Multiresidue Determination of Nonvolatile and Thermally Labile Pesticides in Fruits and Vegetables by Thermospray Liquid Chromatography/Mass Spectrometry

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A multiresidue method using high-performance liquid chromatography/thermospray/mass spectrometry/selected ion monitoring (HPLC/TSP/MS/SIM) to determine 19 thermally labile and nonvolatile pesticides in fruits and vegetables was evaluated. The pesticides were extracted from apples, beans, lettuce, peppers, potatoes, and tomatoes with a slightly modified Luke multiresidue extraction procedure. Aldicarb, aldicarb sulfoxide, bufencarb, carboxin, chlorbromuron, diuron, linuron, methiocarb, methomyl, metobromuron, monuron, neburon, oxamyl, propoxur, and thiodicarb were analyzed by mass spectrometry in the positive ion mode. Fenvalerate, folpet, iprodione, and oryzalin were analyzed in the negative ion mode. The limits of detection of the pesticides in the crops were in range 0.025–1 ppm. For those 14 pesticides with limits of detection of 0.25 ppm and below, recovery studies were performed at the 0.5 ppm fortification level in each of the six crops. Recoveries were between 69 and 110%, except for carboxin, which was recovered between 33 and 54%. Coefficients of variation were between 1.4 and 23.6%, with an average of 9.05%.

INTRODUCTION

Several hundred pesticides are used in the United States on fruits and vegetables, and it is impossible to analyze for every registered pesticide in a reasonable amount of time. This is due, in part, to the myriad number of separate analytical procedures that have been developed over the past several decades.

The Luke extraction procedure (Luke et al., 1981; AOAC, 1985), which can extract more than 230 pesticide residues (Luke et al., 1988) ranging from nonpolar pesticides (e.g., DDT) to the highly polar ones (e.g., methamidofos), is the procedure most widely used by the U.S. Food and Drug Administration (FDA). This method requires no cleanup steps, relying for its specificity on a variety of specific GC detectors. Because of the wide variety of pesticide classes, several specific detectors would be required (each one requiring a separate GC determination) for a complete analysis. Mattern et al. (1990) have shown that it is possible to speed up these analyses by using chemical ionization GC/MS for detection and quantification. GC systems, however, are not capable of determining thermally labile and nonvolatile pesticides, and the method of Mattern et al. is not applicable to such pesticides.

To analyze these pesticides, several more methods, all different, have been developed. Krause (1985) developed a liquid chromatographic multiresidue method using an in-line postcolumn fluorometric detector for the determination of *N*-methylcarbamates in grapes and potatoes. A multiresidue method for the determination of phenylurea herbicides in fruits and vegetables by liquid chromatography with postcolumn photodegradation, chemical derivatization, and spectrofluorometry was reported by Luchtefeld (1987). Both methods require cleanup steps including solvent partitioning and column chromatography.

The FDA official methods for the determination of carboxin and oryzalin in crops are based on chemical derivatization followed by gas chromatography (FDA, 1985). Carboxin is extracted from the crops by Soxhlet extraction with methanol and partitioned into chloroform. Caustic digestion after the evaporation of chloroform cleaves aniline from carboxin, and the aniline is recovered by steam distillation. Carboxin is then determined as aniline by gas chromatography with a microcoulometric nitrogen detector. Oryzalin, on the other hand, is extracted from the crops by blending with methanol and derivatized to a *N*,*N*-dimethyl derivative with methyl iodide after filtration. The *N*,*N*-dimethyl derivative is purified by alumina column chromatography and finally determined by electron capture gas chromatography.

High-performance liquid chromatography is very effective in separating nonvolatile and thermally labile compounds, but conventional detectors, such as ultraviolet absorption and flame ionization, are not sufficiently selective to determine the target pesticides in complex food matrices. A fluorescence detector could not be used in a multiresidue procedure because it would not detect nonfluorescent pesticides. Bellar and Budde (1988) reported the determination of nonvolatile organic compounds in aqueous environmental samples using TSP LC/MS. They concluded that among 52 pesticides and other compounds of environmental interest tested there were 26 compounds for which precision, accuracy, and method detection limits were adequate for environmental monitoring.

In this study, an attempt was made to extend the work of Bellar and Budde to the analysis of fruits and vegetables and to develop methodology that would combine the analyses of phenylureas, carbamates, and several other pesticides into a single procedure.

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EXPERIMENTAL PROCEDURES

Chemicals. Chlorbromuron, diuron, fenvalerate, folpet, iprodione, linuron, methomyl, monuron, neburon, oryzalin, and oxamyl reference standards were purchased from Chem Service, Inc. (West Chester, PA). 2-Fluoro-9-fluorenone was purchased from Aldrich Chemical Co. (Milwaukee, WI). Aldicarb, aldicarb sulfoxide, bufencarb, carboxin, methiocarb, metobromuron, propoxur, and thiodicarb were supplied by the EPA (Research Triangle Park, NC). Sodium chloride, ammonium acetate, anhydrous sodium sulfate, and high-purity HPLC grade acetone, acetonitrile, methanol, petroleum ether, and water were purchased from Fisher Scientific (Springfield, NJ).

Samples. The fruits and vegetables used for this study were collected from New Jersey supermarket distributors and various farms in that state. The samples used for recovery and sensitivity studies were previously determined to be free of the pesticides in this study by unspiked crops under the conditions specified below.

Instrumentation Conditions. A Kratos Spectraflow 400 liquid chromatograph (Kratos, Ramsey, NJ) interfaced to a Vestec Model 201 thermospray LC/MS (Vestec Corp., Houston, TX) and controlled by a Teknivent Vector/One data system (Teknivent Corp., St. Louis, MO) on a Compac Deskpro 286 personal computer was used. A 22 cm × 4.6 mm i.d. Spheri-5 reversed-phase C-18 HPLC column (Brownlee Labs, Santa Clara, CA) with a particle size of 5 μm was used. The mass spectrometer was operated in either the positive ion or negative ion discharge mode. The vaporizer tip temperature was held between 225 and 235 °C, the scan time was 0.5 s, and the sweep width was 0.1 amu for both full-scan and selected ion monitoring (SIM) operations.

For the determinations of aldicarb, bufencarb, carboxin, chlorbromuron, diuron, linuron, methiocarb, methomyl, metobromuron, monuron, neburon, propoxur, oxamyl, and thiodicarb the initial mobile phase composition was 20% acetonitrile, 65% water, and 15% 0.013 M ammonium acetate solution. This was programmed linearly to 80% acetonitrile, 5% water, and 15% 0.013 M ammonium acetate solution in 30 min, and the mass spectrometer was operated in the positive ion discharge mode. For the analyses of fenvalerate, folpet, iprodione, and oryzalin the mobile phase was programmed linearly from 50% acetonitrile and 50% water to 80% acetonitrile and 20% water in 5 min, and the mass spectrometer was operated in the negative ion discharge mode. The flow rate in both cases was 1 mL/min, and the injection volume was 50 μL. The TSP LC/MS spectrum of each analyte and the internal standard was obtained by injection of 250 ng/μL in methanol except for aldicarb sulfoxide (in acetonitrile) and folpet (in acetone).

Selected ion monitoring ions were m/z 157 (aldicarb), 207 (aldicarb sulfoxide), 222 (bufencarb), 236 (carboxin), 295 (chlorobromuron), 233 (diuron), 249 (linuron), 226 (methiocarb), 163 (methomyl, oxamyl, and thiodicarb), 259 (metobromuron), 199 (monuron and 2-fluoro-9-fluorenone), 275 (neburon), and 210 (propoxur) in the positive ion discharge mode and m/e 211 (fenvalerate), 198 (2-fluoro-9-fluorenone), 146 (folpet), 141 (iprodione), and 346 (oryzalin) in the negative ion discharge mode.

Sample Preparation. The Luke procedure (AOAC, 1985) with a slight modification published by Mattern et al. (1990) was followed. One hundred gram chopped samples were extracted with 200 mL of acetone in a Waring blender for 1 min at low speed. The mixture was filtered, and the volume of the filtrate was recorded. This volume is used in the formula for determination of pesticide concentration in food (vide infra). Eighty milliliters of the filtrate was shaken vigorously with 100 mL of petroleum ether and 100 mL of methylene chloride in a 1-L separation funnel. The aqueous phase was transferred to a 125-mL flask. The organic phase was dried by passing it through anhydrous sodium sulfate supported by glass wool in a 4-in. funnel and collected in a 500-mL Kuderna-Danish concentrator. The aqueous phase was saturated with about 7 g of sodium chloride and then extracted with 100 mL of methylene chloride. The organic phase was dried and collected through the same sodium sulfate. The aqueous phase was saturated with sodium chloride and extracted with 100 mL of methylene chloride in the same way. Again, the organic phase was dried and collected through the same sodium sulfate. The aqueous phase was then discarded.

Table I. Ions Observed in the Positive Ion Mode Thermospray LC/MS Spectra of Pesticides Tested

pesticide	MW	base peak	second ion
aldicarb	190	157	208 (40)[a]
aldicarb sulfoxide	206	207	173 (24)
bufencarb	221	222	
carboxin	235	236	
chlorbromuron	292	295	293 (75)
diuron	232	233	235 (66)
linuron	248	249	251 (66)
methiocarb	225	226	169 (13)
methomyl	162	163	
metobromuron	258	259	261 (98)
monuron	198	199	
neburon	274	275	277 (66)
oxamyl	219	163	237 (21)
propoxur	209	210	227 (25)
thiodicarb	354	163	355 (54)

[a] Percent abundance relative to base peak.

The sodium sulfate was washed with an additional 50-mL portion of methylene chloride. A Snyder column was attached to the concentrator, and the solvent was evaporated to about 4 mL on a steam bath. The appropriate internal standard stock solution (40 μL) was added to the final concentrate, and the volume was adjusted to 4 mL.

Preparation of Calibration Curves. Individual solutions of each pesticide at 250 ng/μL were prepared in methanol (except aldicarb sulfoxide in acetonitrile and folpet in acetone). A stock solution of 50 ng/μL was prepared by mixing 1 mL from each individual solution and concentrating to 5 mL. The stock solution was serially diluted, and the appropriate amount of internal standard stock solution (1000 ng/μL) was added. The standard solutions then contained 1, 2, 5, 10, and 20 ng/μL of each pesticide and 10 ng/μL of 2-fluoro-9-fluorenone internal standard. These standard solutions were analyzed two times at each concentration level. Peak areas were obtained from SIM chromatograms of each pesticide, and response factors were calculated by dividing the peak area of each pesticide by that of the internal standard. The response factors of each pesticide were plotted against the amounts of each pesticide in standard solutions on log paper. Linear calibration curves were generated with linear correlation coefficients between 0.930 for propoxur and 0.998 for fenvalerate.

Recovery Studies. Recovery studies were performed at the 0.5 ppm fortification level of each pesticide three times in each of the six crops. These samples were prepared by adding 1.0 mL of 50 ng/μL pesticides stock solutions to 100 g of chopped fruit or vegetable before extraction. The extracts were analyzed as previously described. The relative response factors of each pesticide were applied to the calibration curves, and the concentration (C) of each pesticide in nanograms per microliter in the final extracts was calculated. The concentration of each pesticide in the crops in nanograms per milligram (parts per million) was calculated by using the formula

$$\text{ppm} = \frac{(C \text{ ng of analyte}/\mu\text{L injected}) \times (4000\ \mu\text{L})}{(100 \text{ g of sample}) \times (1000 \text{ mg/g}) \times (80\text{-mL aliquot}/V)} = \frac{CV}{2000}$$

where C is the concentration in nanograms per microliter of pesticide in the solution that was injected and V is the total volume in milliliters of the acetone extract.

Sensitivity Determinations. Appropriate amounts of the pesticide standard solution were added to 1-mL blank extracts of crops. Assuming 100% extraction efficiency, these solutions were made to represent extracts of crops spiked at approximately 0.025, 0.05, 0.1, 0.25, and 1 ppm levels for each pesticide.

RESULTS AND DISCUSSION

Mass spectra were obtained in the positive ion discharge mode operation except for fenvalerate, folpet, iprodione, and oryzalin (negative ion). Table I summarizes the molecular weights, base peaks and second most abundant ions (with relative abundance) of the mass spectra of the

Table II. Ions Observed in the Negative Ion Mode Thermospray LC/MS Spectra of Pescticides Tested

pesticide	MW	base peak	second ion
fenvalerate	419	211	167 (33)[a]
folpet	295	146	
iprodione	329	141	328 (9)
oryzalin	346	346	

[a] Percent abundance relative to base peak.

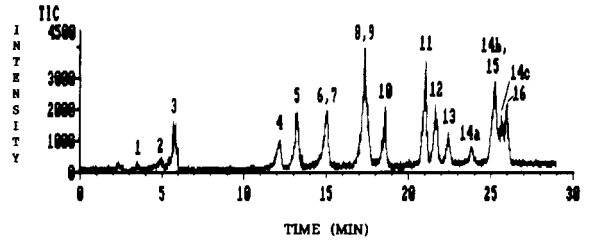

Figure 1. Positive total ion chromatogram of a 50-μL standard solution containing 20 ng/μL of each pesticide and 10 ng/μL of the internal standard aldicarb sulfoxide (1), oxamyl (2), methomyl (3), aldicarb (4), monuron (5), thiodicarb (6), propoxur (7), carboxin (8), diuron (9), metobromuron (10), methiocarb (11), linuron (12), chlorbromuron (13), bufencarb (14a–c), 2-fluoro-9-fluorenone (15), and neburon (16).

15 pesticides that were analyzed in the positive ion discharge mode; Table II summarizes the data for the pesticides analyzed in the negative ion discharge mode.

Base peaks were most often the protonated molecular ions in the positive ion discharge mode. Aldicarb (molecular weight 190), however, had a base peak of m/z 157, corresponding to the addition of acetonitrile to $[CH_3SC(CH_3)_2CH{=}N]^+$, an ion whose identity was confirmed in an LC/MS determination where methanol replaced acetonitrile in the mobile phase. The base peak became m/z 148 (corresponding to the addition of methanol to the same fragment ion), and no m/z 157 peak was observed. Oxamyl had a base peak of m/z 163 which corresponds to a protonated fragment $[(CH_3)_2N{=}C(OH)C(SCH_3){=}NOH]^+$. The second most abundant ion of oxamyl, m/z 237, resulted from the addition of ammonium ion to the oxamyl molecule. Thiodicarb also had a base peak of m/z 163 corresponding to the same protonated fragment as oxamyl. The second most abundant ion of thiodicarb, m/z 355, corresponded to the protonated thiodicarb molecule. For the negative ion mode operation, the base peaks were most often a fragment anion. Oryzalin had a base peak of m/z 346 corresponding to the molecular anion, and no fragmentation was observed.

The total ion current chromatogram of a standard solution containing 20 ng/μL of the pesticides and 10 ng/μL of the internal standard detected by positive ion TSP is shown in Figure 1. Although some analytes coeluted, they could still be analyzed because of the specificity of SIM as shown (Figure 2) for propoxur (m/z 210) and thiodicarb (m/z 163) coeluting at 14.9 min; carboxin (m/z 236) and diuron (m/z 233) at 17.4 min; and bufencarb (m/z 222), 2-fluoro-9-fluorenone (m/z 199), and neburon (m/z 275) at 25.5 min. Bufencarb gave more than one chromatographic peak because it is a mixture of structural isomers.

Figure 3 shows the chromatographic separation of a 10 ng/μL standard solution of the pesticides and the internal standard detected by negative ion TSP. Again, SIM permitted determination of oryzalin, folpet, and the internal standard (2-fluoro-9-fluorenone) coeluting at approximately 7 min.

The selected ion monitoring (SIM) chromatograms for a lettuce sample spiked with some of the pesticides at the

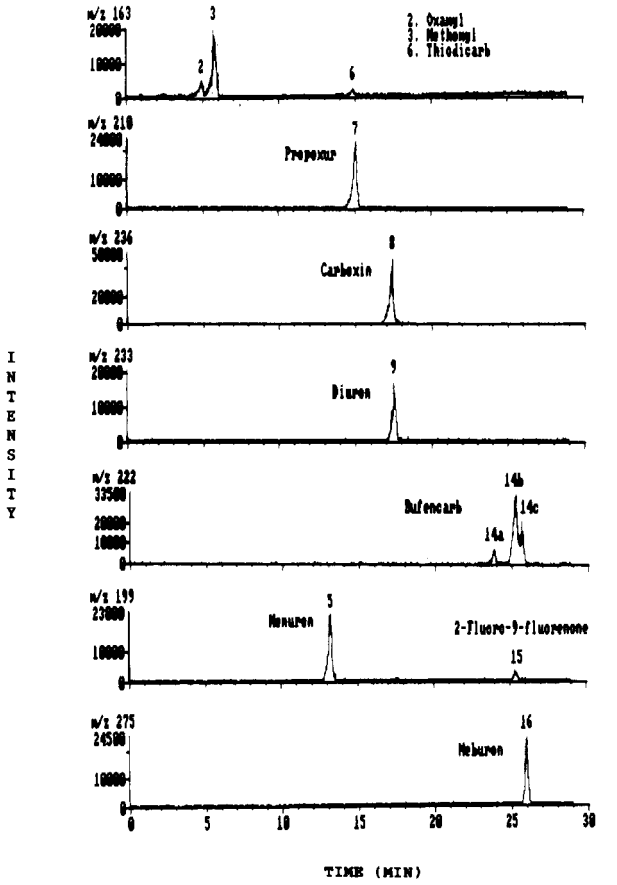

Figure 2. Positive SIM chromatograms of some coeluting pesticides. Amounts injected and concentrations were as in Figure 1.

0.5 ppm level and analyzed in the positive ion mode are shown in Figure 4. Figure 5 shows the SIM chromatograms of an apple sample spiked with some of the other pesticides in this study at the 0.5 ppm level and analyzed with negative ion detection. The results of the recovery studies in each crop for all the analytes at the 0.5 ppm level are given in Table III. Average recoveries were between 69.1 and 110.4% except for carboxin, which gave exceptionally low recoveries (between 33.4 and 54.3%). Coefficients of variation were in range 1.4–23.6%, with an average of 9.05%. The recoveries of aldicarb, aldicarb sulfoxide, methomyl, oxamyl, and thiodicarb in all six crops and chlorbromuron in apples and potatoes at 0.5 ppm fortification level were not obtained because their limits of detection were at the 0.5 ppm level or higher. The recovery of iprodione in potatoes could not be calculated because of the interference by a potato constituent.

The limits of detection of all pesticides in the crops tested are summarized in Table IV. Of the 15 positive ion mode pesticides, aldicarb, aldicarb sulfoxide, methomyl, oxamyl, and thiodicarb had a limit of detection of 1.0 ppm in all six crops. The other pesticides had a limit of detection of 0.25 ppm in all crops tested, except chlorbromuron, which had a limit of detection of 0.5 ppm in apples and potatoes. Fenvalerate, folpet, iprodione, and oryzalin, which were analyzed in the negative ion mode, had limits of detection in the range 0.025–0.1 ppm. Limits of detection were lower than or equal to the tolerances set by the EPA, except chlorbromuron, fenvalerate, metobromuron, and oxamyl in potatoes.

Figure 6 shows the SIM chromatograms of aldicarb, aldicarb sulfoxide, methomyl, oxamyl, and thiodicarb that were spiked into an apple sample at the 1 ppm level. Figure

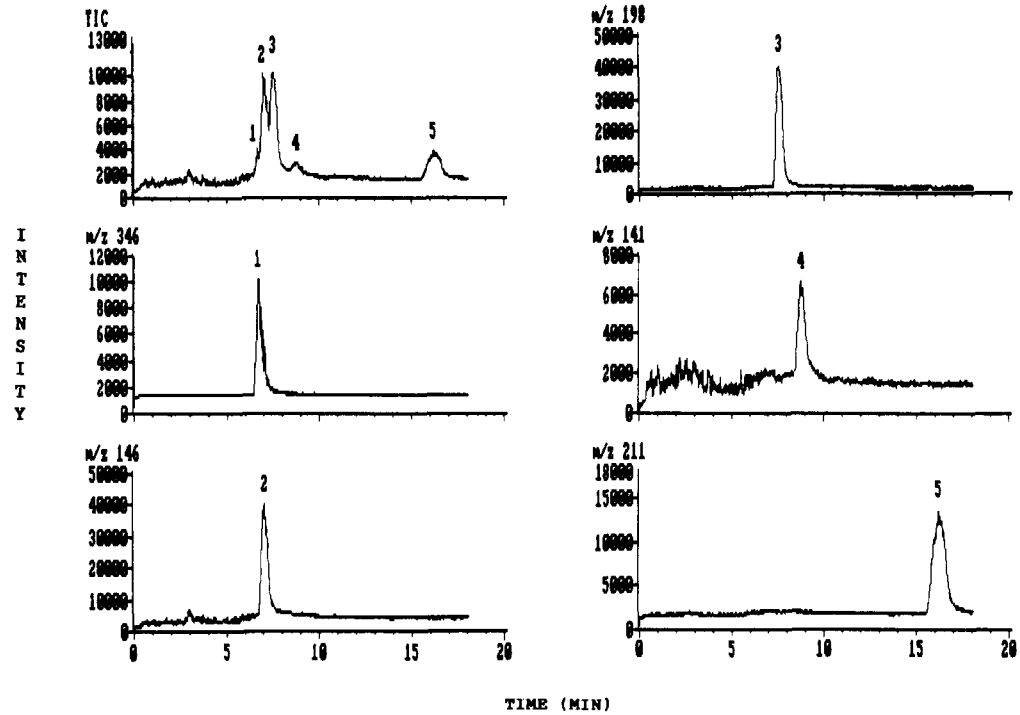

Figure 3. Negative total ion and SIM chromatograms of a 50-μL standard solution containing 10 ng/μL of each pesticide and the internal standard oryzalin (1), folpet (2), 2-fluoro-9-fluorenone (3), iprodione (4), or fenvalerate (5).

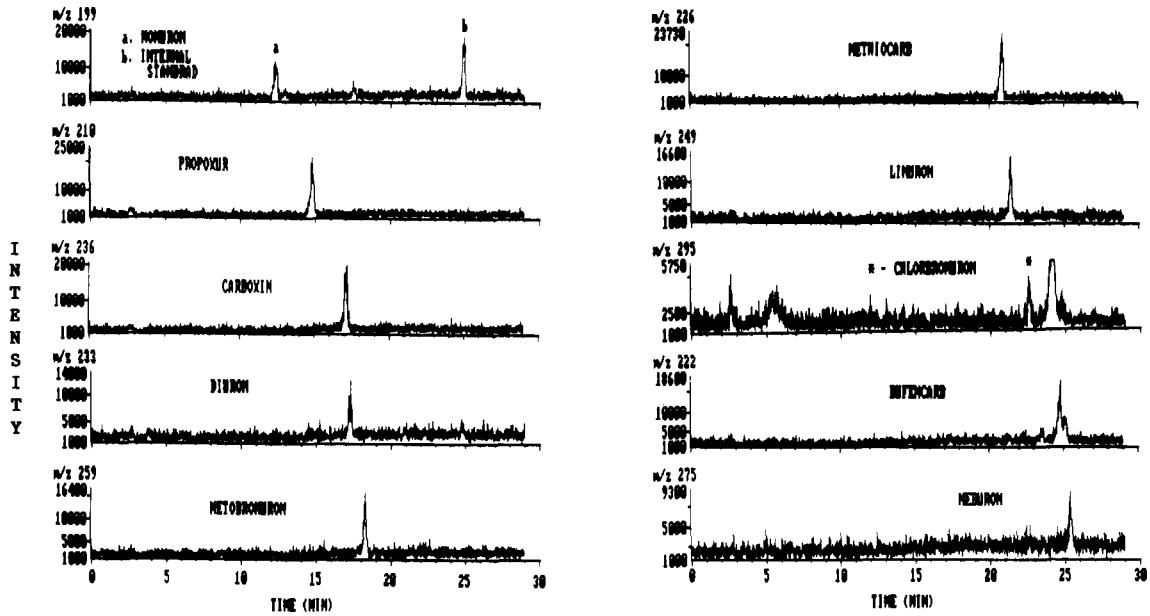

Figure 4. Positive SIM chromatograms for some of the pesticides spiked into lettuce at the 0.5 ppm level before extraction.

7 depicts the SIM chromatograms of linuron, metobromuron, and propoxur spiked into an apple sample at the 0.25 ppm level. Figure 8 shows the SIM chromatograms of fenvalerate, folpet, and oryzalin spiked into a potato sample at the 0.025 ppm level.

Although LC/MS appears to be an excellent technique for most of the pesticides in this study, results for aldicarb, aldicarb sulfoxide, methomyl, oxamyl, and thiodicarb were disappointing in terms of limit of detection. Bellar and Budde (1988) reported good sensitivities for the first four compounds using TSP with both filament and discharge off, but our instrument did not exhibit good sensitivity under these conditions. When we operated the thermospray source in the filament ionization mode, good sensitivities could be obtained but the response was not stable. Operation in the discharge ionization mode provided the best compromise.

The 19 pesticides shown in Tables I and II were selected for several reasons. Carbamates (aldicarb, aldicarb sulfoxide, bufencarb, methiocarb, methomyl, oxamyl, propoxur, and thiodicarb) and phenylurea herbicides (chlorbromuron, diuron, linuron, metobromuron, monuron, and neburon) are too thermally labile to be determined by gas chromatographic (GC) methods. Oryzalin is a nonvolatile compound that has to be analyzed by liquid chromatographic (LC) methods. Fenvalerate, folpet, and iprodione can be determined by GC, but they were found to be less sensitive than most pesticides in the GC/MS multiresidue method previously reported (Mattern et al., 1990). Although carboxin (an N-substituted amide) can be determined by GC/MS, we chose to include it in the LC/MS multiresidue method to see if better sensitivity could be obtained.

The Luke extraction procedure (AOAC, 1985) was used

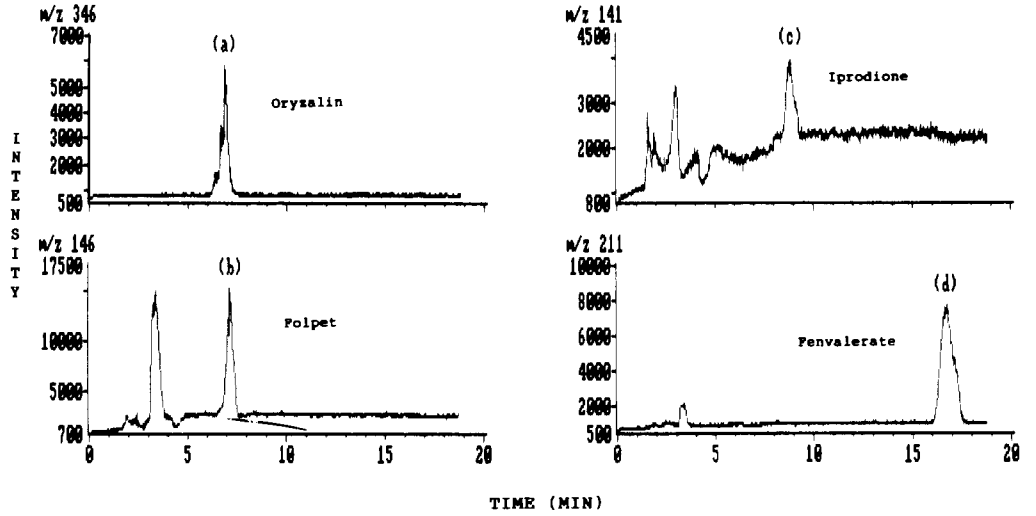

Figure 5. Negative SIM chromatograms for the pesticides spiked into apples at the 0.5 ppm level before extraction.

Table III. Recoveries[a] of Pesticides at the 0.5 ppm Level

pesticide	apples	beans	lettuce	peppers	potatoes	tomatoes
aldicarb	LD[b]	LD	LD	LD	LD	LD
aldicarb sulfoxide	LD	LD	LD	LD	LD	LD
bufencarb	80.3 (6.7)[c]	113.5 (9.4)	89.0 (7.1)	87.6 (9.4)	96.5 (14.4)	105.5 (12.9)
carboxin	54.3 (18.8)	33.4 (7.6)	51.0 (14.6)	39.4 (14.9)	44.1 (11.1)	52.4 (9.3)
chlorbromuron	LD	77.8 (9.4)	90.3 (5.2)	75.9 (3.4)	LD	95.5 (4.4)
diuron	108.5 (11.9)	87.7 (5.7)	101.2 (12.5)	95.0 (5.8)	78.9 (9.9)	103.3 (17.4)
fenvalerate	89.9 (6.7)	91.6 (8.4)	80.1 (5.6)	91.5 (1.7)	80.8 (5.0)	74.3 (4.1)
folpet	81.9 (10.5)	89.1 (10.8)	89.6 (4.6)	96.8 (3.4)	80.8 (4.2)	95.0 (2.8)
iprodione	81.9 (9.8)	78.7 (8.5)	87.0 (7.8)	71.5 (7.9)	I[d]	82.0 (8.9)
linuron	75.3 (5.4)	81.3 (9.8)	79.9 (6.0)	74.7 (9.5)	89.8 (5.4)	82.5 (14.2)
methiocarb	109.3 (10.4)[c]	87.7 (9.8)	108.4 (8.1)	95.4 (10.9)	100.4 (18.5)	110.4 (8.8)
methomyl	LD[b]	LD	LD	LD	LD	LD
metobromuron	85.7 (4.6)	69.1 (3.3)	84.6 (8.1)	82.0 (9.8)	72.0 (8.6)	83.2 (23.6)
monuron	87.5 (8.3)	74.7 (15.2)	93.0 (19.3)	87.5 (10.9)	76.3 (7.7)	94.9 (13.2)
neburon	76.0 (3.5)	79.8 (4.4)	84.7 (6.8)	84.1 (12.0)	84.0 (3.2)	97.8 (6.2)
oryzalin	78.7 (3.3)	96.9 (1.4)	91.3 (5.6)	85.5 (15.0)	78.6 (10.9)	81.2 (15.5)
oxamyl	LD	LD	LD	LD	LD	LD
propoxur	92.3 (8.6)	76.4 (5.4)	93.8 (12.5)	91.7 (17.5)	79.4 (7.3)	93.6 (12.4)
thiodicarb	LD	LD	LD	LD	LD	LD

[a] Average of triplicate. [b] LD, limit of detection is 0.5 ppm or higher. [c] Number in parentheses is the coefficient of variation. [d] I, interference by potato constituent.

Table IV. Limits of Detection (Parts per Million) of Pesticides in Various Crops

pesticide	apples	beans	lettuce	peppers	potatoes	tomatoes
aldicarb	1.0	1.0	1.0	1.0	1.0 (1)[a]	1.0
aldicarb sulfoxide	1.0	1.0	1.0	1.0	1.0	1.0
bufencarb	0.25	0.25	0.25	0.25	0.25	0.25
carboxin	0.25	0.25	0.25	0.25	0.25	0.25
chlorbromuron	0.5	0.25	0.25	0.25	0.5 (0.2)	0.25
diuron	0.25 (1)	0.25	0.25	0.25	0.25 (1)	0.25
fenvalerate	0.05 (2)	0.05 (2)	0.05	0.05 (1)	0.025 (0.02)	0.1 (1)
folpet	0.05 (25)	0.25	0.05 (50)	0.05	0.025	0.1 (25)
iprodione	0.1	0.25	0.1 (15)	0.25	I[b]	0.1
linuron	0.25	0.25	0.25	0.25	0.25 (1)	0.25
methiocarb	0.25	0.25	0.25	0.25	0.25	0.25
methomyl	1.0 (1)[a]	1.0	1.0 (5)	1.0	1.0	1.0 (1)
metobromuron	0.25	0.25	0.25	0.25	0.25 (0.2)	0.25
monuron	0.25	0.25	0.25	0.25	0.25	0.25
neburon	0.25	0.25	0.25	0.25	0.25	0.25
oryzalin	0.05	0.05	0.05	0.05	0.025 (0.05)	0.1
oxamyl	1.0 (2)	1.0	1.0	1.0 (3)	1.0 (0.1)	1.0 (2)
propoxur	0.25	0.25	0.25	0.25	0.25	0.25
thiodicarb	1.0	1.0	1.0	1.0	1.0	1.0

[a] Tolerance (ppm). [b] I, interference by potato constituent.

for the extraction of the pesticides because it is known to be capable of extracting more than 230 pesticides from fruits and vegetables and is thus the most common extraction procedure used by regulatory agencies. We envision a procedure wherein the Luke extraction procedure provides a concentrated solution from which aliquots for both GC/MS *and* LC/MS can be taken.

Discharge ionization requires no volatile buffer, but LC separations were improved when ammonium acetate buffer was incorporated into the mobile phase. However, sen-

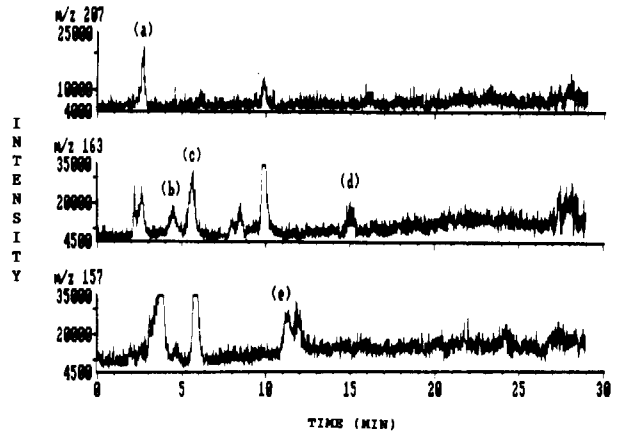

Figure 6. Positive SIM chromatograms of some of the pesticides added to an apple extract to simulate a 1 ppm determination: (a) aldicarb sulfoxide; (b) oxamyl; (c) methomyl; (d) thiodicarb; (e) aldicarb.

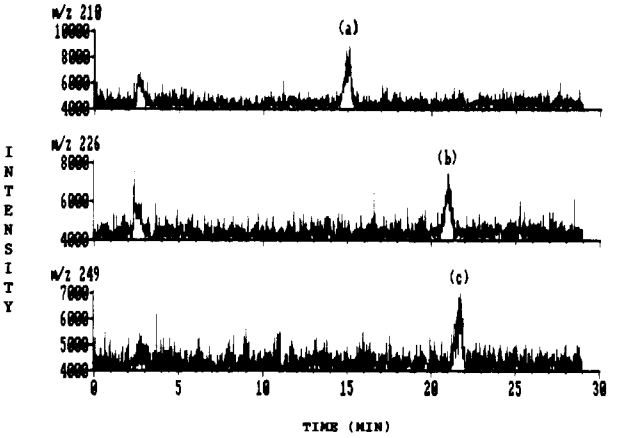

Figure 7. Positive SIM chromatograms of some of the pesticides added to a lettuce extract to simulate a 0.25 ppm determination: (a) propoxur; (b) methiocarb; (c) linuron.

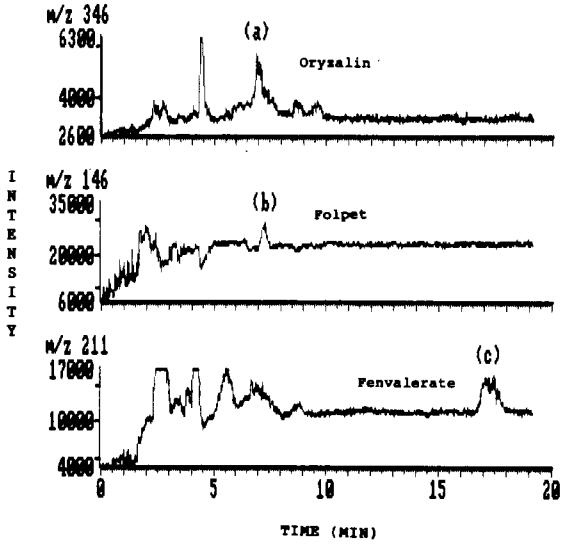

Figure 8. Negative SIM chromatograms of some of the pesticides added to a potato extract to simulate a 0.025 ppm determination.

sitivity losses in the negative ion mode (probably due to acetate having a higher electron affinity than solvent and analyte molecules) restricted the use of ammonium acetate to the positive ion mode. 2-Fluoro-9-fluorenone was chosen as an internal standard because it demonstrated good sensitivity to both positive and negative ion mode operations.

The method discussed in this paper has several advantages over current methods. No derivatization step is required as compared to current official methods for the determination of carboxin and oryzalin. Different classes of pesticides, such as carbamates and phenylureas, are extracted by one procedure. The sensitivity and specificity of mass spectrometry permit the use of the Luke extraction procedure and make unnecessary the cleanup steps in presently used procedures. Furthermore, the use of a mass spectrometer as the detector gives a higher degree of confirmation of molecular identity than methods based on fluorescence or ultraviolet detectors. Finally, multiresidue LC/MS techniques must be incorporated into pesticide analyses because so many pesticide metabolites (which are included in EPA tolerances) cannot be determined by GC. Although some of the current methods may provide better sensitivity for some of the target pesticides than the LC/MS method described, they also require different analyses for each pesticide or each group of pesticides. It is very time- and labor-consuming to analyze each pesticide or each group of pesticides with each official method. Regulatory agencies might perfer the trade-off of being able to analyze many more samples in a given period of time for the disadvantage of not being able to analyze some pesticides at extremely low limits of detection.

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