitable extractant when the recovered compound and metabolite were derivatized with TFAA and TFE prior to GLC-ECD analysis. In the initial stages of our investigation, we attempted extraction with KOH. However, when KOH was used, the resultant derivatized product was a viscous dark-colored solution, and when ECD analysis of this product was attempted, the ^{63}Ni detector foil became contaminated. We suspected this problem to be associated with increased dissolution of the humic fraction of soil by the alkaline extractant which resulted in contamination of the elutant, and therefore we turned our attention to extraction using aqueous triethylamine. The inability of triethylamine to extract all of the GLYPH in soil as demonstrated in this paper is thought to be strongly influenced by the GLYPH–sorbent mixture of the soils used.

We speculate that when triethylamine is used as the extractant, GLYPH dissolved in soil water and weakly held by soil components is determined. Triethylamine apparently does not extract the strongly sorbed GLYPH from soil, which resulted in lower recoveries when soil was extracted 13 h after fortification (Table IV). Extraction of the strongly sorbed GLYPH may be achieved by using a longer shaking period, a larger number of extractions with triethylamine, or a stronger extractant which is compatible with derivatization prior to GLC-ECD analysis. As extraction by triethylamine determines GLYPH dissolved in soil water and that fraction weakly adsorbed by soil components, it may therefore be useful as a method to predict the amount of phytotoxic residues of GLYPH in soil. We have used this procedure to satisfactorily measure decomposition of GLYPH in a number of soils under a range of conditions and have found that results relate closely to the decomposition behavior of [^{14}C]GLYPH as

measured by the evolution of $^{14}CO_2$ in a flow-through system (Eberbach, 1989). Such results will be reported in another paper and indicate that after the initial rapid adsorptive phase, the logarithm of the concentration of triethylamine-extractable GLYPH in soil is linearly related to time and is related to the rate of decomposition. These findings have led us to the conclusion that this procedure extracts the labile or biologically active fraction of GLYPH residues from soil.

ACKNOWLEDGMENT

We thank Monsanto Australia Ltd. for their generous gift of analytical grade glyphosate.

LITERATURE CITED

Bardalaye, P. C.; Wheeler, W. B.; Moye, H. A. Analytical techniques of glyphosate residue analysis. In *The Herbicide Glyphosate*; Grossbard, E., Atkinson, D., Eds.; Butterworths: London, 1985; pp 263–285.

Bretherick, L.; Muir, G. D. Hazardous Chemicals. In *Hazards in the Chemical Laboratory*, 3rd ed.; Bretherick, L., Ed.; The Royal Society of Chemistry: London, 1981; p 520.

Brønstad, J. O.; Friestád, H. O. Method for determination of glyphosate residues in natural waters based on polarography of the *N*-nitroso derivative. *Analyst* **1976**, *101*, 820–824.

Deyrup, C. L.; Chang, S.; Weintraub, R. A.; Moye, H. A. Simultaneous esterification and acylation of pesticides for analysis by gas chromatography. 1. Derivatization of glyphosate and (aminomethyl)phosphonic acid with fluorinated alcohols-perfluorinated anhydrides. *J. Agric. Food Chem.* **1985**, *33*, 944–947.

Eberbach, P. L. Activity of Glyphosate and Other Herbicides in Soil. Ph.D. Dissertation, University of Melbourne, 1989; pp 92–172.

Glass, R. L. Adsorption of glyphosate by soils and clay minerals. *J. Agric. Food Chem.* **1987**, *35*, 497–500.

Hance, R. J. Adsorption of glyphosate by soils. *Pestic. Sci.* **1976**, *7*, 363–366.

Hensley, D. L.; Beuerman, D. S. N.; Carpenter, P. L. The inactivation of glyphosate by various soils and metal salts. *Weed Res.* **1978**, *18*, 287–291.

Lundgren, L. N. New method for the determination of glyphosate and (aminomethyl)phosphonic acid residues in soil. *J. Agric. Food Chem.* **1986**, *34*, 535–538.

McConnell, J. S.; Hossner, L. R. pH dependent adsorption isotherms of glyphosate. *J. Agric. Food Chem.* **1985**, *33*, 1075–1078.

Miles, C. J.; Moye, H. A. Extraction of glyphosate herbicide from soil and clay minerals and determination of residues in soils. *J. Agric. Food Chem.* **1988**, *36*, 486–491.

Moye, H. A.; Miles, C. J.; Scherer, S. J. A simplified high performance liquid chromatographic residue procedure for the determination of glyphosate herbicide and (aminomethyl)-phosphonic acid in fruits and vegetables employing post column fluorogenic labelling. *J. Agric. Food Chem.* **1983**, *31*, 69–72.

Nomura, N. S.; Hilton, H. W. The adsorption and degradation of glyphosate in five Hawaiian sugarcane soils. *Weed Res.* **1977**, *17*, 113–121.

Parish, R. C.; Stock, L. M. A method for the esterification of hindered acids. *J. Org. Chem.* **1965**, *30*, 927–929.

Pesticide Analytical Manual; Food and Drug Administration: Washington, DC, 1977; Pesticide Regulation Section 180.364.

Roy, D. N.; Konar, S. K. Development of an analytical method for the determination of glyphosate and (aminomethyl)phosphonic acid residues in soil by nitrogen-selective gas chromatography. *J. Agric. Food Chem.* **1989**, *37*, 441–443.

Shoval, S.; Yariv, S. The interaction between Roundup (glyphosate) and montmorillonite. Pt I. Infrared study of the sorption of glyphosate by montmorillonite. *Clays Clay Miner.* **1979**, *27*, 19–28.

Sprankle, P.; Meggitt, W. F.; Penner, D. Adsorption, mobility and microbial degradation of glyphosate in the soil. *Weed Sci.* **1975a**, *23*, 229–234.

Sprankle, P.; Meggitt, W. F.; Penner, D. Rapid inactivation of glyphosate in the soil. *Weed Sci.* **1975b**, *23*, 224–228.

Received for review December 11, 1990. Revised manuscript received May 13, 1991. Accepted June 3, 1991.

Registry No. GLYPH, 1071-83-6; AMPA, 1066-51-9; triethylamine, 121-44-8.