Determination of Pesticide Residues in Foods by Fluorine-19 Fourier Transform Nuclear Magnetic Resonance Spectroscopy

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Pesticide residues have been determined at, or near, tolerance levels in certain foods by fluorine-19 Fourier transform nuclear magnetic resonance spectroscopy. ^{19}F NMR spectral data are reported for a series of common fluorine-containing pesticides. Practical lower concentration limits for sample screening are also established for pesticides containing the trifluoromethyl group. It is further demonstrated that usable spectra can be obtained from certain concentrated crop extracts and an incurred residue in fish.

In studies to ascertain the feasibility of using Fourier transform nuclear magnetic resonance (FT-NMR) spectroscopic techniques for trace residue analysis, we have applied ^{19}F FT-NMR methods to the determination of fluorine-containing pesticide residues. This new approach was evaluated because a large group of polar fluorinated pesticides exists that could be determined by the technique. The paucity of naturally occurring fluorine compounds and the high NMR sensitivity of the ^{19}F nucleus suggested this method for identifying fluorinated pesticide residues in complex matrices. The same considerations have led to the characterization of trifluoroacetyl derivatives of a wide variety of organic compounds by ^{19}F NMR (Sleevi et al., 1979). Sample cleanup, which is a critical and often time-consuming step for effective gas–liquid chromatographic pesticide residue analysis, is largely unnecessary. As such, this technique presents the potential for rapid sample analysis. In this paper we report ^{19}F NMR spectral data for a series of common fluorine-containing pesticides, practical lower concentration limits for sample screening, analysis of selected crop extracts fortified with trifluralin [4-(trifluoromethyl)-2,6-dinitro-*N*,*N*-dipropylaniline], and analysis of a fish sample with an incurred trifluralin residue.

EXPERIMENTAL SECTION

^{19}F NMR spectra, described by 4096 data points, were obtained at 75 MHz on a Varian Associates FT-80A NMR spectrometer. Spectral widths of 8 kHz were used, which correspond to acquisition times of approximately 0.5 s. Pulse widths of 18 μs were employed, which correspond to tip angles of approximately 40° with 10-mm sample tubes. Sample volumes of 3 mL were used for detection of fluorine signals at 0.1, 1, 10, and 100 ppm.

The extraction methodology used for carrots and peanuts was that described in "Pesticide Analytical Manual" (1978, Vol. II). The method for soybeans was that outlined in "Pesticide Analytical Manual" (1978, Vol. II, Method I, Extraction A) for profluralin. Recoveries by these procedures were greater than 80%. The procedures were used as indicated with the following exceptions: (1) sample sizes were increased to 100 g with commensurately larger volumes of extraction solvent, (2) no sample cleanups were performed, (3) samples were transferred to NMR tubes with deuteriochloroform with a final volume of 3 mL, and (4) ^{19}F FT-NMR was used as the determinative step.

The analytical methodology used for the fish sample was that described in "Pesticide Analytical Manual" (1978, Vol. I, Section 211.13f). Two 40-g samples of fish were used.

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Table I. Fluorine Chemical Shifts for 25 Compounds and Metabolites

compound	functional group	solvent	chemical shift[a,b]
trifluralin	$ArCF_3$	$CDCl_3$	−63.5
benefin	$ArCF_3$	$CDCl_3$	−63.5
Pregard	$ArCF_3$	$CDCl_3$	−63.5
fluchloralin	$ArCF_3$	$CDCl_3$	−63.7
fluchloralin metabolite	$ArCF_3$	$CDCl_3$	−63.7
dinitramine	$ArCF_3$	$CDCl_3$	−63.3
2-chloro-1-(4-nitrophenyl)-4-(trifluoromethyl)benzene	$ArCF_3$	$CDCl_3$	−63.6
oxyfluorfen	$ArCF_3$	$CDCl_3$	−63.6
Preforan	$ArCF_3$	$CDCl_3$	−63.8
norflurazon	$ArCF_3$	$CDCl_3$	−63.9
desmethyl norflurazon	$ArCF_3$	$(CD_3)_2CO$	−62.9
fluometuron	$ArCF_3$	$CDCl_3$	−64.0
Lamprecide	$ArCF_3$	$CDCl_3$	−61.5
Fenazaflor	$ArCF_3$	$CDCl_3$	−63.8
Fenazaflor metabolite 1	$ArCF_3$	$(CD_3)_2CO$	−64.8
Fenazaflor metabolite 2	$ArCF_3$	$(CD_3)_2CO$	−64.5
fluoridamid	$ArNHSO_2CF_3$	$(CD_3)_2CO$	−77.3
mefluidide	$ArNHSO_2CF_3$	$(CD_3)_2CO$	−77.3
perfluidone	$ArNHSO_2CF_3$	$CDCl_3$	−77.5
N-methyl-perfluidone	$ArNHSO_2CF_3$	$CDCl_3$	−75.4
2,4-dimethyl-aniline–HFBA derivative	$R–CF_3$	$CDCl_3$	−81.9
dimefox	$FP(O)[N(CH_3)_2]_2$	$CDCl_3$	−84.0
diflubenzuron	Ar–F	Me_2SO-d_6	−114.0
cryolite	Na_3AlF_6	D_2SO_4	−157[c]
sodium fluoroacetate	CH_2FCO_2Na	D_2O	−222[c]

[a] NMR solutions: approximately 50 mg/3 mL of solvent in a 10-mm tube. [b] Parts per million from $CFCl_3$ internal standard except as noted. [c] External reference.

The combined 6% ethyl ether in petroleum ether eluates from a Florisil column were concentrated to dryness, transferred to an NMR tube with deuteriochloroform, and diluted to a final volume of 3 mL.

The fluorinated pesticide standards were obtained from the U.S. Environmental Protection Agency (EPA), Reference Standards Section, Health Effects Research Laboratory, Environmental Toxicology Division, Research Triangle Park, NC 27711.

RESULTS AND DISCUSSION

Fluorine chemical shifts for most of the compounds investigated occur, as expected (Mooney, 1970; Wray, 1980), between −60 and −80 ppm (Table I). This provides a relatively narrow and convenient detection window for the majority of fluorinated pesticides. The ^{19}F NMR

Table II. Determination Levels for Trifluralin in Standard Solutions and Crop Matrices

concn, ppm	sample	no. of scans	time	S/N
100	standard	10	5 s	62
10	standard	100	1 min	20
1	standard	1000	9 min	6
0.1	standard	58000	8 h	5
1	carrots	1000	9 min	5
1	peanuts	58000	8 h	3
1	soybeans	58000	8 h	3

spectra of 23 of these compounds consist of sharp, well-resolved single lines. Although different functional group classes of fluorine-containing compounds, e.g., (trifluoromethyl)aryl, fluoroaromatic, and inorganic fluorine, can readily be distinguished, the chemical shift data are not sufficient for specific compound identification because of very small chemical shift differences between members of certain functional group classes and substantial solvent dependency exhibited by ^{19}F chemical shifts in general (Emsley and Phillips, 1971). Tetramethylphosphorodiamidic fluoride (dimefox), however, gives a doublet due to coupling to phosphorus. Sodium hexafluoroaluminate (cryolite) was soluble only in deuteriosulfuric acid and then appeared to decompose rapidly None of the other compounds exhibited similar decomposition.

Most of the fluorinated pesticides contain the trifluoromethyl (CF_3) group. The most common of these is trifluralin; for this reason it was selected to determine the practical lower concentration limits for sample screening. Standard solutions of trifluralin in $CDCl_3$ gave sharp, well-resolved signals at concentrations of 100, 10, 1, and 0.1 ppm. The number of scans and data accumulation times required to produce definitive spectra at these concentrations are given in Table II. Because of the favorable signal-to-noise (S/N) values given in Table II and the fact that fortification recovery levels for the methods employed were found to be greater than 80%, concentration levels as low as 0.10 ppm are sufficient to permit detection of the majority of fluorinated pesticides, viz., those that contain trifluoromethyl groups (Martin et al., 1980) in relatively oil-free crops (vide infra).

Since tolerances for fluorinated pesticide residues are generally above 0.05 ppm, this technique will provide an adequate detection level for a large percentage of the fluorinated pesticides currently in use.

Trifluralin was also used to determine whether usable spectra could be obtained from concentrated crop extracts. Three crops were chosen on which this pesticide is currently registered for use: carrots, peanuts, and soybeans. Samples were treated as described under Experimental Section, and the concentrated crop was analyzed by ^{19}F FT-NMR. Samples were first examined by NMR to establish control levels (100000-scan blanks) and then fortified. Times required to obtain good spectra from low to high fortification levels were then determined. An additional study in which carrot samples were fortified before extraction was also performed. Recovery levels comparable to those reported were obtained.

In multiresidue screening analyses of samples of fresh water fish, a gas chromatographic peak with a retention time identical with that of trifluralin was detected by the Food and Drug Administration District Laboratory in Minneapolis, MN. Preliminary electron impact mass spectral analyses could not confirm the identity of this component. A sample of this fish was extracted and cleaned up on a Florisil column. ^{19}F NMF analysis (8 h) indicated the presence of trifluralin, by a signal at −62.8 ppm, at a concentration of about 0.1 ppm, based on comparison with external standards. Subsequent negative ion chemical ionization mass spectral studies confirmed the presence of trifluralin (W. C. Brumley, Food and Drug Administration, personal communication, 1983).

Good spectra were obtained for trifluralin in carrots. Extracts from samples fortified at the tolerance level of 1 ppm (3-mL sample volume) gave a well-defined signal in approximately 15 min. Such analysis times make this an attractive technique for rapid screening. Green leafy vegetables should also be amenable to this method of analysis. Conversely, extracts of 100-g samples of those crops having relatively high oil contents, e.g., peanuts and soybeans, could not be concentrated to the 3-mL volume required for most efficient NMR examination. As a result, samples fortified at the 1-ppm level required longer (8 h) accumulation of data for adequate sensitivity. For samples that contain an appreciable amount of oil, improving the detection limit requires some form of sample cleanup before NMR analysis. However, for samples that are relatively oil free, this NMR method is a rapid screening technique that permits detection of fluorinated pesticide residues at, or near, tolerance levels.

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Registry No. Trifluralin, 1582-09-8; benefin, 1861-40-1; Pregard, 26399-36-0; fluchloralin, 33245-39-5; dinitramine, 29091-05-2; 2-chloro-1-(4-nitrophenyl)-4-(trifluoromethyl)benzene, 90791-27-8; oxyfluorfen, 42874-03-3; Preforan, 15457-05-3; norflurazon, 27314-13-2; desmethyl norflurazon, 23576-24-1; fluometuron, 2164-17-2; Lamprecide, 654-66-0; Fenazaflor, 14255-88-0; fluoridamid, 47000-92-0; mefluidide, 53780-34-0; perfluidone, 37924-13-3; *N*-methylperfluidone, 62059-53-4; dimefox, 115-26-4; diflubenzuron, 35367-38-5; cryolite, 15096-52-3; sodium fluoroacetate, 62-74-8.

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