GC/MS and LC/MS Determination of 20 Pesticides for Which Dietary Oncogenic Risk Has Been Estimated

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The National Research Council has estimated dietary oncogenic risk for 28 pesticides registered for use in the United States. We report a rapid analytical procedure for 20 of these pesticides in a variety of crops based on a single extraction step and the use of mass spectrometry for detection and quantification. Recovery and sensitivity studies were performed in various commodities (apples, peaches, potatoes, tomatoes, peppers, spinach, lettuce, snap beans, and sweet corn) for the suspected oncogens acephate, alachlor, azinphos-methyl, captafol, captan, chlordimeform, chlorothalonil, cypermethrin, diclofop-methyl, ethalfluralin, metolachlor, oxadiazon, parathion, permethrin, pronamide, *o*-phenylphenol, terbutryne, folpet, linuron, and oryzalin. All pesticides were determined by gas chromatography/chemical ionization mass spectrometry (GC/CIMS) except the last three, for which high-performance liquid chromatography/mass spectrometry (HPLC/MS) was used. Average recoveries at the 0.5 ppm fortification level were between 70 and 123%, with an average coefficient of variation of 13%. Sensitivity studies demonstrated that most pesticides could be detected at 0.05 or 0.10 ppm in the crops, but some limits of detection were 0.25 ppm or greater.

INTRODUCTION

The Environmental Protection Agency (EPA) has published cancer potency values (Q^*) for 28 pesticides currently registered for use in the United States, and these values have been used to calculate human cancer risk (National Research Council, 1987). The State of California has recently enacted legislation that fruits and vegetables sold there be analyzed for these pesticides. Given the diverse chemical nature of the oncogenic pesticides, numerous determinations would have to be performed in every crop. In this paper, we describe a procedure based on the widely used Luke extraction procedure (AOAC, 1985), GC/CIMS (Mattern et al., 1990), and HPLC/MS (Liu et al., 1991) to determine 20 of these pesticides in various crops. Current methods of analysis for these 20 pesticides would require at least five separate GC determinations and two additional HPLC determinations.

EXPERIMENTAL PROCEDURES

Chemicals. Acephate, alachlor, azinphos-methyl, captafol, captan, chlordimeform, chlorothalonil, d_{12}-chrysene, diclofop-methyl, ethalfluralin, folpet, linuron, metolachlor, oryzalin, oxadiazon, pronamide, *o*-phenylphenol, and terbutryne reference standards were purchased from Chem Service (West Chester, PA). *cis*- and *trans*-permethrin reference standards were supplied by FMC (Princeton, NJ). Fluorene and 2-fluoro-9-fluorenone were purchased from Aldrich Chemical (Milwaukee, WI). Cypermethrin and parathion reference standards were supplied by the EPA (Research Triangle Park, NC). Sodium chloride, ammonium acetate, anhydrous sodium sulfate, and high-purity HPLC grade acetone, methanol, petroleum ether, dichloromethane, ethyl ether, water, and acetonitrile were purchased from Fisher Scientific (Springfield, NJ).

Crop Samples. The fruits and vegetables used for this study were collected from New Jersey supermarket distributors and various farms in New Jersey. The samples used for recovery and sensitivity studies were previously determined to be free of any of the pesticides in this study.

GC/CIMS. A Varian Model 3400 gas chromatograph (Varian Associates, Walnut Creek, CA) interfaced to a Finnigan MAT ion trap detector in the chemical ionization mode (Finnigan MAT, San Jose, CA) and controlled by an IBM PC/AT was used. The analyses and quantifications were performed with Finnigan Ion Trap software version 3.15. A splitless on-column injector held at 50 °C was used, and a 2 m × 0.53 mm (i.d.) deactivated fused silica precolumn was fitted between the injector and capillary column. Approximately 45 cm of the precolumn was removed after every five injections because of the accumulation of nonvolatile sample components. A new, 2-m precolumn was installed after every 20 injections. A 30 m × 0.25 mm i.d. J&W (Rancho Cordova, CA) DB-1 fused-silica capillary column (1-μm film thickness) was held at 50 °C for 1 min and then temperature-programmed from 50 to 280 °C at 15 °C/min. For analysis with a 15-m column, the column temperature was programmed from 80 to 260 °C at 20 °C/min. Carrier gas (He) velocity was 25 cm/s, and the injection volume was 1 μL. A 15-cm syringe needle was used for the on-column injections. The mass spectrometer was operated in the chemical ionization mode using isobutane reagent gas at a source pressure that gave a 2/1 ratio for m/z 43–57. The filament voltage and current were 70 eV and 80 μA, respectively. Electron multiplier gain was 10^5. Scan range was from 100 to 420 amu at 1 s/scan. Transfer line and manifold temperatures were 250 and 220 °C, respectively.

HPLC/MS. A Kratos Spectraflow 400 liquid chromatograph (Kratos, Ramsey, NJ) containing a 22 cm × 4.6 mm i.d. Spheri-5 reversed-phase C-18 HPLC column (Brownlee Laboratories, Santa Clara, CA) with a particle size of 5 μm was interfaced to a Vestec Model 201 thermospray LC/MS (Vestec, Houston, TX). The system was controlled by a Teknivent Vector/One data system (Teknivent, St. Louis, MO) on a Compac Deskpro 286 personal computer. A mobile phase consisting of 20% acetonitrile, 65% water, and 15% 0.013 M ammonium acetate linearly programmed to 80% acetonitrile, 5% water, 15% 0.013 M ammonium acetate in 30 min was used for the elution of linuron, which was analyzed by selected ion monitoring (m/z 249) in the positive ion discharge mode. A mobile phase linearly programmed from 50% acetonitrile/50% water to 80% acetonitrile/20% water in 5 min was used for the elution of folpet and oryzalin, which were analyzed by selected ion monitoring at m/z 346 and 146,

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Table I. Percent Recoveries (Percent Coefficients of Variation)[a] for Pesticides at 0.5 ppm Determined by GC/CIMS

pesticide	peppers	spinach	lettuce	beans	corn
acephate	117.8 (6.8)	79.1 (7.4)	101.1 (25.5)	116.1 (7.6)	NR[b]
alachlor	108.5 (14.5)	74.0 (11.8)	109.2 (19.9)	109.5 (13.1)	72.5 (13.0)
azinphos-methyl	78.8 (11.6)	71.5 (7.7)	84.0 (27.1)	76.3 (8.2)	NR
captafol	NP[c]	NP	NP	NP	NR
captan	116.8 (7.7)	122.7 (4.3)	120.9 (7.0)	115.6 (6.3)	NR
chlordimeform	87.8 (24.2)	72.6 (7.9)	99.7 (24.5)	94.7 (25.2)	NR
chlorothalonil	81.0 (6.3)	LD[d]	73.2 (6.8)	LD	NR
cypermethrin	LD	LD	LD	LD	LD
diclofop-methyl	79.1 (10.0)	70.3 (5.3)	117.2 (11.6)	83.2 (23.5)	NR
ethalfluralin	110.8 (16.2)	85.3 (5.1)	77.4 (8.4)	117.1 (5.0)	110.9 (14.5)
folpet	76.5 (8.6)	LD	112.4 (6.3)	LD	NR
metolachlor	113.7 (15.3)	79.3 (5.5)	112.1 (21.2)	109.8 (15.6)	82.4 (20.9)
o-phenylphenol	118.6 (8.2)	82.9 (7.3)	112.0 (5.9)	82.1 (15.2)	74.7 (6.8)
oxadiazon	72.6 (6.6)	72.9 (6.6)	108.7 (13.6)	108.6 (13.6)	103.7 (19.2)
parathion	76.1 (10.0)	73.0 (9.9)	71.6 (11.0)	88.8 (13.8)	87.5 (22.9)
permethrin[e]	78.9 (6.3)	LD	LD	76.3 (8.5)	74.2 (8.7)
pronamide	97.4 (11.3)	86.3 (14.3)	106.5 (24.9)	79.8 (13.6)	91.3 (19.1)
terbutryne	92.7 (17.6)	77.3 (8.3)	106.7 (22.0)	97.3 (17.6)	NR

[a] Average of three determinations. [b] NR, not recovered from corn when the Florisil cleanup procedure was used. [c] NP, analysis not performed. [d] LD, limit of detection is 0.5 ppm or higher. [e] Amount of permethrin is sum of cis and trans isomers.

Table II. Percent Recoveries (Percent Coefficients of Variation)[a] for Pesticides at 0.5 ppm Determined by HPLC/MS

pesticide	apples	beans	lettuce	peppers	potatoes	tomatoes
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)
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)
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)

[a] Average of three determinations.

respectively, in the negative ion discharge mode. The flow rate, injection volume, scan time, and sweep width were 1 mL/min, 50 μL, 0.5 s, and 0.1 amu, respectively. The vaporizer tip temperature was held between 225 and 235 °C.

Preparation of Calibration Curves. A 25-mg portion of each reference standard (for GC analysis) was dissolved in 500 mL of dichloromethane to give a 50 μg/mL stock solution. A 50 μg/mL stock solution of linuron and oryzalin was prepared in methanol. The stock solutions were serially diluted, and the appropriate amount of internal standard stock solution was added. The standard solutions then contained 0.25, 0.5, 1, 2.5, 5, 10, 25, and 50 ng/μL of each pesticide and 25 ng/μL of the internal standard(s). Fluorene (for acephate, alachlor, captafol, chlordimeform, chlorothalonil, ethalfluralin, metolachlor, parathion, *o*-phenylphenol, pronamide, and terbutryne) and d_{12}-chrysene (for azinphos-methyl, captan, cypermethrin, diclofop-methyl, folpet, oxadiazon, and permethrin) were the internal standards used in the GC/CIMS analyses. 2-Fluoro-9-fluorenone was the internal standard for folpet, linuron, and oryzalin in the HPLC/MS analyses. These standard solutions were analyzed two to three times at each concentration level. Response factors (area of pesticide/area internal standard) were calculated by the computers. Peak areas were obtained from mass chromatograms of each analyte's quantification ion, except for the HPLC/MS analyses, where selected ion monitoring (SIM) chromatograms were used. Linear calibration curves were generated with linear correlation coefficients between 0.91 for chlorothalonil and 0.99 for acephate, cypermethrin, chlordimeform, *o*-phenylphenol, and terbutryne.

Ions chosen for detection/quantification were those that exhibited the strongest intensities in the isobutane CI/MS spectra of the pesticides and were as follows: acephate, m/z 184; alachlor, m/z 238; azinphos-methyl, m/z 160; captafol, m/z 312; captan, m/z 264; chlordimeform, m/z 197; chlorothalonil, m/z 267; d_{12}-chrysene, m/z 241; cypermethrin, m/z 191; diclofop-methyl, m/z 281; ethalfluralin, m/z 334; 2-fluorofluorenone, m/z 199 (positive ion discharge mode) and m/z 198 (negative ion discharge mode); folpet, m/z 260 (GC/CIMS) and m/z 146 (HPLC/MS); linuron, m/z 249; metolachlor, m/z 284; oryzalin, m/z 346; oxadiazon, m/z 345; parathion, m/z 292; permethrin, m/z 183; *o*-phenylphenol, m/z 171; pronamide, m/z 256; terbutryne, m/z 242. Confirmation ions used were as follows: acephate, m/z 143; alachlor, m/z 240 and 270; azinphos-methyl, m/z 132 and 318; captafol, m/z 314 and 278; captan, m/z 266, 236, and 153; chlordimeform, m/z 199; chlorothalonil, m/z 265 and 269; cypermethrin, m/z 193 and 208; diclofop-methyl, m/z 283 and 341; folpet, m/z 262 and 148 (GC/MS only); linuron, m/z 251 and 253 (GC/MS only); metolachlor, m/z 286 and 252; oxadiazon, m/z 347 and 349; permethrin, m/z 365 and 355. Oryzalin and linuron have ions at 345 and 251, respectively, that could be used for confirmation during LC/MS analysis. Ethalfluralin, parathion, *o*-phenylphenol, and terbutryne (GC/MS) and folpet (LC/MS) gave no significant confirmation ions.

Sample Preparation. Our modification of the Luke extraction procedure has been published previously (Mattern et al., 1990). For all commodities, except corn, the Luke procedure (AOAC, 1985) was followed exactly up to the step when petroleum ether and acetone are added through the Snyder column and the solution is reconcentrated. Instead, 50 mL of dichloromethane was added through the Snyder column, and the solution was reconcentrated to approximately 2 mL. The internal standard stock solutions (40 μL each) containing 2.5 mg/mL each of the internal standards were added, and the final volume were adjusted to 4 mL. For corn analysis, the Luke extraction procedure was followed even more closely up until the last step, when we omitted the addition of acetone, thus leaving the corn constituents dissolved in petroleum ether. Corn extracts were cleaned up prior to GC/CIMS analysis using a Florisil column solid-phase extraction procedure. For each sample, a 1-g Florisil column (Supelco, Bellefonte, PA) was attached to a solid-phase extraction manifold (J. T. Baker Chemical Co., Phillipsburg, NJ). The column was conditioned with 1 column volume of petroleum ether, and the extract was added before the column became dry. After the extract eluted, the column was washed with 1 column volume of petroleum ether and the latter was discarded. Pesticides were then eluted from the Florisil column with two 1-mL aliquots of ethyl ether/dichloromethane/petroleum ether (1:1:1). The eluates were combined, 40 μL of the internal standards solution was added, and the solution was diluted to 4 mL.

Recovery Studies. Recovery studies were performed at the 0.5 ppm level. The results obtained in apples, peaches, potatoes, and tomatoes for acephate, azinphos-methyl, captafol, captan, chlorothalonil, and permethrin have been previously reported (Mattern et al., 1990). In this work, we obtained recovery data for these pesticides (except for captafol, which was inadvertently omitted from the standard pesticide solution) as well as for alachlor, chlordimeform, chlorothalonil, cypermethrin, diclofop-methyl, ethalfluralin, metolachlor, *o*-phenylphenol, oxadiazon, parathion, permethrin, pronamide, and terbutryne in beans, corn, lettuce, peppers, and spinach. Recovery studies for those

Table III. Limits of Detection and Tolerances for Oncogogenic Pesticides in Crops Analyzed

pesticide	crop	tolerance, ppm	limit of detection, ppm
acephate	apples		0.10
	beans	3.0	0.10
	lettuce	10.0	0.10
	peaches		0.10
	peppers	4.0	0.10
	potatoes		0.10
	spinach		0.25
	tomatoes		0.10
alachlor	beans		0.05
	corn	0.05	0.05
	lettuce		0.10
	peppers		0.05
	potatoes	0.1	NP[a]
	spinach		0.10
azinphos-methyl	apples	2.0	0.10
	beans	2.0	0.10
	lettuce		0.10
	peaches	2.0	0.10
	peppers	0.3	0.05
	potatoes	0.3	0.10
	spinach	2.0	0.25
	tomatoes	2.0	0.10
captafol	apples	0.25	0.10
	beans		0.25
	corn	0.1	NR[b]
	lettuce		0.25
	peaches	30.0	0.10
	peppers		0.25
	potatoes	0.5	0.10
	spinach		0.50
	tomatoes	15.0	0.10
captan	apples	25.0	0.10
	beans		0.10
	corn	2.0	NR
	lettuce	100.0	0.25
	peaches	50.0	0.10
	peppers	25.0	0.25
	potatoes		0.10
	spinach	100.0	0.50
	tomatoes	25.0	0.10
chlordimeform	apples	3.0	NP
	beans		0.05
	lettuce		0.05
	peaches	5.0	NP
	peppers		0.05
	tomatoes	1.0	NP
	spinach		0.10
chlorothalonil	apples		0.10
	beans	5.0	0.50
	corn	1.0	NR
	lettuce		0.25
	peaches	0.5	0.10
	potatoes	0.1	0.10
	peppers		0.10
	spinach		0.50
	tomatoes	5.0	0.10
cypermethrin	beans		1.0
	lettuce		1.0
	peppers		1.0
	spinach		1.0
diclofop-methyl	beans		0.10
	lettuce		0.10
	peppers		0.10
	spinach		0.25
ethalfluralin	beans	0.05	0.05
	corn		0.05
	lettuce		0.05
	peppers		0.05
	spinach		0.05
folpet	apples	25.0	0.05[c]
	beans		0.50
	lettuce	50.0	0.10, 0.10[c]
	peppers		0.25, 0.05[c]
	potatoes		0.025[c]
	spinach		1.0
	tomatoes	25.0	0.10[c]
linuron	apples		0.25[c]
	beans		0.25[c]
	corn	0.25	NP
	lettuce		0.25[c]
	peppers		0.25[c]
	potatoes	1.0	0.25,[c] 0.10[d]
	tomatoes		0.25[c]
metolachlor	beans		0.05
	corn	0.1	0.05
	lettuce		0.10
	peppers	0.5	0.05
	potatoes	0.2	NP
	spinach		0.05
oryzalin	apples		0.05[c]
	beans		0.05[c]
	lettuce		0.05[c]
	peaches	0.05	NP
	peppers		0.05[c]
	potatoes	0.05	0.025[c]
	tomatoes		0.10[c]
oxadiazon	beans		0.10
	corn		0.10
	lettuce		0.10
	peppers		0.05
	spinach		0.25
parathion	apples	1.0	NP
	beans	1.0	0.05
	corn	1.0	0.05
	lettuce	1.0	0.05
	peaches	1.0	NP
	peppers	1.0	0.05
	potatoes	0.1	NP
	spinach	1.0	0.10
	tomatoes	1.0	NP
permethrin	apples	0.05	0.10
	beans		0.10
	corn	0.1	0.25
	lettuce	20.0	0.50
	peaches	5.0	0.10
	peppers	1.0	0.10
	potatoes	0.05	0.10
	spinach	20.0	0.50
	tomatoes	2.0	0.10
o-phenylphenol	apples	25.0	NP
	beans		0.10
	corn		0.05
	lettuce		0.05
	peaches	20.0	NP
	peppers	10.0	0.10
	spinach		0.05
	tomatoes	10.0	NP
pronamide	apples	0.1	NP
	beans		0.05
	corn		0.05
	lettuce	1.0	0.05
	peaches	1.0	NP
	peppers		0.05
	spinach		0.05
terbutryne	beans		0.05
	lettuce		0.05
	peppers		0.05
	spinach		0.10

[a]NP, analysis not performed. [b]NR, not recovered from Florisil column. [c]Quantification by LC/MS (Liu et al., 1990a). [d]Data from Mattern et al. (1989).

pesticides determined by HPLC/MS (folpet, linuron, and oryzalin) were performed in apples, beans, lettuce, peppers, potatoes, and tomatoes. For those pesticides determined by GC/CIMS, pesticide concentrations (nanograms per microliter) were obtained by the instrument software, where the relative responses of each pesticide were applied to the calibration curves. For the HPLC/MS analyses, response factors were calculated manually. The amounts of each pesticide (parts per million) in the crops were calculated as in the Luke procedure.

Sensitivity Determinations. Samples were spiked at levels ranging from 0.025 to 0.25 ppm. For a pesticide to be considered detectable at a certain level, it had to give a signal to noise ratio of at least 3 with the mass chromatographic or selected ion monitoring peak being distinguishable from background and/or sample components.

RESULTS AND DISCUSSION

While most pesticides can be determined by GC/MS, some are too polar or too thermally labile for this technique. HPLC/MS can be used for the determination of such pesticides (Liu et al., 1991) (as well as their metabolites), and we have used that procedure for the determination of folpet, linuron, and oryzalin. Folpet is usually determined by GC, but we have found that HPLC/MS was more sensitive to some crops toward folpet than GC/CIMS. Linuron may be determined by GC/MS if a shorter GC capillary column is used (Mattern et al., 1989); the HPLC/MS determination reported here is part of a multiresidue procedure for phenylureas and carbamates (Liu et al., 1991).

Table I summarizes the results of the recovery studies obtained for those pesticides analyzed by GC/MS in beans, corn, lettuce, peppers, and spinach at the 0.5 ppm fortification level. Recoveries were between 70 and 123% (average 93%) with an average coefficient of variation of 13%. Recovery of cypermethrin could not be determined because its limit of detection was higher than 0.5 ppm. The sensitivity of pesticides such as cypermethrin, permethrin, fenvalerate, and bufencarb is reduced in determinations involving high-resolution GC compared to packed-column GC because the diasteroisomers of these materials are separated into several peaks. Recoveries for acephate, azinphos-methyl, captafol, captan, chlorothalonil, and permethrin in apples, peaches, potatoes, and tomatoes have been reported previously (Mattern et al., 1990). Recoveries for these pesticides in these crops were in the range 74–118% (average, 91%) with an average coefficient of variation of 12%. Table II summarizes the recoveries obtained for the pesticides detected by HPLC/MS (folpet, linuron, and oryzalin) in apples, beans, peppers, potatoes, lettuce, and tomatoes. These recoveries ranged from 74 to 97% (average, 85%) with an average coefficient of variation of 8%. Table III provides a summary of the limits of detection of the suspected oncogenic pesticides in the crops they were determined together with a listing of the EPA tolerances, if applicable. Most limits of detection were 0.05–0.10 ppm. Corn and spinach were the most difficult crops in this study because they gave the dirtiest extracts, resulting in higher limits of detection for certain pesticides. Interferences in corn extracts necessitated the incorporation of a Florisil cleanup step, a procedure that was not completely successful because some pesticides could not be recovered from the adsorbent. In spite of these shortcomings, all limits of detection were lower than the tolerances, except for permethrin in corn (limit of detection 0.25 ppm), and chlorothalonil, captan, and captafol which were not recovered from corn using the Florisil cleanup procedure.

Figure 1 shows some of the mass chromatograms obtained from the GC/CIMS analysis of peppers spiked with 0.05 ppm of each pesticide. Figure 2 shows the SIM chromatograms of 0.10 ppm linuron in corn and 0.025 ppm folpet and oryzalin in potatoes obtained by HPLC/MS analysis.

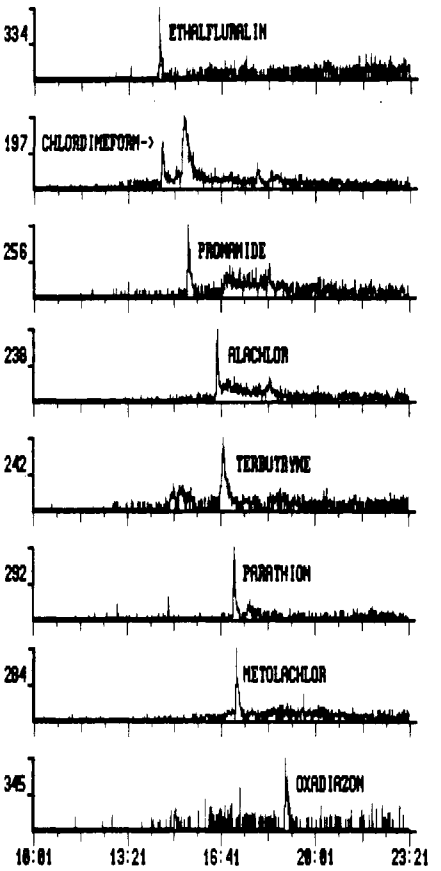

Figure 1. Mass chromatograms of some of the pesticides spiked into peppers at the 0.05 ppm level before extraction and determined by GC/CIMS on a 30-m capillary column.

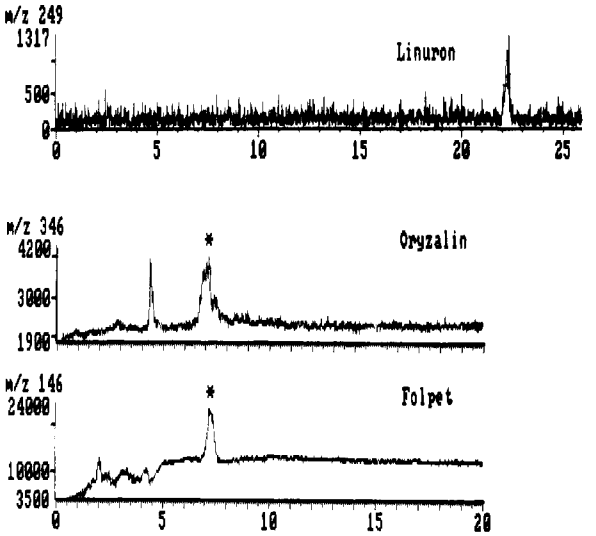

Figure 2. Selected ion monitoring (SIM) chromatograms of linuron (0.5 ppm), folpet (0.10 ppm), and oryzalin (0.10 ppm) spiked into potatoes before extraction and determined by HPLC/MS. An asterisk denotes the pesticides when there is more than one peak.

Of the 28 pesticides for which oncogenic risk has been calculated by the National Research Council, 20 could be determined by the procedure outlined in this paper. Eight of the listed pesticides could not be determined for various reasons: the ethylene bis(dithiocarbamate)s (EBDC's) mancozeb, maneb, metiram, and zineb require conversion

to carbon disulfide before analysis; cyromazine, fosetyl Al, and glyphosate are not extractable by the Luke procedure; benomyl is unstable in solution and must first be converted to its hydrolysis product (Liu et al., 1990).

This study vividly demonstrates the advantages of using mass spectrometry for detection and quantification of pesticides in a multiresidue determination. Five different detectors would be required for the 19 pesticides that are determined by gas chromatography. A flame photometric detector would be needed to determine acephate, azinphos-methyl, and parathion; a Hall detector (halogen mode) would be needed to determine alachlor, captafol, captan, chlordimeform, chlorothalonil, cypermethrin, diclofop-methyl, ethalfluralin, folpet, metolachlor, oxadiazon, permethrin, and pronamide; a Hall detector (nitrogen mode) would be needed to determine terbutryne; a flame ionization detector would be needed to determine *o*-phenylphenol. Two additional analyses at higher column temperature would be required because azinphos-methyl, cypermethrin, and permethrin take too long to chromatograph under the packed-column conditions usually employed for multiresidue pesticide analysis. Finally, two more separate, time-consuming methods would be required to determine linuron and oryzalin. The method described in this paper requires only one extraction and one GC/MS and two LC/MS determinations. One of the LC/MS determinations could be eliminated by determining all the volatile pesticides on a 15-m GC column instead of a 30-m column so that linuron could be included in the GC/MS determination. A 15-m column was tested by analyzing the same 0.05 ppm spiked pepper extract used to obtain Figure 1. This extract was additionally spiked with linuron at the 0.05 ppm level. Linuron was easily detectable, and the other pesticides gave results similar to those generated by using the 30-m column, with the added advantage of shortening the analysis time from 30 to 16 min.

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LITERATURE CITED

AOAC. *Changes in Official Methods of Analysis*, 1st Supplement, 14th ed.; Association of Official Analytical Chemists: Arlington, VA, 1985; Sections 29A01–29.A04.

Liu, C.-H.; Mattern, G. C.; Yu, X.; Rosen, J. D. Determination of Benomyl by High Performance Liquid Chromatography/Mass Spectrometry/Selected Ion Monitoring. *J. Agric. Food Chem.* **1990**, *38*, 167–171.

Liu, C.-H.; Mattern, G. C.; Yu, X.; Rosen, R. T.; Rosen, J. D. Multiresidue Determination of Nonvolatile and Thermally Labile Pesticides in Fruits and Vegetables by Thermospray Liquid Chromatography/Mass Spectrometry. *J. Agric. Food Chem.* **1991**, *39*, 718–723.

Mattern, G. C.; Singer, G. M.; Louis, J.; Robson, M.; Rosen, J. D. Determination of Linuron in Potatoes Using Capillary Column Gas Chromatography/Mass Spectrometry. *J. Assoc. Off. Anal. Chem.* **1989**, *72*, 970–974.

Mattern, G. C.; Singer, G. M.; Louis, J.; Robson, M.; Rosen, J. D. Determination of Several Pesticides With a Chemical Ionization Ion Trap Detector. *J. Agric. Food Chem.* **1990**, *38*, 402–407.

National Research Council. *Regulating Pesticides In Foods: The Delaney Paradox*; National Academy Press: Washington, DC, 1987; p 68.

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Registry No. Acephate, 30560-19-1; alachlor, 15972-60-8; azinphos-methyl, 86-50-0; captafol, 2425-06-1; captan, 133-06-2; chlordimeform, 6164-98-3; chlorothalonil, 1897-45-6; cypermethrin, 52315-07-8; diclofop-methyl, 51338-27-3; ethalfluralin, 55283-68-6; folpet, 133-07-3; metolachlor, 51218-45-2; *o*-phenylphenol, 90-43-7; oxadiazon, 19666-30-9; parathion, 56-38-2; permethrin, 52645-53-1; pronamide, 23950-58-5; terbutryne, 886-50-0; linuron, 330-55-2; oryzalin, 19044-88-3.