Analysis of Pendimethalin Residues in Fruit, Nuts, Vegetables, Grass, and Mint by Gas Chromatography

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Pendimethalin [*N*-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine], in the formulation of Prowl (a commercial herbicide), was applied to various crops. Analysis of pendimethalin and its metabolite [4(1-ethylpropyl)amino-2-methyl-3,5-dinitrobenzyl alcohol] was accomplished by utilizing liquid−liquid partitioning, gel permeation chromatography (GPC) for nuts and mint, solid-phase extraction (SPE) cleanup, and gas chromatography (GC) with a nitrogen−phosphorus detector (NPD). Method validation recoveries for fruits, nuts, vegetables, grass, and mint are given for both compounds. Pendimethalin average recoveries ranged from 71% to 126% over two levels of fortification. Pendimethalin metabolite average recoveries ranged from 69% to 123% over two levels of fortification. The quantitation limit for all crops except mint was 0.050 ppm. The quantitation limit for mint and mint oil was 0.10 ppm. Residues greater than the limit of quantitation were found for pendimethalin in apple pomace, fresh and dry fig, grass screenings, mint oil, almond hulls, green onion, and tomato pomace (wet and dry). Residues greater than the limit of quantitation were found for pendimethalin metabolite in grass screenings, grass straw, and almond hulls. All other crop analyses for pendimethalin and its metabolite were below the limit of quantitation.

Keywords: *Pendimethalin; Prowl; pendimethalin metabolite; herbicide; GC−NPD; GPC*

INTRODUCTION

Pendimethalin [*N*-(1-ethylpropyl)-3,4-dimethyl 2,6-dinitrobenzenamine] is a dinitroaniline herbicide with selective, preemergence characteristics used extensively for control of a large variety of grasses and broadleaf weeds (*1*). Pendimethalin disrupts the mitotic sequence by inhibiting the production of the microtubule protein, tubulin (*2*, *3*). Translocation of pendimethalin in the crop plant is minimal from the root to the top of the plant (*4*).

Several methods for analysis of pendimethalin utilizing gas chromatography (GC) with electron capture detector (ECD), nitrogen−phosphorus detector (NPD), or mass selective detector (MSD) have been reported (*5*−*10*). Column cleanup and use of florisil have been reported by several authors (*7*, *11*−*13*). In addition, high performance liquid chromatography (HPLC) determination of pendimethalin was reported in soil and water by Cabras and Melis (*14*) and in grass by others (*15*). Most methods are part of a multi-residue, often multi-matrix, scenario, and are not specific to pendimethalin. Pendimethalin recoveries have been reported using some of the above-mentioned methods (*11*, *12*, *16*−*18*).

Published analyses of pendimethalin residues on treated crops are limited. Balasubramanion and Sankaran (*19*) reported no pendimethalin residues in cotton seed crop treated with 1.00−3.00 kg/ha. Sugiyama et al. (*20*) found residues of 0.01 ppm in field treated cabbages. Pendimethalin residues in young onion were 0.239 ppm and in ripe onion 0.113 ppm (*21*).

Most studies by other researchers present only results of pendimethalin analysis. It has been determined that the pendimethalin metabolite is of toxicological importance (*21*). In the present study, pendimethalin and its metabolite were analyzed in a large variety of crops. The aim of the present work is to report the general method of analysis for pendimethalin and its metabolite in various crops and matrixes. Residues of pendimethalin and its metabolite found in some crops collected from IR-4 testing fields have also been summarized. IR-4 is a federal agriculture program that carries out the research needed for the registration of pest control materials on minor crops. IR-4 prepares and submits petitions to the EPA requesting tolerances or exemptions for a pest control product on minor crops.

MATERIALS AND METHODS

Materials. Pendimethalin (98.4% purity) and pendimethalin metabolite (CL 202,347, 97% purity) were acquired from American Cyanamid Company (Princeton, NJ). All solvents and reagents were residue grade or better. Specifications for columns used for analysis are cited below.

Preparation of Standard Solutions. Stock solutions (1 mg/mL) were prepared by dissolving ca. 102.1 mg of pendimethalin or 103.2 mg of pendimethalin metabolite in separate 100-mL volumetric flasks and diluting them to volume with ethyl acetate. Various dilutions were made from the stock solutions, in ethyl acetate, for fortification standard solutions and standard solutions for GC analysis. GC standards were made up weekly and typically consisted of 250, 125, 62.5, and 31.2 pg/μL mixed standard containing both pendimethalin and pendimethalin metabolite. All stock and fortification solutions were kept at -16 ± 6 °C until use.

Collection of Field Samples. Prowl 3.3 EC herbicide formulation of pendimethalin (EPA Reg. No. 241-337, CAS #40487-42-1) was used for application in these field studies.

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Table 1. Average Recoveries of Pendimethalin in Fruits, Nuts, Vegetables, Grass, and Mint

type	crop/matrix	level 1 ppm	% ± SD	level 2 ppm	% ± SD	level 3 ppm	% ± SD
fruit	apple/fruit	0.05	90 ± 5 (n = 10)[a]	0.5	89 ± 3 (n = 10)	n/a	n/a
fruit	apple/juice	0.05	72 ± 6 (n = 4)	0.5	77 ± 3 (n = 4)	n/a	n/a
fruit	apple/pomace	0.05	98 ± 4 (n = 4)	0.5	89 ± 5 (n = 4)	n/a	n/a
fruit	cherry	0.05	90 ± 5 (n = 6)	0.5	90 ± 4 (n = 6)	n/a	n/a
fruit	fig/dry	0.05	98 ± 3 (n = 3)	0.5	89 ± 8 (n = 5)	n/a	n/a
fruit	fig/fresh	0.05	92 ± 4 (n = 4)	0.5	93 ± 5 (n = 5)	n/a	n/a
fruit	grape/fruit	0.05	82 ± 3 (n = 3)	0.5	77 ± 8 (n = 10)	n/a	n/a
fruit	grape/juice	0.05	81 ± 5 (n = 3)	0.5	84 ± 14 (n = 3)	n/a	n/a
fruit	grape/raisins	0.05	95 ± 2 (n = 3)	0.5	85 ± 5 (n = 3)	n/a	n/a
fruit	kiwifruit	0.05	100 ± 7 (n = 7)	0.5	98 ± 1 (n = 3)	n/a	n/a
fruit	peach	0.05	90 ± 2 (n = 6)	0.5	89 ± 2 (n = 8)	n/a	n/a
fruit	pear	0.05	94 ± 4 (n = 7)	0.5	88 ± 4 (n = 5)	n/a	n/a
fruit	plum/dried	0.05	97 ± 3 (n = 3)	0.5	97 ± 2 (n = 5)	n/a	n/a
fruit	plum/fresh	0.05	93 ± 3 (n = 5)	0.5	92 ± 7 (n = 7)	n/a	n/a
fruit	pomegranate	0.05	94 ± 18 (n = 12)	0.5	92 ± 4 (n = 8)	n/a	n/a
fruit	strawberry	0.05	82 ± 1 (n = 3)	0.5	78 ± 5 (n = 5)	n/a	n/a
grain	grass/screenings	0.05	102 ± 23 (n = 6)	1.0	80 ± 4 (n = 3)	10	84 ± 3 (n = 3)
grain	grass/seed	0.05	86 ± 6 (n = 6)	1.0	87 ± 1 (n = 3)	10	90 ± 2 (n = 3)
grain	grass/straw	0.05	108 ± 14 (n = 6)	1.0	85 ± 4 (n = 3)	10	70 ± 4 (n = 3)
grain	grass/forage	0.05	104 ± 13 (n = 6)	1.0	81 ± 1 (n = 3)	10	78 ± 16 (n = 8)
mint	mint/fresh	0.10	116 ± 20 (n = 6)	1.0	102 ± 19 (n = 8)	10	93 ± 6 (n = 3)
mint	mint/oil	0.10	112 ± 8 (n = 3)	1.0	94 ± 9 (n = 4)	10	92 ± 6 (n = 3)
nut	almond/hulls	0.05	80 ± 2 (n = 3)	0.5	75 ± 4 (n = 5)	n/a	n/a
nut	almond/meat	0.05	91 ± 3 (n = 3)	0.5	85 ± 3 (n = 7)	n/a	n/a
nut	pecans	0.05	88 ± 13 (n = 6)	0.5	84 ± 4 (n = 6)	n/a	n/a
nut	pistachio	0.05	97 ± 2 (n = 3)	0.5	85 ± 7 (n = 6)	n/a	n/a
vegetable	asparagus	0.05	84 ± 5 (n = 11)	0.5	77 ± 2 (n = 4)	n/a	n/a
vegetable	broccoli	0.05	102 ± 17 (n = 13)	0.5	86 ± 2 (n = 3)	n/a	n/a
vegetable	carrot	0.05	81 ± 8 (n = 8)	0.5	80 ± 5 (n = 11)	5	78 ± 6 (n = 6)
vegetable	greens (mustard)	0.05	95 ± 26 (n = 6)	0.1	99 ± 26 (n = 9)	0.5	91 ± 4 (n = 5)
vegetable	greens (turnip)/roots	0.05	97 ± 5 (n = 3)	0.5	84 ± 6 (n = 8)	n/a	n/a
vegetable	greens (turnip)/tops	0.05	110 ± 2 (n = 3)	0.5	89 ± 7 (n = 9)	n/a	n/a
vegetable	kenaf /dry	0.05	72 ± 2 (n = 3)	0.5	81 ± 9 (n = 5)	n/a	n/a
vegetable	kenaf /fresh	0.05	109 ± 2 (n = 3)	0.5	91 ± 3 (n = 5)	n/a	n/a
vegetable	leek	0.05	98 ± 8 (n = 3)	0.1	83 ± 3 (n = 3)	n/a	n/a
vegetable	onion/green	0.05	116 ± 4 (n = 3)	0.1	90 ± 11 (n = 3)	n/a	n/a
vegetable	peppers/bell	0.05	92 ± 11 (n = 3)	0.1	87 ± 7 (n = 6)	0.5	74 ± 9 (n = 3)
vegetable	peppers/non-bell	0.05	78 ± 6 (n = 3)	0.5	83 ± 12 (n = 5)	n/a	n/a
vegetable	tomato/whole	0.05	124 ± 7 (n = 3)	0.5	99 ± 10 (n = 4)	5	94 ± 12 (n = 3)
vegetable	tomato/juice	0.05	105 ± 7 (n = 3)	0.5	104 ± 9 (n = 4)	5	81 ± 4 (n = 3)
vegetable	tomato/paste	0.05	116 ± 10 (n = 3)	0.5	98 ± 10 (n = 4)	5	85 ± 2 (n = 3)
vegetable	tomato/puree	0.05	108 ± 9 (n = 3)	0.5	101 ± 11 (n = 4)	5	91 ± 2 (n = 3)
vegetable	tomato/wet pomace	0.05	126 ± 5 (n = 3)	0.5	98 ± 3 (n = 4)	5	90 ± 4 (n = 3)
vegetable	tomato/dry pomace	0.05	71 ± 14 (n = 3)	0.5	97 ± 15 (n = 4)	5	98 ± 5 (n = 3)

[a] Values are mean percent recovered ± standard deviation; n is the number of duplications.

This test substance was applied in a manner that represents and/or simulates the major application techniques that are used by commercial growers. Samples were collected from IR-4 field testing sites throughout the United States. (For specific information, contact IR-4 Project, Center for Minor Crop Pest Management, Technology Centre of New Jersey, 681 U. S. Highway #1 South, North Brunswick, NJ 08902−3390). The rates of Prowl application are shown later in Table 3.

Each test site usually consisted of one untreated (control) and one treated plot. Individual plots were of adequate size to ensure that no more than 50% of the plot would be needed to provide the necessary plant material for residue sampling. Adequate buffer zones were employed between plots to prevent contamination.

Typically, duplicate samples were harvested from each plot. Each sample was collected in a manner to ensure a representative, impartial sample. The sample was placed in a plastic-lined cloth bag that was labeled with complete identification. After collection, samples were usually placed in a cooler, then frozen within 24 h of harvesting. Samples were kept frozen during shipping, and held at −20 ± 6 °C at the laboratory until analysis.

Sample Preparation. The crop was chopped with equal amounts of dry ice using a Hobart food chopper (Hobart Corporation, Troy, OH). For some seeds and nuts, a small food chopper or Wiley mill (Arthur Thompson Co., Philadelphia, PA) was used. Each chopped sample was stored in a labeled ca. 1-L jar, and a lined lid was loosely closed on top to allow the dry ice to dissipate during storage at −20 ± 6 °C. For juice, oil, and some processed samples, aliquots were measured directly from the original containers.

Stability Study. A minimum of six control samples were fortified with pendimethalin and pendimethalin metabolite at 0.5 ppm level for each matrix. At least three samples were analyzed after a storage period equivalent to the number of days between harvest and analysis, and the remaining samples were retained for long-term storage.

Extraction. Ten or twenty grams of fruit (except raisins) and vegetables (except greens, kenaf, and peppers) were extracted by blending twice with 200 mL of methanol. Grasses, mint, and the exceptions noted above were extracted by blending twice with 50% methanol/water (v/v). Nut meats (10 g) were extracted by blending twice with 200 mL of 25% 2-propanol in hexane.

After filtration, a 2.5- or 5-g aliquot of crop extract was transferred to a 250-mL TurboVap tube (Zymark Corporation, Hopkinton, MA) and extraction solvent was evaporated in the TurboVapII concentration station, at 35 °C; or the filtered extract was transferred to a round-bottomed flask and then rotary-evaporated to near dryness, or until all methanol was removed. For all crops except raisins, mustard greens, kenaf, mint, and leeks, the residue was transferred with distilled water and partitioned two times with hexane. For the exceptions, no additional water was needed. The hexane partitions were pooled in a 250-mL TurboVap tube and evaporated as above to dryness.

Table 2. Average Recoveries of Pendimethalin Metabolite in Fruits, Nuts, Vegetables, Grass, and Mint

type	crop/matrix	level 1 ppm	% ± SD	level 2 ppm	% ± SD	level 3 ppm	% ± SD
fruit	apple/fruit	0.05	86 ± 8 (n = 10)[a]	0.5	93 ± 6 (n = 10)	n/a	n/a
fruit	apple/juice	0.05	94 ± 6 (n = 4)	0.5	94 ± 3 (n = 4)	n/a	n/a
fruit	apple/pomace	0.05	87 ± 4 (n = 4)	0.5	91 ± 9 (n = 4)	n/a	n/a
fruit	cherry	0.05	89 ± 14 (n = 6)	0.5	96 ± 8 (n = 11)	n/a	n/a
fruit	fig/dry	0.05	86 ± 2 (n = 3)	0.5	87 ± 7 (n = 5)	n/a	n/a
fruit	fig/fresh	0.05	96 ± 3 (n = 4)	0.5	94 ± 3 (n = 5)	n/a	n/a
fruit	grape/fruit	0.05	97 ± 10 (n = 3)	0.5	94 ± 8 (n = 10)	n/a	n/a
fruit	grape/juice	0.05	95 ± 12 (n = 3)	0.5	110 ± 7 (n = 3)	n/a	n/a
fruit	grape/raisins	0.05	114 ± 3 (n = 3)	0.5	114 ± 3 (n = 3)	n/a	n/a
fruit	kiwifruit	0.05	91 ± 13 (n = 7)	0.5	75 ± 6 (n = 3)	n/a	n/a
fruit	peach	0.05	81 ± 11 (n = 6)	0.5	89 ± 8 (n = 8)	n/a	n/a
fruit	pear	0.05	111 ± 14 (n = 7)	0.5	88 ± 4 (n = 5)	n/a	n/a
fruit	plum/dried	0.05	110 ± 3 (n = 3)	0.5	101 ± 5 (n = 5)	n/a	n/a
fruit	plum/fresh	0.05	102 ± 14 (n = 5)	0.5	93 ± 7 (n = 7)	n/a	n/a
fruit	pomegranate	0.05	103 ± 17 (n = 12)	0.5	93 ± 5 (n = 8)	n/a	n/a
fruit	strawberry	0.05	94 ± 1 (n = 3)	0.5	90 ± 3 (n = 5)	n/a	n/a
grain	grass/screenings	0.05	90 ± 7 (n = 6)	1.0	116 ± 3 (n = 3)	10	108 ± 19 (n = 3)
grain	grass/seed	0.05	96± 23 (n = 6)	1.0	107 ± 26 (n = 3)	10	119 ± 2 (n = 3)
grain	grass/straw	0.05	84 ± 13 (n = 6)	1.0	112 ± 17 (n = 3)	10	93 ± 21 (n = 3)
grain	grass/forage	0.05	93 ± 15 (n = 6)	1.0	88 ± 8 (n = 3)	10	93 ± 10 (n = 8)
mint	mint/fresh	0.10	98 ± 14 (n = 6)	1.0	94 ± 11 (n = 8)	10	103 ± 3 (n = 3)
mint	mint/oil	0.10	88 ± 26 (n = 3)	1.0	87 ± 3 (n = 4)	10	87 ± 8 (n = 3)
nut	almond/hulls	0.05	83 ± 3 (n = 3)	0.5	89 ± 4 (n = 5)	n/a	n/a
nut	almond/meat	0.05	69 ± 7 (n = 3)	0.5	84 ± 2 (n = 7)	n/a	n/a
nut	pecans	0.05	81 ± 7 (n = 6)	0.5	82 ± 3 (n = 6)	n/a	n/a
nut	pistachio	0.05	84 ± 5 (n = 3)	0.5	84 ± 5 (n = 6)	n/a	n/a
vegetable	asparagus	0.05	101 ± 7 (n = 11)	0.5	95 ± 5 (n = 4)	n/a	n/a
vegetable	broccoli	0.05	111 ± 7 (n = 13)	0.5	104±2 (n = 3)	n/a	n/a
vegetable	carrot	0.05	85 ± 13 (n = 8)	0.5	95 ± 5 (n = 6)	5	93 ± 6 (n = 6)
vegetable	greens (mustard)	0.05	120 ± 11 (n = 6)	0.1	109 ± 13 (n = 9)	0.5	99 ± 10 (n = 5)
vegetable	greens (turnip)/roots	0.05	91 ± 2 (n = 3)	0.5	94 ± 7 (n = 8)	n/a	n/a
vegetable	greens (turnip)/tops	0.05	103 ± 2 (n = 3)	0.5	95 ± 6 (n = 9)	n/a	n/a
vegetable	kenaf /dry	0.05	110 ± 7 (n = 3)	0.5	71 ± 16 (n = 5)	n/a	n/a
vegetable	kenaf /fresh	0.05	117 ± 4 (n = 3)	0.5	107 ± 17 (n = 5)	n/a	n/a
vegetable	leek	0.05	117 ± 7 (n = 3)	0.1	85 ± 5 (n = 3)	n/a	n/a
vegetable	onion/green	0.05	120 ± 6 (n = 3)	0.1	119 ± 9 (n = 3)	n/a	n/a
vegetable	peppers/bell	0.05	100 ± 3 (n = 3)	0.1	97 ± 7 (n = 6)	0.5	93 ± 6 (n = 3)
vegetable	peppers/non-bell	0.05	123 ± 10 (n = 3)	0.5	102 ± 8 (n = 5)	n/a	n/a
vegetable	tomato/whole	0.05	107 ± 3 (n = 3)	0.5	96 ± 7 (n = 4)	5	89 ± 16 (n=3)
vegetable	tomato/juice	0.05	119 ± 5 (n = 3)	0.5	96 ± 4 (n = 4)	5	85 ± 5 (n = 3)
vegetable	tomato/paste	0.05	115 ± 8 (n = 3)	0.5	108 ± 16 (n = 4)	5	77 ± 4 (n = 3)
vegetable	tomato/puree	0.05	117 ± 9 (n = 3)	0.5	101 ± 12 (n = 4)	5	90 ± 2 (n = 3)
vegetable	tomato/wet pomace	0.05	113 ± 5 (n = 3)	0.5	95 ± 8 (n = 4)	5	84 ± 7 (n = 3)
vegetable	tomato/dry pomace	0.05	98 ± 9 (n = 3)	0.5	91 ± 16 (n = 4)	5	76 ± 4 (n=3)

[a] Values are mean percent recovered ± standard deviation; n is the number of duplications.

Gel Permeation Chromatography (GPC). Sample cleanup of nuts, fresh mint, and mint oil was accomplished with gel permeation chromatography (GPC). The GPC system consisted of a Kontes Chromaflex gel permeation column (Kontes, Vineland, NJ), a Foxy 200 X-Y fraction collector (Isco, Inc., Lincoln, NE), and a Benchmate II workstation (Zymark Corporation, Hopkinton, MA). The GPC system was programmed to automatically weigh, vortex, and filter (PTFE, 0.45-μm Millipore filter disk, Millipore Corporation, Bedford, MA) each sample prior to injection into the GPC column. The column consisted of a 2.5 cm i.d. × 62 cm glass column, packed with 50 g (200/400 mesh) of S-X3 Bio-Beads (Bio Rad, Richmond, CA) to a bed length of 29 cm. The mobile phase was dichloromethane/cyclohexane (DCM-CH) 15:85 (v/v) with a flow rate of 5.0 mL/min (after firmly packed).

For mint oil analysis, no extraction was needed, and a 2-g aliquot of oil was dissolved in 10 mL of the DCM-CH mobile phase. For nuts and fresh mint, crop residue was loaded (i.e., after the hexane extract was evaporated to dryness) by quantitatively transferring the residue into a 10-mL volumetric flask with DCM-CH and bringing the volume to 10 mL.

For analysis on the GPC, the sample was transferred to a culture tube, put on the rack, and automatically sampled. By using a 5-mL injection loop, one-half of the total aliquot of crop was cleaned up. After injection onto the column, the sample was eluted with the DCM-CH mobile phase. The first portion of eluate [15 min, 75 mL] was discarded. The pendimethalin-containing portion of eluate [15−30 min, 76−150 mL] was collected in a TurboVap tube. The pendimethalin metabolite-containing portion of eluate [30−50 min, 151−250 mL] was collected in a second TurboVap tube. The GPC column was regenerated with 100 mL of the DCM-CH mobile phase, then the next sample on the rack was injected.

Solid-Phase Extraction (SPE) Florisil Cartridge Cleanup. For crops that were not injected on the GPC, crop matrix was cleaned up, and pendimethalin and its metabolite were collected separately from a SPE Florisil cartridge (Supelco LC-Florisil, Bellefonte, PA). The cartridge was pre-washed with hexane to remove any contaminants. The sample was loaded in 5 mL of hexane, and the hexane eluate discarded. The pendimethalin-containing fraction was eluted with 5 mL of 10% ethyl acetate in hexane into a TurboVap tube. The pendimethalin metabolite-containing fraction was eluted with 10 mL of 20% ethyl acetate in hexane into a TurboVap tube. The samples were evaporated to near dryness, then transferred with ethyl acetate and made to the appropriate volume for GC analysis.

Nuts and Mint SPE Cleanup. For the pendimethalin-containing fraction, the GPC eluate was evaporated just to dryness with conditions as above (~45 min). The SPE Florisil cartridge was pre-washed with 5 mL of hexane. The sample residue was loaded with approximately 5 mL of hexane. The hexane eluate was discarded. Pendimethalin was eluted from the SPE column with 5 mL of 10% ethyl acetate in hexane into a TurboVap tube. The SPE pendimethalin-containing

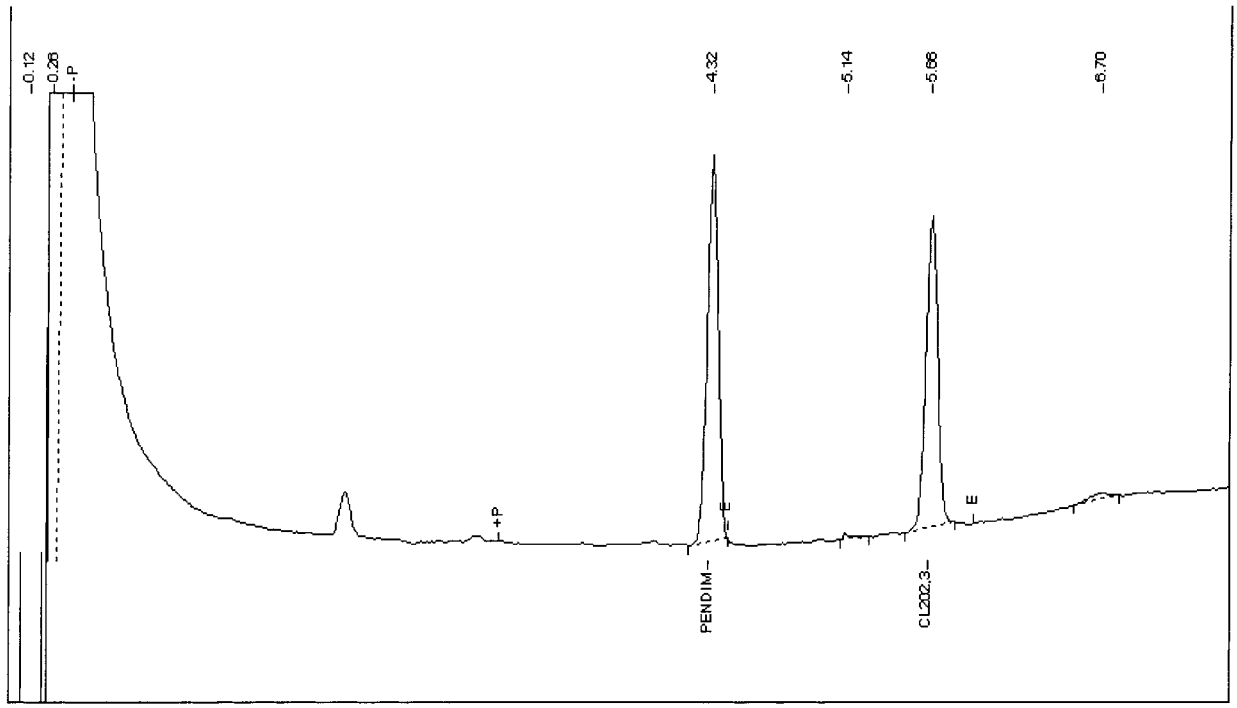

Figure 1. Sample chromatogram of pendimethalin and pendimethalin metabolite (250 pg/μL × 3 μL), fig analysis, retention times 4.32 and 5.66 min, respectively.

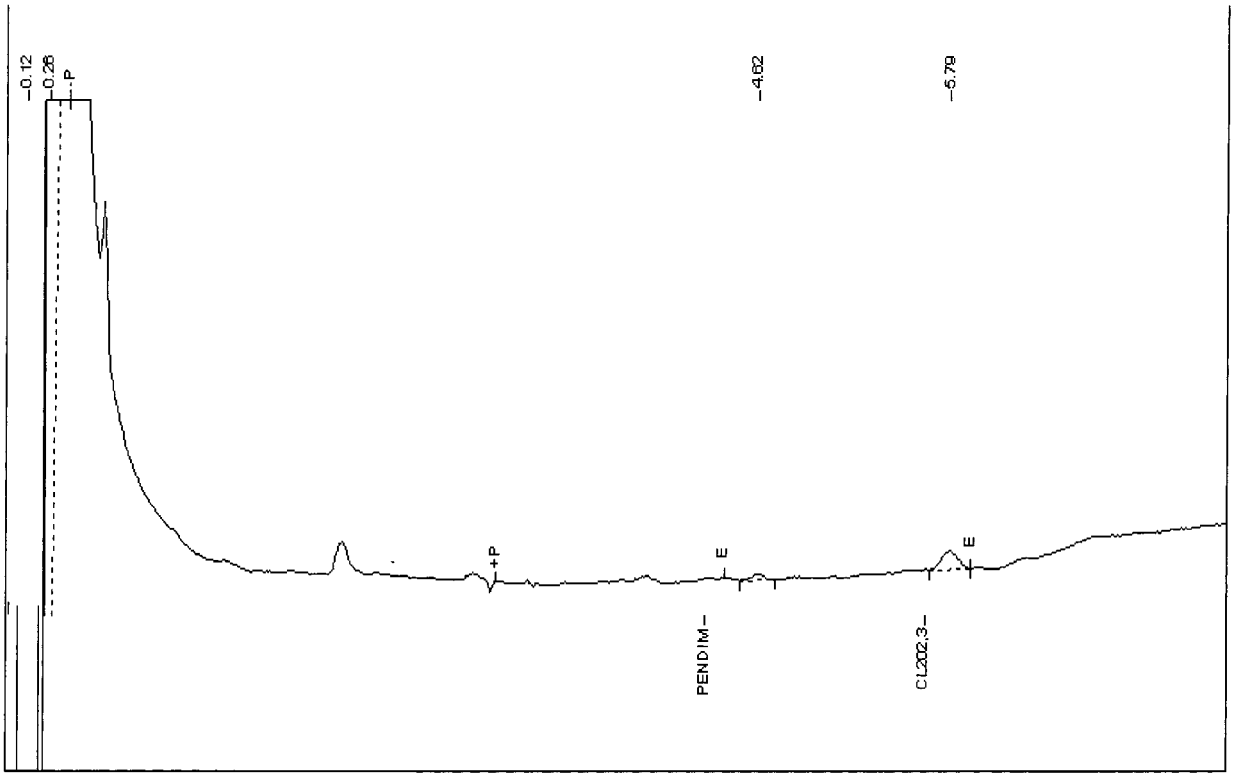

Figure 2. Sample chromatogram of control fig, pendimethalin fraction (3.75 mg injected).

fraction was evaporated to dryness (~10 min). The residue was dissolved in an appropriate amount of ethyl acetate for GC analysis.

The GPC eluate containing the pendimethalin metabolite was evaporated just to dryness with conditions as above (~60 min). The SPE Florisil cartridge was prewashed with 5 mL of 10% ethyl acetate in hexane. The sample residue was loaded with approximately 5 mL of 10% ethyl acetate in hexane. The 10% ethyl acetate in hexane eluate was discarded. The pendimethalin metabolite was eluted with 10 mL of 20% ethyl acetate in hexane into a TurboVap tube. The sample was evaporated to dryness (~15 min). The residue was dissolved in an appropriate amount of ethyl acetate for GC analysis.

Instrumentation. A Perkin-Elmer Autosystem (Perkin-Elmer, Norwalk, CT) or Hewlett-Packard gas chromatograph (Agilent, Loveland, CO) with a nitrogen−phosphorus detector (NPD) was used. Megabore (0.53 mm i.d.) analytical columns used included a XTI-5 (Restek Corp. Bellefonte, PA); DB-XLB, or DB-5 (J & W Scientific, Folsom, CA), 15 or 30 m long. The Perkin-Elmer Turbochrom data acquisition package was used

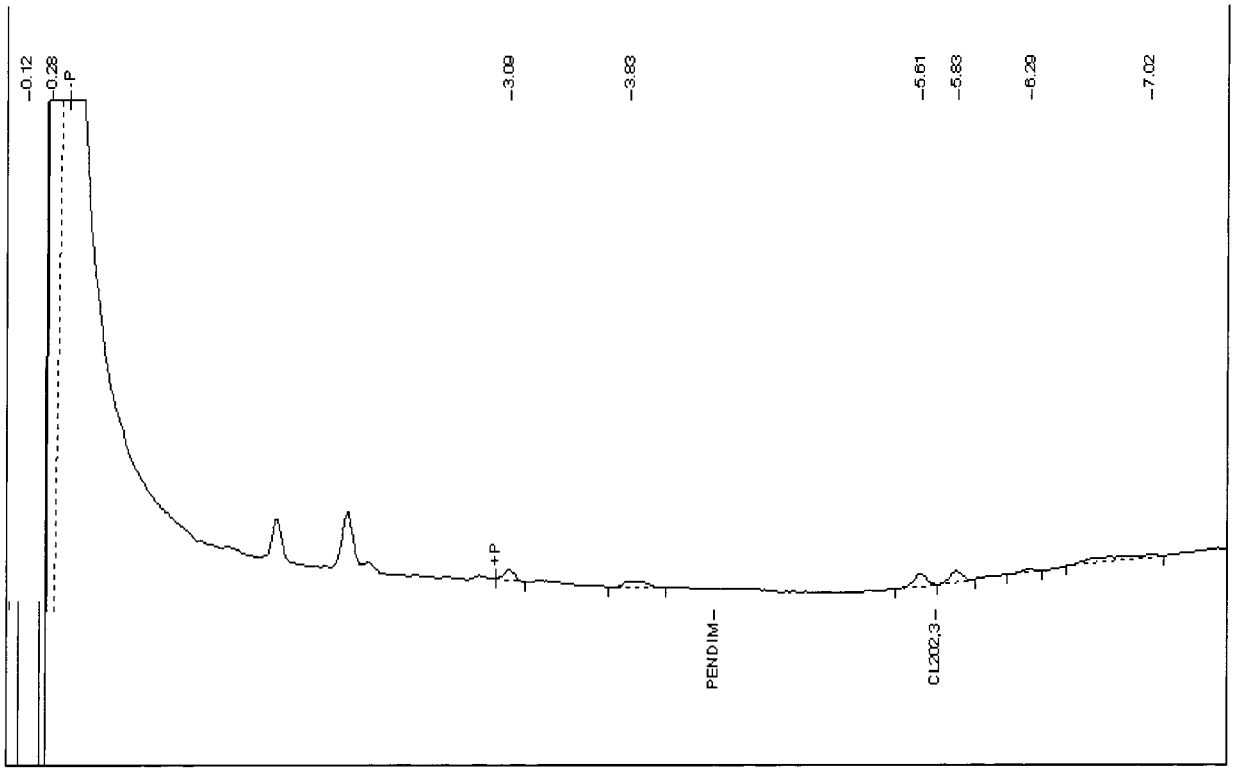

Figure 3. Sample chromatogram of control fig, pendimethalin metabolite fraction (3.75 mg injected).

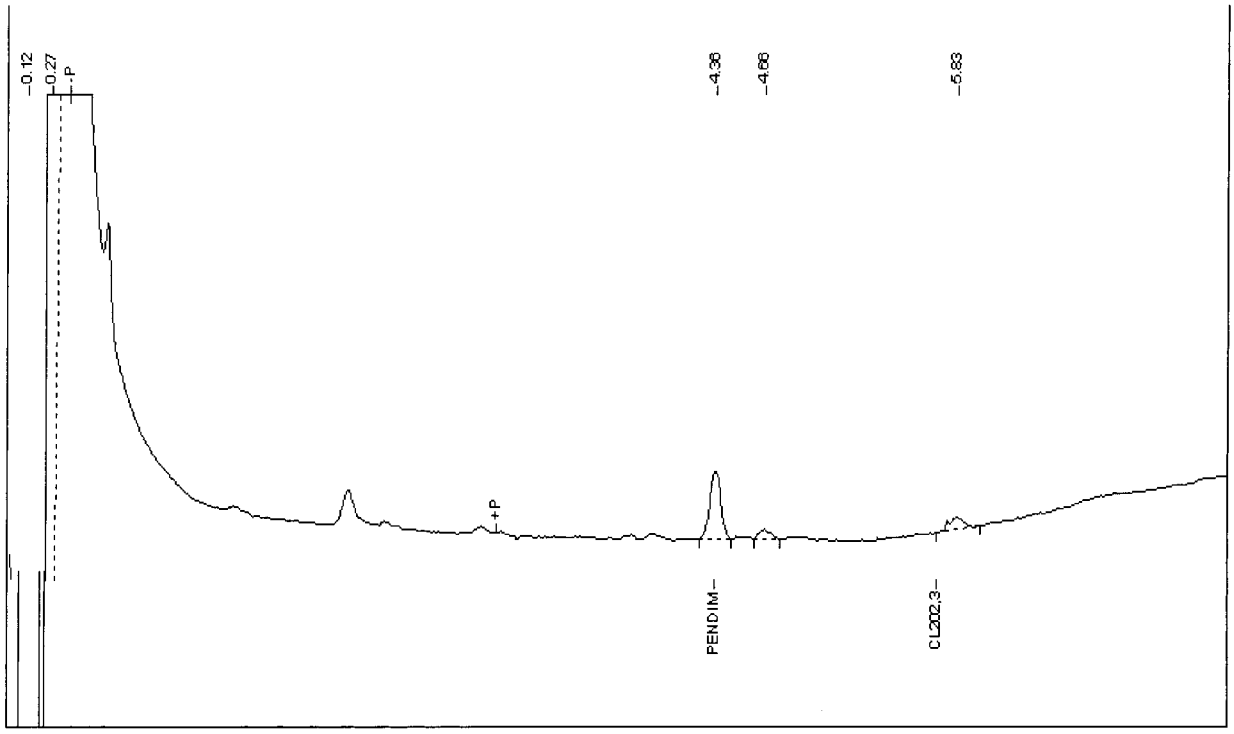

Figure 4. Sample chromatogram of fortified fig, pendimethalin fraction (3.75 mg injected, 87% recovery).

for accumulating data and the Excel spreadsheet program was used for calculations. Parameters for GC analysis included a column temperature of 160 °C or higher. A typical temperature program was 160 °C, hold 1 min, ramp 20 °C/min to 270 °C and hold for 1 min. The detector temperature was 280 °C. Injector temperature for on-column injection tracked oven temperature or for splitless was 250 °C. Gas flows were 10−20 mL/min for the helium carrier gas, ca. 100 mL/min for air, and ca. 2 mL/min for hydrogen. Retention time for pendimethalin was about 4.3 min and for pendimethalin metabolite was about 5.6 min.

RESULTS AND DISCUSSION

Recoveries for pendimethalin are shown in Table 1. For fruits, average pendimethalin recoveries ranged from 72−100% over two fortification levels (0.05 and 0.5 ppm). Vegetables ranged from 71−126%, and nuts

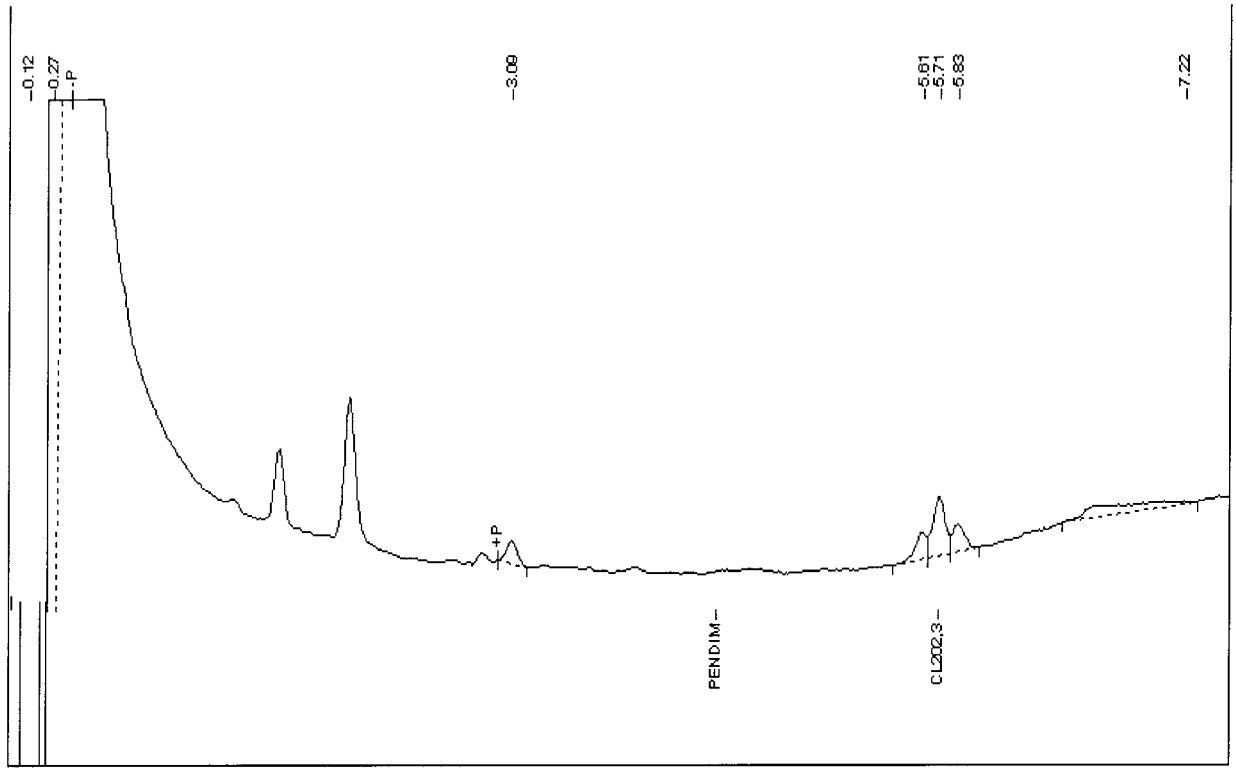

Figure 5. Sample chromatogram of fortified fig, pendimethalin metabolite fraction (3.75 mg injected, 99% recovery).

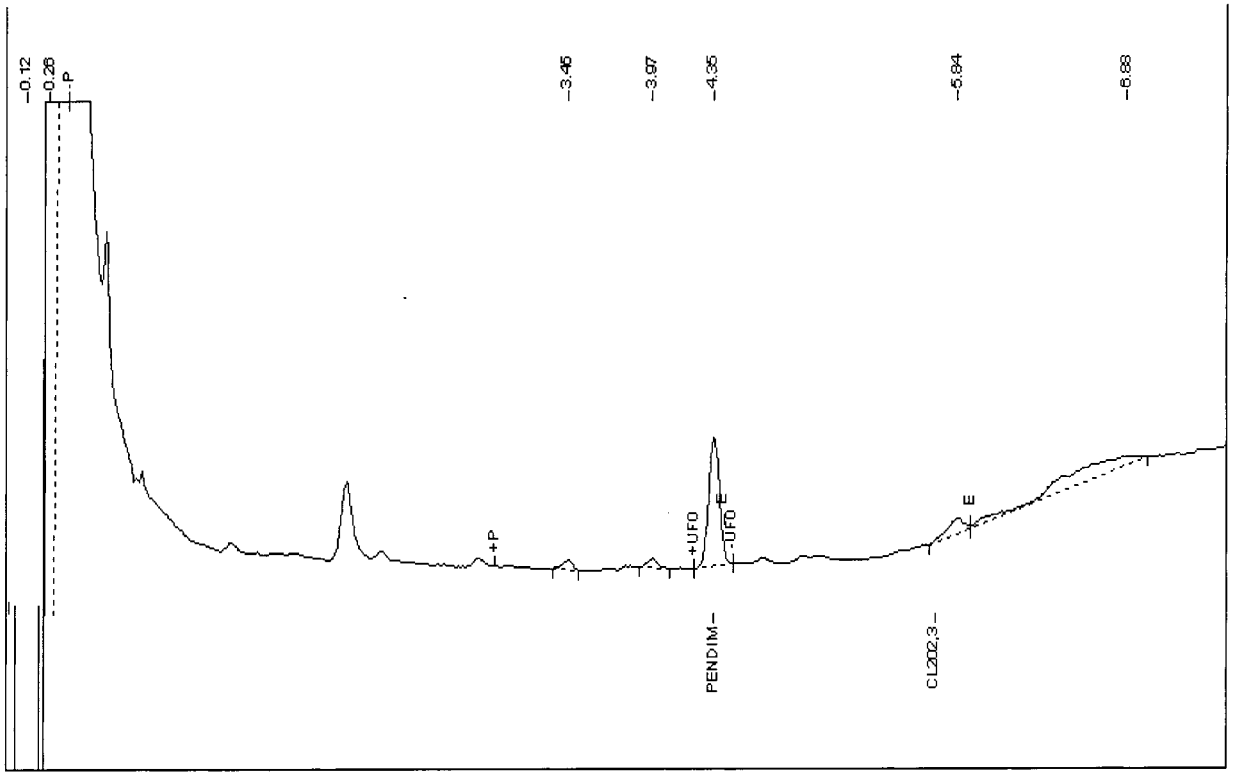

Figure 6. Sample chromatogram of treated fig, pendimethalin fraction (3.75 mg injected, 0.057 ppm found).

ranged from 75−97% over two fortification levels (0.05 and 0.1 or 0.5 ppm). The average pendimethalin recovery range for grass matrixes was 70−108% (for 0.05, 1.0, and 10 ppm), and mint matrixes ranged from 94−116% over three fortification levels (0.10, 1.0, and 10.0 ppm).

Recoveries for pendimethalin metabolite are shown in Table 2. For fruits, average metabolite recoveries ranged from 75−114% over two fortification levels. Vegetables ranged from 71−123%, and nuts ranged from 69−89% over two fortification levels. The average metabolite recovery range for grass matrixes was 84−119%, and mint matrixes ranged from 87−103% over three fortification levels. The method sensitivity was 0.05 ppm for all crops except mint which had a method sensitivity of 0.10 ppm. The limit of detection (LOD),

Table 3. Application Rates and Residue Results of Pendimethalin Analysis in Fruits, Nuts, Vegetables, Grass, and Mint

			pendimethalin		metabolite	
type	crop/matrix	rate[a] (a.i. lb/A)	control (ppm)	treated 1× (ppm)	control (ppm)	treated 1× (ppm)
fruit	apple/fruit	4.0	<0.050	<0.050	<0.050	<0.050
fruit	apple/juice	4.0	<0.050	<0.050	<0.050	<0.050
fruit	apple/pomace	4.0	<0.050	0.14, 0.21	<0.050	<0.050
fruit	cherry	4.0	<0.050	<0.050	<0.050	<0.050
fruit	fig /dry	4.0	<0.050	<0.050−0.071	<0.050	<0.050
fruit	fig /fresh	4.0	<0.050	<0.050−0.075	<0.050	<0.050
fruit	grape/fruit	6.0	<0.050	<0.050	<0.050	<0.050
fruit	grape/juice	6.0	<0.050	<0.050	<0.050	<0.050
fruit	grape/raisins	6.0	<0.050	<0.050	<0.050	<0.050
fruit	kiwifruit	6.0	<0.050	<0.050	<0.050	<0.050
fruit	peach	4.0	<0.050	<0.050	<0.050	<0.050
fruit	pear	4.0	<0.050	<0.050	<0.050	<0.050
fruit	plum/dried	4.0	<0.050	<0.050	<0.050	<0.050
fruit	plum/ fresh	4.0	<0.050	<0.050	<0.050	<0.050
fruit	pomegranate	4.0	<0.050	<0.050	<0.050	<0.050
fruit	strawberry	1.5	<0.050	<0.050	<0.050	<0.050
grain	grass/forage	3.0	<0.050	<0.05	<0.050	<0.05
grain	grass/screenings	3.0	<0.050	<0.05−0.22	<0.050	<0.05−0.81
grain	grass/seed	3.0	<0.050	<0.050	<0.050	<0.050
grain	grass/straw	3.0	<0.050	<0.050	<0.050	<0.05−0.55
mint	mint/fresh	2.0	<0.100	<0.100	<0.100	<0.100
mint	mint/oil	2.0	<0.100	0.51, 0.61	<0.100	<0.100
nut	almond/hulls	6.0	<0.050	<0.05−0.21	<0.050	<0.050−0.11
nut	almond/meat	6.0	<0.050	<0.05	<0.050	<0.050
nut	pecans	6.0	<0.050	<0.050	<0.050	<0.050
nut	pistachio	6.0	<0.050	<0.050	<0.050	<0.050
vegetable	asparagus	4.0	<0.050	<0.050, 0.050	<0.050	<0.050
vegetable	broccoli	1.0	<0.050	<0.050	<0.050	<0.050
vegetable	carrot	1.0	<0.050	<0.050	<0.050	<0.050
vegetable	greens (mustard)	0.5	<0.050	<0.050	<0.050	<0.050
vegetable	greens (turnip)/roots	0.5	<0.050	<0.050	<0.050	<0.050
vegetable	greens (turnip)/tops	0.5	<0.050	<0.050	<0.050	<0.050
vegetable	kenaf/dry	1.0	<0.050	<0.050	<0.050	<0.050
vegetable	kenaf/fresh	1.0	<0.050	<0.050	<0.050	<0.050
vegetable	leek	3.3	<0.050	<0.050	<0.050	<0.050
vegetable	onion, green	1.0	<0.050	<0.050−0.133	<0.050	<0.050
vegetable	peppers/bell	1.5	<0.050	<0.050	<0.050	<0.050
vegetable	peppers/non-bell	1.5	<0.050	<0.050	<0.050	<0.050
vegetable	tomato/whole	3.0	<0.050	<0.050	<0.050	<0.050
vegetable	tomato/juice	3.0	<0.050	<0.050	<0.050	<0.050
vegetable	tomato/paste	3.0	<0.050	<0.050	<0.050	<0.050
vegetable	tomato/puree	3.0	<0.050	<0.050	<0.050	<0.050
vegetable	tomato/wet pomace	3.0	<0.050	0.107	<0.050	<0.050
vegetable	tomato/dry pomace	3.0	<0.050	0.357	<0.050	<0.050

[a] Rate = application rate in pounds of active ingredient/acre (±5%).

defined as 10% below the lowest point on the standard curve, was 0.022 ppm for all crops except mint which had a LOD of 0.045 ppm. Although the data are not presented here, analysis by our laboratory showed no significant degradation of pendimethalin or pendimethalin metabolite in stability fortification studies on any of the crops analyzed.

Metabolism of pendimethalin by photodegradation and microbial activities have been studied by several researchers (*15*, *17*, *22*−*25*). Adsorption and degradation of pendimethalin and other dinitroaniline herbicides in soil has also been the subject of many studies (*26*−*29*). Pendimethalin adsorbs rapidly and strongly to soil because of its high potential for hydrogen bonding. Its persistence in the soil is affected by cultivation, soil temperature, and moisture conditions (*30*). Various reports of pendimethalin residues in turf grasses are highly dependent on soil type, moisture content, and microbial activity (*15*, *17*, *31*).

The USDA IR-4 Program (United States Department of Agriculture Interregional Research Project No. 4, Minor Use Pesticide Registration Program) initiated these projects starting in 1993 to obtain residue data for submission of registration petitions to the U.S. Environmental Protection Agency (EPA). All field and laboratory work was conducted as close as possible to the Good Laboratory Practice Standards mandated by the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), Federal Register 40 CFR Part 160.

Although several multi-matrix, multi-pesticide methods have been published for pendimethalin, we feel that the above method was rugged and versatile, and gave good recoveries for a variety of crops. Our method also allowed for simultaneous analysis of pendimethalin and pendimethalin metabolite.

Figures 1 to 5 show typical gas chromatograms of pendimethalin, CL202,347 and control and fortified samples from the fig analysis study. Figure 1 shows pendimethalin and pendimethalin metabolite standards with a retention time of 4.3 and 5.6 min., respectively. Figures 2 and 3 depict separate control fractions of fresh fig. Figures 4 and 5 represent recoveries of fortified fig with pendimethalin recovery at 87% and pendimethalin metabolite recovery at 99%.

Residue results of pendimethalin analysis in fruits, nuts, vegetables, grass, and mint are shown in Table 3. Residues greater than the limit of quantitation were found for pendimethalin in apple pomace, fresh and dry

fig, grass screenings, mint oil, almond hulls, green onion, and tomato pomace (wet and dry). Figure 6 is an example of pendimethalin residues in treated fig at a level of 0.057 ppm. Residues greater than the limit of quantitation were found for pendimethalin metabolite in grass screenings, grass straw, and almond hulls. Pendimethalin and its metabolite residues on the crops mentioned above can be explained by two separate phenomena. The first is concentration. Mint oil and pomace are concentrated matrixes of the original fresh crop, and some concentration of the pesticide levels could be expected. The other phenomenon is the direct contact of crop and treated soil. For example, when figs and almonds were harvested, the fruit and nuts were shaken from the trees and then raked up into piles for collection. Therefore, contamination from pendimethalin-treated soil was likely. Another example is when grass straw was cut and then field dried, allowing for contact with the soil for 10 days prior to sampling. Grass screenings or chafe could collect soil in the awns of the chafe which would explain the higher levels of pendimethalin and its metabolite in screenings that are not seen in the seeds or in the fresh-cut grass. Residues found on crops that had direct contact with soil could result from pendimethalin present in the crop matrix or from contaminated soil adhering to the crop material.

Sharma and Mehta (*32*) reported 0.103 ppm in onion at harvest when the pendimethalin treatment was 2.0 kg/ha. Tsiropoulos and Miliadis (*25*) reported 0.054 ppm in onions treated at 2.0 kg/ha. Our field study showed pendimethalin residues in green onion at 0.120 and 0.133 ppm. Residues were found only in green onions grown in Michigan. We also analyzed onions from Washington, Ohio, New York, and Arkansas, and found no residues above the limit of quantitation. As discussed previously, soil contact, microbial action, soil moisture, and photodecomposition can affect pendimethalin residue levels found in the harvested crop.

The present study shows that pendimethalin and pendimethalin metabolite can be analyzed in several types of matrixes with the above method. We have also reported that, for most crops, pendimethalin and its metabolite residue levels were below the limit of quantitation of 0.05 ppm.

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