Determination of Imidacloprid and Triadimefon in White Pine by Gas Chromatography/Mass Spectrometry

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Imidacloprid is one of a new class of highly systemic chloronicotinyl insecticides with significant activity against a wide range of insects. The triazole fungicides, triadimefon and triadimenol, are also systemic and highly effective in controlling a variety of economically important fungal diseases. A sensitive and reliable method for the determination of these compounds by GC/MS has been developed. Imidacloprid was converted to the heptafluorobutyryl derivative, whereas triadimefon and triadimenol were determined directly. Quantitation of all three analytes in white pine foliar extracts was performed in selected ion monitoring mode, by comparison with an external standard in sample matrix. Limits of quantitation were 0.01 ppm (10 pg injected) for imidacloprid and 0.1 ppm (100 pg injected) for both triadimefon and triadimenol. Overall mean recovery was 85.78 ± 5.20% (6.06%). This method has been successfully applied to quantify in-planta residues after treatment of white pine seedlings with a controlled-release pellet containing imidacloprid and triadimefon for control of white pine weevil and white pine blister rust, respectively. Mean recoveries for QC samples were 85.62 ± 9.34% (10.9%).

Keywords: *Imidacloprid; triadimefon; triadimenol; residue analysis; white pine*

INTRODUCTION

Imidacloprid, 1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine), is a new chloronicotinyl insecticide with properties that make it very attractive as a tool in integrated pest management. These properties include favorable environmental and toxicological characteristics, excellent systemic activity against a wide variety of insects on a wide range of crops, and a novel mode of action that addresses the problem of pesticide resistance—it is an agonist of the nicotinergic acetylcholine receptor (Moffat, 1993; Mullins, 1993, and references cited therein; Kagabu and Medej, 1995). Imidacloprid is marketed under several trade names, including Provado, Admire 2, and Merit. The structure of imidacloprid is illustrated in Figure 1.

The triazoles, triadimefon and triadimenol, are sterol-biosynthesis-inhibiting fungicides that also exhibit plant growth regulating properties (Fletcher, 1985; Fletcher et al., 1986; Davis et al., 1988). Once applied, triadimefon, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)butanone, is degraded into two diastereomers of triadimenol, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4,-triazol-1-yl)-2-butan-2-ol: (+)-1*R*,2*S*;(−)-1*S*,2*R* (triadimenol A) and (+)-1*R*,2*R*;(−)-1S,2S (triadimenol B). The reduction of triadimefon to triadimenol may be regarded as an activation because the metabolite possesses greater fungicidal activity than the parent compound (Gasztonyi and Josepovits, 1979). Triadimefon and triadimenol are registered under the trade names Bayleton and Baytan, respectively. The structures of these compounds are shown in Figure 1.

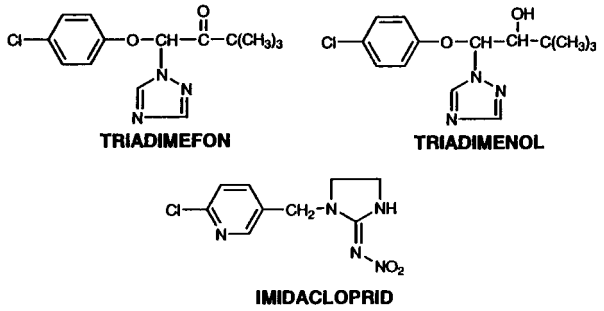

Figure 1. Structures of triadimefon, triadimenol, and imidacloprid.

These compounds were considered to be excellent pest management candidates for studies on white pine (*Pinus strobus* L.). White pine is considered one of the most valuable conifer species in the eastern temperate forests of North America; however, its re-establishment is severely limited by two major pests—the white pine weevil [*Pissodes strobi* (Peck)] and white pine blister rust (*Cronartium ribicola* J. C. Fisch.). Reliable, cost-effective, and environmentally acceptable methods of prevention and/or control are not available. Consistent with the expected systemic activity of imidacloprid and triadimefon, within white pine, a controlled-release pellet was developed in cooperation with Bayer Corp. and Vigoro Industries Inc. The pellet, applied at the time of planting, would provide a delivery mechanism in the root zone. Availability of the pesticides during root activity would maximize uptake while minimizing contamination of the surrounding soil volume and exposure of nontarget organisms. To evaluate the potential of this approach, field efficacy trials were established at two sites in central Ontario, Canada, in 1993 and 1994.

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A sensitive, multiresidue analytical method was required to quantify imidacloprid and triadimefon residues in small (5 g) samples of white pine foliage. Nondestructive sampling was employed so that the same young trees could be sampled repeatedly over time. Data representative of the mean would be obtained because each treatment was replicated 50 times. Residue data, acquired over a period of at least five years, would permit assessment of uptake, translocation, and foliar persistence, which could then be correlated with insect and disease control as well as overall crop growth response. Little or no data were available, at the time this study was begun, as to either rates of incorporation or dissipation of imidacloprid and triadimefon in white pine; therefore, it was important to develop as sensitive a method as possible.

In 1993, when this work was initiated, one method was available for the HPLC-UV determination of imidacloprid in plants (Placke and Weber, 1993), and several GC methods were available for triadimefon and triadimenol (Brennecke, 1984; Newsome et al., 1989; García-G., 1991) in various matrixes. These methods were considered to be too lengthy, solvent consumptive, or less sensitive than required. Mass spectrometry in selected ion monitoring (SIM) mode was the detection system of choice because of its inherent ability to provide sensitivity, selectivity, and confirmation of analytes in the analysis of complex environmental matrixes.

Several methods for the determination of imidacloprid have been published since 1993. The limit of positive identification of imidacloprid in vegetables by HPLC-DAD is 2 ng injected, and the limit of detection (LOD) by HPLC-MS (thermospray) is 500 pg in SIM mode (Fernández-Alba et al., 1996). Ishii et al. (1994) report a similar limit of quantitation (LOQ) in their HPLC-UV method for crops and soil. Vilchez et al. (1996) have reported a simple method for the determination of imidacloprid in water and soil by GC/MS(SIM) after alkaline hydrolysis of the parent to the imidazolidin-2-one. LOQ and LOD are 60 pg and 8 pg injected; however, applicability of their method, which involves little sample cleanup, to more complex environmental matrixes is unknown. Rouchaud et al. (1994) prepared the trifluoroacetyl derivative of imidacloprid for the determination of residues in soil and sugar beets by GC-ECD. Mass spectrometry data are given for the parent compound, which was introduced directly; however, no structural confirmation of the derivative by GC/MS is given nor is there any validation data for the method. The absence of these data is not conducive to a significant level of confidence in the methodology presented. This paper describes a sensitive, multiresidue analytical method based on GC/MS(SIM) for the determination of imidacloprid and triadimefon residues in planta. Imidacloprid was converted to the heptafluorobutyryl (HFB) derivative, whereas triadimefon and triadimenol were determined directly. Electron capture negative ion mass spectrometry was not used in the determination of imidacloprid as the highly electronegative HFB derivative because our instrument did not have that capability.

MATERIALS AND METHODS

Reagents. All reagents were of analytical quality. Analytical standards of imidacloprid (96.9%), [*methylene*-^{14}C]-imidacloprid (99.0%), [*phenyl*-^{14}C]triadimefon (99.4%), and [*phenyl*-^{14}C]triadimenol (1:1 isomers A:B) were obtained from Bayer Corp., Stillwell, KS. Triadimefon and triadimenol A (both 99.0%) were obtained from Riedel-de Haën (Caledon Lab., Georgetown, ON). Standards were prepared in ethyl acetate (triazoles) or acetonitrile (imidacloprid). Heptafluorobutyric acid anhydride (HFAA) and pyridine (silylation grade) were obtained from Pierce (Chromatographic Specialties, Brockville, ON).

^{14}C Recovery Studies. ^{14}C-Labeled analogues were used during method development to optimize extraction efficiency and recovery during cleanup and column chromatography. Radiolabeled compounds, in water, were evenly applied to 5 g samples of very finely divided white pine needles, equilibrated at room temperature for 2 h and then held at −20 °C for at least 48 h. Extraction with various solvent combinations was performed using a high-speed homogenizer (Omni-Mixer, Sorvall, Norwalk, CT). Radioactivity recovered during extraction and subsequent steps was measured on a liquid scintillation counter (Beckman LS6000SE). Personnel were trained in the use of radiolabeled compounds, and procedures consistent with their use were followed.

Storage of Field Samples. All field samples were stored at −20 °C until analyzed. Stability tests on imidacloprid stored for two years under these conditions indicated no degradation (Placke and Weber, 1993). Long-term storage data were not available for the triazoles; however, both compounds are very stable to hydrolysis, with half-lives at 22 °C and pH 3 of >1 year (Brennecke, 1984). Standards, in matrix, showed no degradation over several months, if refrigerated. The very large number of field samples made it necessary for some to be stored for up to 15 months before analysis. White pine foliage for method development, validation, and QCs was collected from control trees on both field sites at the same time as the treated trees were sampled. All trees were 3-year-old seedlings outplanted from 2-year-old containerized stock grown in Multipot 45s.

Extraction and Cleanup. Five grams of finely divided white pine needles was weighed into a 100 mL glass bottle containing 50 mL of 70:30 methanol/0.04% aqueous sulfuric acid (pH 3.3) and macerated for 3 min. Samples were vacuum filtered through Whatman No. 1 paper, and the filter cake was washed twice with 10 mL of 70:30 methanol/water. The combined filtrate was transferred to a 250 mL round-bottom flask and the methanol distilled off on a rotary evaporator at 40 °C. The aqueous remainder (10−12 mL) was diluted with 3 mL of water and transferred to a C18 Sep-Pak Plus cartridge (Waters, Mississauga, ON). The cartridge, preconditioned with 10 mL each of methanol and water, was attached to a 10 mL disposable syringe containing a glass fiber filter (Gelman Type A/E, 13 mm; Fisher Scientific Canada, Toronto, ON) and a glass wool plug. The flask was rinsed twice with 5 mL of water, which was added to the Sep-Pak. The cartridge was then washed with 5 mL of 0.05 M potassium carbonate and dried under vacuum for 30 min or until completely dry. All three analytes were then eluted with 5 mL of methylene chloride.

Column Chromatography. Additional cleanup and analyte separation were accomplished by loading the methylene chloride eluate onto a Florisil minicolumn. The minicolumns were prepared by packing disposable large-volume Pasteur pipets (14.5 cm × 7.5 mm i.d.; Fisher Scientific Canada) plugged with glass wool with Florisil (1.5 g, activated at 650 °C, 60−100 mesh, J. T. Baker, Phillipsburg, NJ). Florisil was stored at 130 °C until immediately before use. The columns were preconditioned with 10 mL of methylene chloride. The initial column eluate was discarded. The triazoles were eluted first with 20 mL of 75:25 ethyl acetate/hexane followed by imidacloprid, with 5 mL of acetonitrile. The triazole fraction was evaporated to dryness under nitrogen, and residues were recovered in ethyl acetate for GC/MS analysis. The imidacloprid fraction was concentrated to 1.0 mL under nitrogen in preparation for derivatization. These operations were performed in a fume hood.

Preparation of HFB Derivative of Imidacloprid. Experiments to determine and optimize the efficiency of the derivatization reaction were performed with imidacloprid in

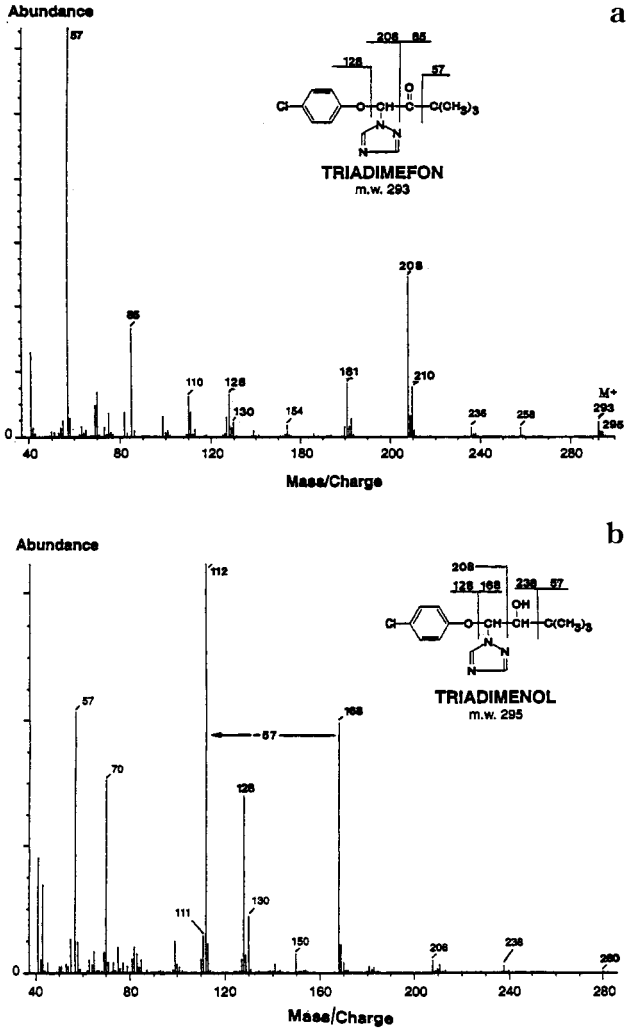

Figure 2. (a) Full-scan EI spectrum of triadimefon. (b) Full-scan EI spectrum of triadimenol.

acetonitrile and in matrix blanks. Matrix blanks were processed from initial extraction of white pine needles through elution from Florisil and concentration of the acetonitrile fraction. Optimum production of the derivative was achieved by adding 100 μL each of silylation grade pyridine and HFAA to the acetonitrile concentrate and heating for 2 h at 60 °C. Excess reagent was removed by evaporation to dryness under a gentle stream of nitrogen. The derivative was recovered in ethyl acetate for GC/MS. These operations were performed in a fume hood. HFAA should be handled carefully, as with most derivatizing reagents.

Gas Chromatography/Mass Spectrometry. GC/MS analyses were performed on a Hewlett-Packard 5989A. A DB-17ht column (30 m × 0.25 mm i.d. × 0.15 μm film; Chromatographic Specialties, Brockville, ON) with a deactivated fused silica guard column (1.0 m × 0.56 mm i.d.) was used for the determination of all three analytes. For triadimefon and triadimenols A and B, the column temperature was programmed from 60 to 235 °C at 25 °C/min, then to 250 °C at 5 °C/min, and finally to 300 °C at 30 °C/min and held for 10 min. Injection was on-column at 60 °C using an HP7673 autosampler. For the HFB derivative of imidacloprid the column temperature was programmed from 150 to 300 °C at 20 °C/min and held for 10 min. Injections were performed manually at 250 °C. The transfer line and source temperatures were 280 and 275 °C, respectively.

Confirmation and quantification were performed by selected ion monitoring (SIM) of structurally significant ions as determined from the full-scan 70 eV electron ionization (EI) spectra (Figures 2 and 3). Ions selected for confirmation of the presence of each analyte and the ion selected for quantitation

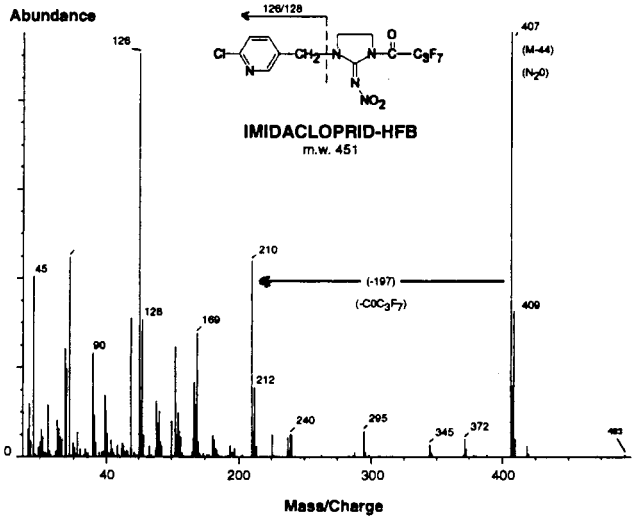

Figure 3. Full-scan EI spectrum of imidacloprid HFB derivative.

were, respectively, as follows: triadimefon, *m/z* 181, 208/210, 293/295 and *m/z* 208; triadimenol, *m/z* 128/130, 168 and *m/z* 168; and imidacloprid HFB, *m/z* 126/128, 210/212, 407/409 and *m/z* 407. The base peak of triadimenol, *m/z* 112, could not be used reliably at low residue levels (<50 ppb) due to the presence of this ion at the same t_R in some matrix blanks.

Method Validation. Very finely divided needles (5 g) were spiked at 10.0, 1.0, and 0.1 ppm with triadimefon and triadimenol and additionally at 0.01 ppm with imidacloprid. Standards were evenly distributed over the foliage in 1.0 mL of deionized water. Samples were equilibrated at room temperature for 2 h and frozen at −20 °C overnight prior to processing as described above. Each concentration was replicated five times for all analytes. Quantitation of all three analytes was performed in SIM mode by comparison with an external standard in sample matrix. A stock of white pine sample matrix was prepared from field control foliage processed as described to yield an ethyl acetate fraction equivalent to that containing the triazoles and an acetonitrile concentrate (1.0 mL) corresponding to the imidacloprid-containing fraction. These were then spiked with the triazoles in ethyl acetate and imidacloprid in acetonitrile at the concentrations to be validated. The control matrix was analyzed to ensure that there were no ion interferences at the relevent retention times over the concentration range of interest for all compounds. In the case of imidacloprid, the control was treated with HFAA.

RESULTS AND DISCUSSION

Radiolabeled compounds were used during method development to determine and optimize extraction efficiencies, elution patterns, and recoveries. Various extraction solvents and times were tried. Maceration with 70:30 methanol/water (pH 3.3) for 3 min provided high (>90%) extraction efficiency and minimized coextractive interference. The addition of sulfuric acid was required to maximize recovery of imidacloprid. Complete removal of methanol prior to loading the aqueous remainder on C18 was essential to retention of all analytes on the cartridge. This was accomplished if the volume of solvent in the round-bottom flask was 10−12 mL. It should be noted that recoveries were reduced if the aqueous remainder was allowed to sit long enough (2−3 h) for solids to settle out before loading on C18. Washing with 0.05 M potassium carbonate served to remove phenolics and other acidic compounds. Complete drying of the cartridge was essential for quantitative elution of the analytes with methylene chloride.

Column chromatography on Florisil separated the triazoles from imidacloprid and further cleaned up the

sample, particularly the imidacloprid fraction. No losses were observed when the triazole-containing fraction was taken to dryness with nitrogen prior to recovery in ethyl acetate. Both fractions could be stored under refrigeration for at least two months with no degradation.

Imidacloprid itself could not be analyzed directly by GC because of its thermolability and polarity. During the course of our investigations, a variety of derivatization reactions were attempted, including methylation, silylation, and acylation. In all cases substitution of the acidic hydrogen of the imidazolidine amine group occurred, but with varying degrees of success and consistency. Acylation with HFAA provided the derivative most suitable for GC/MS. The derivative was consistently and efficiently produced and free from interferences at environmental concentrations. The potential for loss of imidacloprid caused by evaporation of the derivative to dryness prior to recovery in ethyl acetate was examined during method development. Losses were determined to be minimal. Once derivatized, samples should be analyzed the same day to avoid any chance of hydrolysis. We found a significant decline in response (30−50%) and peak broadening for samples reinjected 18−24 h later. Injections of large numbers of samples (30−40) also affected chromatographic performance, probably as a result of sample acidity and/or matrix coextractives adhering to the guard column. This could be remedied by removing 6−8 cm from the head of the guard column. Attempts to form the HFB derivative with the corresponding imidazole, which has the distinct advantage of producing no acidic byproducts, were unsuccessful, presumably because of steric effects. Manual injection resulted in significantly better peak shape and reproducibility than was obtained with the HP7673 autosampler. This was attributed to longer needle residence time. Multiple injections of the triadimefon/triadimenol fraction had no negative effect on chromatographic quality.

The EI mass spectrum of the heptafluorobutyryl derivative is shown in Figure 3. We postulate that the base peak at *m*/*z* 407 arises from $[M - N_2O]^+$, a rearrangement reaction which produces the stable cyclic urea. Other important fragmentation pathways are also illustrated. An alternative explanation for the mass spectrum is that the parent compound is acid hydrolyzed to the imidazolidin-2-one during the derivatization and that this product is derivatized. The literature indicates that whereas imidacloprid is subject to alkaline hydrolysis at elevated temperatures, it is not hydrolyzed under acidic conditions (Kagabu et al., 1995; Vilchez et al., 1996). In fact, we attempted to hydrolyze it but were unsuccessful (pH 3.0, 80 °C, for 0.5, 1.0, and 2.0 h). The pH of the reaction mixture was 3.5.

Quantitation was performed by comparison with external standards in sample matrix. We found during method development that there was an enhanced response (~35%) for the imidacloprid HFB derivative prepared in matrix as compared to the derivative prepared in solvent alone. This enhancement was not due to coextractive interference as there were no peaks observed at the retention time of the derivative in either solvent or matrix blanks when treated with HFAA. It is not known whether this *matrix effect* is due to the matrix actually enhancing conversion to the derivative or to increased transfer of analyte induced by the matrix during injection. Enhanced response of the detector to the analyte in the presence of matrix is also a possibility.

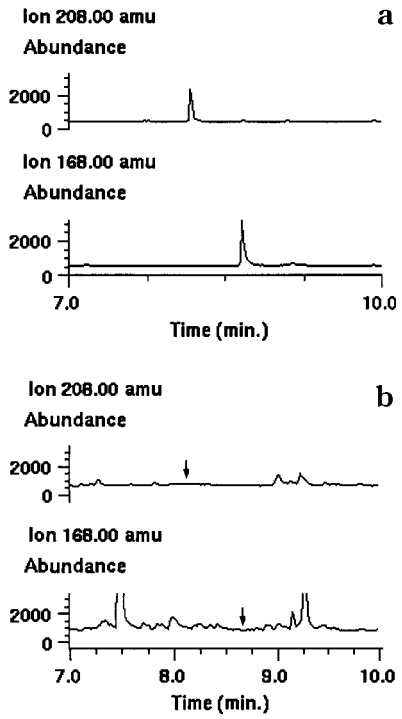

Figure 4. (a) Chromatogram of a white pine sample containing triadimefon (*m*/*z* 208) and triadimenol (*m*/*z* 168) at 100 ppb (100 pg injected). (b) Chromatogram of a white pine matrix blank−triazole fraction.

No enhancement was noted for the triazoles. Matrix-induced peak enhancement has been reported increasingly over the past several years, and the use of calibration standards prepared in sample matrix has been recommended as a means of compensation (Erney et al., 1997, and references cited therein; Headley et al., 1996).

The above method was validated for triadimefon and triadimenol in fortified white pine needles at 10, 1.0, and 0.1 ppm. LOQs were 100 pg on-column, with LODs conservatively set at 50 pg. A validation trial was performed at 0.01 ppm with less than satisfactory results [114.46 ± 12.3% (10.74%), $n = 4$]. Figure 4a shows ion chromatograms obtained at the lowest validated concentration of 0.1 ppm. Baseline resolution was achieved for triadimefon and both triadimenol diastereomers under the GC conditions described. Quantitation of imidacloprid was validated at the above levels as well as at 0.01 ppm, which is equivalent to 10 pg injected. LOD has been set at 5 pg. A representative chromatogram obtained at 10 ppb is shown in Figure 5a. Overall mean recovery was 85.18 ± 5.20% (6.06%), $n = 50$. Response was linear over the concentration range of interest. Chromatograms of matrix blanks at the lowest validated concentrations are illustrated in Figures 4b and 5b. Recoveries for individual fortification levels are presented in Table 1. These values compare favorably with or, in most cases, exceed those of other analytical methods. The LOD for imidacloprid by HPLC-MS is 500 pg in SIM mode (Fernández-Alba et al., 1996). Ishii et al. (1994) report a similar LOQ in their HPLC-UV method for crops and soil. Vilchez et al. (1996) have described a method for the determination of imidacloprid in water and soil, as the imidazolidin-2-one hydrolysis product, by GC/MS(SIM). LOQ and LOD are 60 pg and 8 pg injected, respectively.

The method presented here has been applied to the analysis of hundreds of field samples collected in 1993

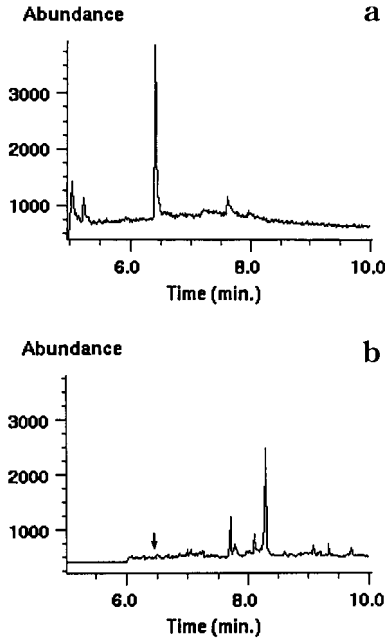

Figure 5. (a) Chromatogram of white pine sample containing imidacloprid as HFB derivative (*m*/*z* 407) at 10 ppb (10 pg injected). (b) Chromatogram of a white pine matrix blank—imidacloprid fraction.

Table 1. Recovery Efficiency for Imidacloprid, Triadimefon, and Triadimenol from White Pine Foliage

analyte	fortifn level (ppm)	mean rec eff (%; $n = 5$)	SD	CV (%)
imidacloprid	10.00	80.59	7.12	8.83
	1.00	81.68	6.59	8.07
	0.10	84.83	8.87	10.45
	0.01	88.89	0.28	11.56
triadimefon	10.00	87.77	8.24	9.39
	1.00	77.16	8.63	11.19
	0.10	86.61	6.72	7.77
triadimenol	10.00	87.77	8.24	9.39
	1.00	84.15	7.23	8.59
	0.10	92.40	12.04	13.03

and is currently being used to determine residues in samples collected in 1995 and 1997. Mean recoveries for QC samples analyzed in conjunction with 1993 field samples are comparable to those obtained during method validation, 85.62 ±9.34% (10.9%). These data will be published at the termination of the field experiments. This analytical method has also been applied in greenhouse bioassays with potted white pine trees artificially infested with white pine weevil. In these experiments imidacloprid was incorporated at various rates into the soil in which white pine seedlings had been planted. Residues were determined in the needles and correlated with efficacy against white pine weevil. These data will be published elsewhere.

CONCLUSIONS

Results from this study demonstrate a sensitive and selective method to determine imidacloprid, triadimefon, and triadimenol residues in white pine foliage. LOQ and LOD are 10 pg and 5 pg on-column for imidacloprid and 100 pg and 50 pg on-column for both triadimefon and triadimenol. LOD has been conservatively set. Overall mean recoveries are 85.78 ± 5.20% (6.06%). We are confident that this procedure can be applied to the determination of imidacloprid, triadimefon, and triadimenol in a variety of other environmental matrixes given the complexity of the white pine matrix. Quantification of triadimefon and triadimenol by SIM at levels below 0.1 ppm in white pine may be achievable with additional cleanup of the Florisil eluate to remove coextractives or with further refinement of the eluents. Electron capture negative-ion mass spectrometry and GC-ECD are options for the imidacloprid HFB derivative which could lower the quantitation and detection limits to parts per trillion levels. MS/MS to filter out the chemical background is an option that could lower the LOQ of all compounds to parts per trillion levels.

ABBREVIATIONS USED

SIM, selected ion monitoring; HPLC-UV, high-performance liquid chromatography with ultraviolet detection; GC/MS, gas chromatography/mass spectrometry; HPLC-DAD, HPLC with diode array detection; LOQ, limit of quantitation; LOD, limit of detection; GC-ECD, gas chromatography with electron capture detection; HFB, heptafluorobutyryl; HFAA, heptafluorobutyric acid anhydride.

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LITERATURE CITED

Brennecke, R. Method for gas chromatographic determination of residues of Bayleton and Bayfidan fungicides in plant material, soil and water. *Pflanzenschutz- Nachr. Bayer*. **1984**, *37* (1), 68−93.

Davis, T. D.; Steffens, G. L.; Sankhla, N. Triazole Plant Growth Regulators. In *Horticultural Reviews*; Janick, J., Ed.; Timber Press: 1988; Vol. 10.

Erney, R. D.; Pawlowski, T. M.; Poole, C. F. Matrix-Induced Peak Enhancement in Gas Chromatography: Is There a Solution? *J. High Resolut. Chromatogr.* **1997**, *20*, 375−378.

Fernández-Alba, A. R.; Valverde, A.; Agüer, A.; Contreras, M.; Chiron, S. Determination of imidacloprid in vegetables by high-performance liquid chromatography with diode-array detection. *J. Chromatogr. A* **1996**, *721*, 97−105.

Fletcher, R. A. Plant Growth Regulating Properties of Sterol-inhibiting Fungicides. In *Hormonal Regulation of Plant Growth and Development*; Purohit, S. S., Ed.; Martinus Nijhoff: Dordrecht, The Netherlands, 1985; Vol. 2.

Fletcher, R. A.; Hofstra, G.; Gao, J. Comparative Fungitoxic and Plant Growth Regulating Properties of Triazole Derivatives. *Plant Cell Physiol.* **1986**, *27* (2), 367−371.

García-G., J. E. Improved method for the determination of triadimefon, triadimenol-A and triadimenol-B in wheat plants (*Triticum aestivum* l.) and soil samples by gas chromatography. *Fresenius' J. Anal. Chem*. **1991**, *339*, 402−404.

Gasztonyi, M.; Josepovits, G. The Activation of Triadimefon and its Role in the Selectivity of Fungicide Action. *Pestic. Sci.* **1979**, *10*, 57−65.

Headley, J. V.; MacDonald, L.; Peru, K. M. GC/MS Determination of Metsulfuron Methyl and Chlorsulfuron in Natural Waters − Matrix Effects. *Proceedings of the 44th ASMS Conference on Mass Spectrometry and Allied Topics*; American Society for Mass Spectrometry: Santa Fe, NM, 1996; p 516.

Ishii, Y.; Kobori, I.; Araki, Y.; Kurogochi, S.; Iwaya, K.; Kagabu, S. HPLC Determination of the New Insecticide Imidacloprid and Its Behavior in Rice and Cucumber. *J. Agric. Food Chem*. **1994**, *42*, 2917−2921.

Kagabu, S.; Medej, S. Stability Comparison of Imidacloprid and Related Compounds under Simulated Sunlight, Hydrolysis Conditions and Oxygen. *Biosci., Biotechnol., Biochem*. **1995**, *59* (6), 980−985.

Moffat, A. S. New Chemicals Seek to Outwit Insect Pests. *Science* **1993**, *261*, 550−551.

Mullins, J. W. Imidacloprid—A New Nitroguanidine Insecticide. In *Pest Control with Enhanced Environmental Safety*; ACS Symposium Series 524; Duke, S. O., Menn, J. J., Plimmer, J. R., Eds.; American Chemical Society: Washington, DC, 1993.

Newsome, W. H.; P. Collins. Multiresidue method for fungicides in fruit and vegetables. *J. Chromatogr.* **1989**, *472*, 416−421.

Placke, F. J.; Weber, E. Method of determining imidacloprid residues in plant materials. *Pflanzenschutz-Nachr. Bayer.* **1993**, *46* (2), 109−182.

Rouchaud, J.; Gustin, F.; Wauters, A. Soil Biodegradation and Leaf Transfer of Insecticide Imidacloprid Applied in Seed Dressing in Sugar Beet Crops. *Bull. Environ. Toxicol.* **1994**, *53*, 344−350.

Vilchez, J. L.; El-Khattabi, R.; Fernández, J.; González-Casado, A.; Navalón, A. Determination of imidacloprid in water and soil samples by gas chromatography-mass spectrometry. *J. Chromatogr. A* **1996**, *746*, 289−294.

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