SPECIAL GUEST EDITOR SECTION

Determination of Imidacloprid and Benzimidazole Residues in Fruits and Vegetables by Liquid Chromatography–Mass Spectrometry after Ethyl Acetate Multiresidue Extraction

AMADEO R. FERNÁNDEZ-ALBA[1], ANA TEJEDOR[2], and ANA AGÜERA[1]
University of Almería, 04071 Almería, Spain
MARIANO CONTRERAS
COEXPHAL—Cosecheros y Exportadores de Hortalizas de Almería, El Viso, 04070 Almería, Spain
JUAN GARRIDO
Centro Nacional de Alimentación, Dep. Análisis Residuos Fitosanitarios, Crta. Majadahonda-Pozuelo, 28220 Majadahonda, Madrid, Spain

A simple and sensitive method based on liquid chromatography–atmospheric pressure ionization–mass spectrometry is described for the determination of 4 benzimidazole pesticides (carbendazim, thiabendazole, benomyl, and thiophanate-methyl) and imidacloprid in vegetables and fruits. Food samples were typically extracted with ethyl acetate to draw the analytes into the organic phase. No cleanup step was necessary before injection into the liquid chromatographic (LC) system with electrospray mass spectrometric detection. The analytes were separated on a reversed-phase C_8LC column. Limits of detection for the compounds were in the µg/L range. Results are reported for validation studies with fortified pear and tomato samples and for residues of the target compounds found in the pesticide residue monitoring program during 1998.

Gas chromatography (GC) still appears to be the major analytical technique for monitoring pesticide residues in agricultural foods, because of its high separation power and the presence of GC-amenable pesticides in a wide variety of samples. The ease of coupling GC columns to a mass spectrometer and the large number of standardized electron impact spectra obtained by laboratories involved in pesticide residue analysis have increased the prevalence of GC over other analytical techniques (1).

However, the number of compounds that cannot be determined directly by GC because of their poor volatility, high polarity, and/or thermal instability has grown dramatically in the last few years (2), and the use of only GC-based techniques is not sufficient in most cases. Thus, the complementary use of liquid chromatography (LC) coupled with diode-array detection (DAD) or fluorescence spectrophotometry is also common for screening purposes and prevents some of these problems (3, 4).

Unfortunately, the application of LC-based techniques to residue analysis is hampered mainly by problems in sample preparation because of the insensitivity of DAD and the large amounts of interferents from vegetable extracts (5–7). As a result, it is usually necessary to develop specific sample handling procedures or sophisticated cleanup strategies for these LC- amenable compounds. Moreover, it can be difficult to identify and quantitate the analytes in many commodity/pesticide combinations (5, 7, 8).

Because of its selectivity and high specificity, mass spectrometry (MS) combined with LC may be used for future analyses of food for pesticide residues. MS can determine pesticides that do not produce a chromophore response, and the presence of interferences in the sample matrix is not a problem. For simplicity and low cost, it is useful to keep the extraction procedure for pesticides determined by GC in methods developed for LC–MS.

Consequently, LC–MS is gaining acceptance for pesticide monitoring (9, 10). With the ready availability in recent years of atmospheric-pressure ionization (API), LC–MS interfaces such as atmospheric-pressure chemical ionization (APCI) and electrospray (ES) provide structural information and sensitivity and overcome the limitations of other LC devices (11). LC–MS allows the confirmation and quantitation of highly polar, less volatile, and thermally labile compounds; because it can be used afer "classical" multiresidue extraction procedures, additional and tedious partitioning or solid-phase extraction steps are avoided (12).

A large number of multiresidue extraction methods (MRMs) for the determination of pesticides in fruits and vegetables have been published in the last 20 years. Most MRMs are based on the use of acetone or ethyl acetate as extraction

Guest edited as a special report on "Chromatographic Pesticide Residue Analysis" by Antonio Valverde.
[1]Pesticide Residue Research Group.
[2]Mass Spectrometry Service.

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solvents (13, 14). The low recoveries of very polar pesticides such as Methamidophos are a major disadvantage of the acetone method. Previous works have evaluated the efficacy of ethyl acetate for extraction of a wide variety of pesticide residues in fruit horticultural samples before determination by GC (15–17). Ethyl acetate extraction followed by an extra cleanup has been applied to reversed-phase LC with ultraviolet (UV) detection for determination of the most frequently used non-GC-amenable pesticides such as the benzimidazoles (8); however, the difficulties in applying these MRMs to LC are considerable because of the large amounts of coextractives obtained (5, 7, 8).

The benzimidazoles and imidacloprid represent a group of very important pesticides in monitoring programs. Several LC methods have been reported for their determination (8, 18–21). Nevertheless, most of these methods involve labor-intensive sample cleanup and the use of UV and fluorescence (FL) detectors. This paper describes the fine tuning of the ethyl acetate MRM for the determination of imidacloprid and benzimidazoles in fruit and vegetable samples with separation by reversed-phase LC and detection by MS–API, which minimizes or eliminates the need for further cleanup steps. The peformance of the whole method was evaluated with spiked samples and a large number of real samples analyzed in our regulatory laboratory during 1998.

Experimental

Apparatus

(**a**) *Food processor*.—Model UM 12 (Stephan, Hameln, Germany).

(**b**) *Homogenizer*.—Polytron Model PT-2000 (Kinematic AG, Littau, Switzerland).

(**c**) *Porcelain Büchner funnel*.—9 cm dia.

(**d**) *Vacuum rotary evaporator*.—Model VV 2000 (Heidolph, Germany).

(**e**) *Liquid chromatograph*.—HP Series 1100 (Hewlett-Packard, Palo Alto, CA).

(**f**) *LC column*.—Zorbax SB-C8, 150 × 4.6 mm id, 3.5 μm particle size (Hewlett-Packard).

(**g**) *Mass detector*.—API mass spectrometer. Hewlett-Packard 1100 MSD. G1946A equipped with ES G1948A and APCI G1947A interfaces.

Reagents

(**a**) *Acetonitrile*.—LC grade (Merck, Darmstadt, Germany).

(**b**) *Water*.—LC grade (Merck).

(**c**) *Ethyl acetate*.—Pestiscan grade (Lab-Scan, Dublin, Ireland).

(**d**) *Sodium sulfate*.—Anhydrous (Scharlau, Barcelona, Spain).

(**e**) *Glass fiber filter*.—9 cm dia.

(**f**) *Nitrogen*.—99.998% pure, for API interfaces (Air Liquid, Barcelona, Spain).

(**g**) *Mobile phase components*.—Solvent A: acetonitrile. Solvent B: 50 mM ammonium formate in purified water–acetonitrile (95 + 5), acidified with formic acid (pH 4).

(**h**) *Pesticide standards*.—Primary standards of carbendazim, thiabendazole, benomyl, thiophanate-methyl, and imidacloprid of the highest avalilable purity (Ehrenstorfer, Augsburg, Germany, or Riedel de Haen, Seelze, Germany).

(**i**) *Standard stock solutions*.—Stock solutions (50 :g/mL) of all of pesticides except benomyl were prepared in acetonitrile, and they were stable for ≥6 months in a freezer at −18°C. A stock solution of benomyl (50 μg/mL) was prepared in methanol and was stable for ≥1 month in a freezer at −18°C.

(**j**) *Calibration solution*.—A 200 μL aliquot of each stock solution was diluted to 100 mL with acetonitrile–water (50 + 50), acidified with formic acid to pH 4 for a final concentration of 0.1 μg/mL. This calibration solution was prepared daily for benomyl.

Sample Preparation

Prepare laboratory sample (e.g., by removing adhering soil, stems, etc.) as described in Council Directive 90/642/EEC (22). Chop analytical sample into small pieces and homogenize thoroughly in food processor.

Extraction

Weigh 15 g analytical portion into blender tube, and add 60 mL ethyl acetate and 15 g sodium sulfate. Homogenize mixture for 30 s, using Polytron. Decant ethyl acetate phase, and filter with light suction through Büchner funnel fitted with glass fiber filter covered by 8 g sodium sulfate. Repeat extraction procedure once with 25 mL ethyl acetate, and rinse filter with 5 mL ethyl acetate. Transfer 60 mL extract (10 g sample) to round-bottom flask, and reduce volume to about 1 mL with rotary evaporator and water bath at 40°C. Quantitavely transfer residue with ethyl acetate to precalibrated test tube. Rinse round-bottom flask with methanol, and adjust volume to 3 mL. Evaporate final extract in water bath (60°C) with gentle nitrogen stream to near dryness. Let remaining solvent evaporate in air, and redissolve residue in 2 mL acetonitrile–water (50 + 50). Filter through 0.45 μm filter, and inject 20 μL into LC system.

LC Analysis

LC analyses were performed with an HP Series 1100 liquid chromatograph. The chromatographic separation was performed with a Zorbax SB-C8 column (150 × 4.6 mm id, 3.5 μm particle size). The gradient elution was carried out with a binary gradient composed of LC solvent A (acetonitrile) and LC solvent B (50mM ammonium formate in water–acetonitrile [95 + 5] acidified by adding formic acid) according to the following program: 4 min at 100% B, then to 0% B in 12 min. After 3 min at 100% acetonitrile, the mobile phase

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was returned to the initial conditions. The flow rate was kept at 1 mL/min.

Mass Spectrometry

Liquid chromatography–atmospheric pressure ionization–mass spectrometry (LC–API–MS) with APCI and ES interfacing techniques with positive and negative modes of operation were used. The ES interface consists of a nebulizer, which extends into the spray chamber so that the nozzle is inside the field generated by the mesh electrode. The operating parameters were a drying gas flow rate of 10 L/min and a nebulizer pressure of 50 psi. The capillary voltage was set at 3000 V and the drying gas temperature, at 325°C. The APCI interface consists of a nebulizer and a heater vaporizer and is equipped with a corona discharge pin. The operating parameters were a drying gas flow rate of 6 mL/min and a nebulizer pressure of 50 psi. The drying gas temperature was set at 325°C, and the capillary voltage and the corona current, at 2500 V and 4 μA, respectively.

The chromatograms were recorded under full-scan (SCAN) and selected-ion monitoring (SIM) conditions in the positive ionization mode of operation. For SCAN conditions, the m/z range was 100–400, and for SIM conditions, the ions corresponding to the typical fragments of carbendazim, thiabendazole, thiphanate-methyl, benomyl, and imidacloprid were selected.

The influence of vaporizer temperature (APCI interface) and fragmentor voltage (both interfaces, APCI and ES) on ion abundance and fragmentation was studied by applying 6 different temperatures, ranging from 250° to 500°C, and 8 fragmentor voltages, ranging from 20 to 160 V, as follows: (*1*) vaporizer temperatures of 250°, 300°, 350°, 400°, 450°, and 500°C, with the fragmentor voltage at 50 V, in the APCI source; and (*2*) extraction voltages of 20, 40, 60, 80, 100, 120, 140, and 160 V (with the vaporizer temperature constant at 400°C for the APCI source).

Method Validation

For recovery experiments homogenized, untreated pear and tomato samples were spiked with carbendazim, thiabendazole, benomyl, thiophanate-methyl, and imidacloprid at 0.05 and 0.5 mg/kg. With a graduated microsyringe of 15 μL (0.75 μg) or 150 μL (7.50 μg) of the 50 μg/mL pesticide stock solution was added to 15 g blank matrix in a blender tube. Samples were mixed and allowed to stand for 1 h before extraction. For each fortification level, 10 replicates were analyzed.

Results and Discussion

Selection of Interface Technique and Ionization Mode

Preliminary evaluations were carried out for the selected pesticides. Typically, a 5 μg/μL solution of the pesticide of interest was injected directly into the mass spectrometer, and data were acquired in the SCAN mode (ca 50–350 amu). As briefly discussed, adjustment of ES and APCI extraction voltages and APCI probe temperature can be used to opti-

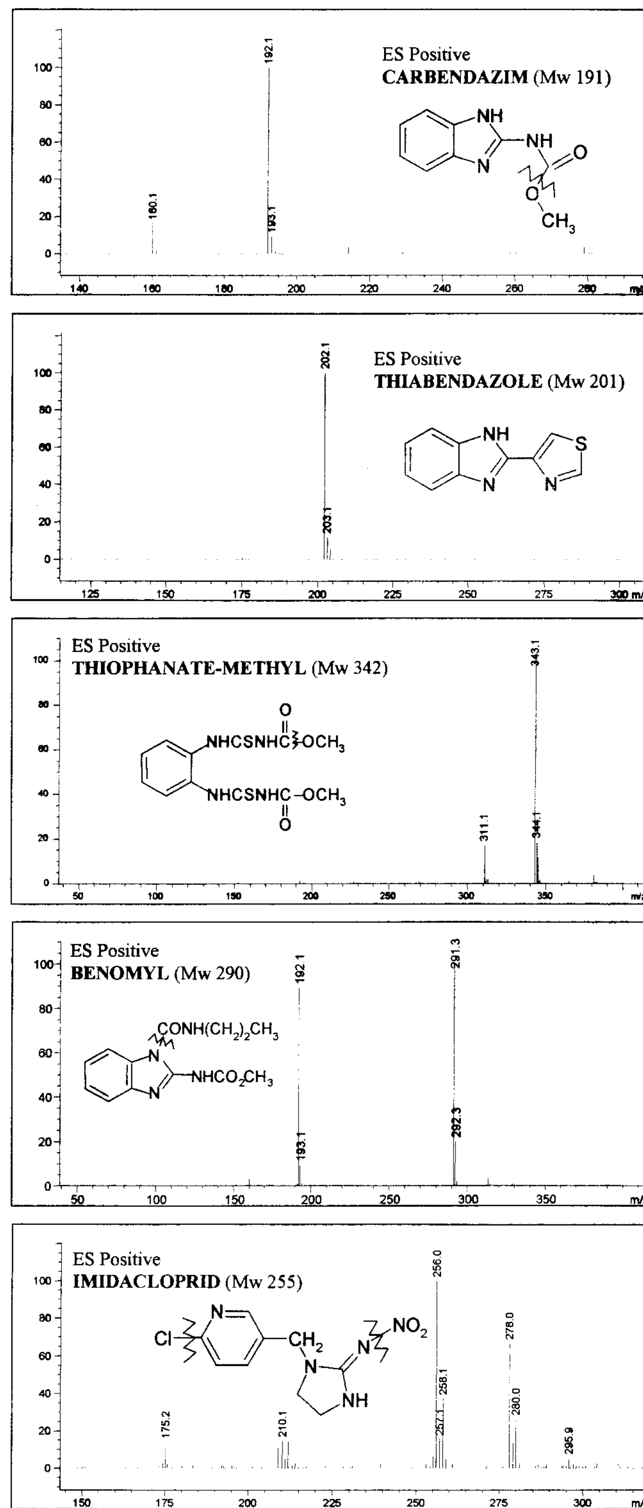

Figure 1. Mass spectra of carbendazim, thiabendazole, thiophanate-methyl, benomyl, and imidacloprid, obtained by LC–ES–MS using positive ionization ES in the SCAN mode (fragmentor voltage, 80 V).

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Table 1. Calibration data obtained with LC–ES–MS in the full-scan and selected-ion monitoring positive ionization modes for carbendazim, thiabendazole, imidacloprid, thiophanate-methyl, and benomyl

Compound	Calibration equation	r^{2a}	LOD, mg/L[b]
	Full-scan monitoring		
Carbendazim	y = 42219x + 5377.9	0.997	0.01
Thiabendazole	y = 217985x + 3320.1	0.999	0.005
Imidacloprid	y = 32182x – 57.216	0.999	0.01
Thiophanate-methyl	y = 4515618x + 2641.5	0.999	0.05
Benomyl	y = 11102x + 366.13	0.997	0.05
	Selected-ion monitoring		
Carbendazim	y = 2E + 0.6x + 15283	0.999	0.001
Thiabendazole	y = 3E + 0.6x + 3163.7	0.999	0.0005
Imidacloprid	y = 885020x + 2770.5	0.999	0.001
Thiophanate-methyl	y = 2E + 0.6x – 24425	0.998	0.0025
Benomyl	y = 275243x + 6013.4	0.995	0.0025

[a] Correlation coefficient.
[b] LOD = limit of detection.

mize the formation of ions of interest (e.g., [M+H]+) to obtain and optimize the compromise between enough fragmentation for identification purposes and sensitivity.

Thiabendazole.—Poor ionization of thiabendazole was observed in the APCI negative ionization mode, whereas positive ionization APCI and ES produced an intense protonated molecule (M+H)+ (m/z 202; Figure 1). Variation of the vaporizer temperature had only a slight influence on fragmentation. The protonated molecule was fragmented at extraction voltages of >120 V, producing a fragment ion in low abundance at m/z 175 when APCI was used. A similar effect on fragmentation was observed when ES was used.

Carbendazim.—It was not possible to form a deprotonized molecule for carbendazim when negative ionization was used. As with thiabendazole, positive ionization ES and APCI produced an intense protonated molecule (m/z 192; Figure 1). Increasing the temperature to >400°C in APCI produced a simple fragmentation that yielded a characteristic ion (m/z 160; Figure 1). This fragment is due to the loss of the methoxy group. The same fragment was obtained when the extraction voltage was increased to >60 V, and a base peak was obtained at >100 V by using APCI and ES sources.

Thiophanate-methyl.—Once again, positive ionization produced a much more intense quasi molecular ion (m/z 343; Figure 1) than did negative mode. In this case, fragmentation at m/z 311 due to the loss of the methoxy group was observed at a lower temperature (300°C) and a lower voltage (40 V) in both APCI and ES with respect to the temperature and voltage required for corresponding fragmentation of the other benzimidazoles.

Benomyl.—It was not possible to form an intense deprotonized molecule in negative mode. The protonated molecule (m/z 291; Figure 1) for benomyl always appeared as main fragment with an intense ion occurring in positive mode at 192 (Figure 1). This fragment may be formed by cleavage of the amide group in the MS system, or it can be formed as a consequence of the fast transformation of this fungicide into carbendazim even in organic solvents [23]. The total disappearance of the 291 ion and the increase of the 192 mean the complete conversion into carbendazim, which ocurred 48 hours after preparing the standard solution.

Imidacloprid.—Imidacloprid yielded intense protonated

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Table 2. Mean recoveries[a] of thiabendazole, carbendazim, thiophanate-methyl, benomyl, and imidacloprid from fortified pear and tomato samples[b]

Compound	Spiking level, mg/kg	Pear SCAN		Pear SIM		Tomato SCAN		Tomato SIM	
Thiabendazole	0.05	102	(12)	108	(9)	99	(15)	98	(10)
	0.5	108	(8)	97	(9)	103	(10)	95	(7)
Carbendazim	0.05	102	(14)	98	(10)	99	(11)	97	(8)
	0.5	99	(12)	101	(8)	107	(14)	93	(12)
Thiophanate-methyl[c]	0.05	96	(18)	105	(16)	90	(10)	99	(9)
	0.5	95	(8)	91	(15)	93	(5)	94	(10)
Benomyl[d]	0.05	101	(12)	90	(9)	91	(12)	100	(9)
	0.5	108	(8)	96	(5)	109	(11)	110	(9)
Imidacloprid	0.05	107	(14)	89	(10)	104	(16)	100	(9)
	0.5	103	(13)	92	(8)	108	(12)	91	(7)

[a] n = 10; CVs are in parentheses.
[b] The ions at 192, 202, 256, and 343 were selected.
[c] Sum of carbendazim and thiophanate-methyl.
[d] Calculated as carbendazim.

and deprotonized molecules (m/z 256 and 254) when ES was used in the positive and negative ionization modes, respectively. However, it was not possible to form a deprotonized molecule when negative ionization APCI was used, whereas positive ionization in both ES and APCI produced a more sensitive protonated molecule (m/z 256; Figure 1). The fragments at m/z 210 and 175 corresponding to $(M + H - NO_2)+$ and $(M + H - NO_2 - Cl)+$, respectively, were observed for a broad range of voltages with both APCI and ES interfaces. Typical cluster ions (m/z 278 and 296; Figure 1) corresponding to (M + Na)+ (M + K)+ as a consequence of potassium impurities present in the mobile phase was also observed when the ES interface was used.

Because results were very similar with regard to sensitivity when the positive ionization mode and fragmentation with the 2 interfaces were used, ES in the positive ionization mode was selected to avoid high temperatures, which could produce undesirable degradation processes in the pesticides. The extraction voltage selected for the formation of the protonated molecules and the formation of other fragments in the analytical procedure was 80 V.

Detector Response

Table 1 shows the linear calibration data (ca 0.01–5 µg/mL) obtained for standards in acetonitrile by using ES in the positive ionization SCAN and SIM modes. Detection limits were calculated by extracting or monitoring the ions at m/z 192,

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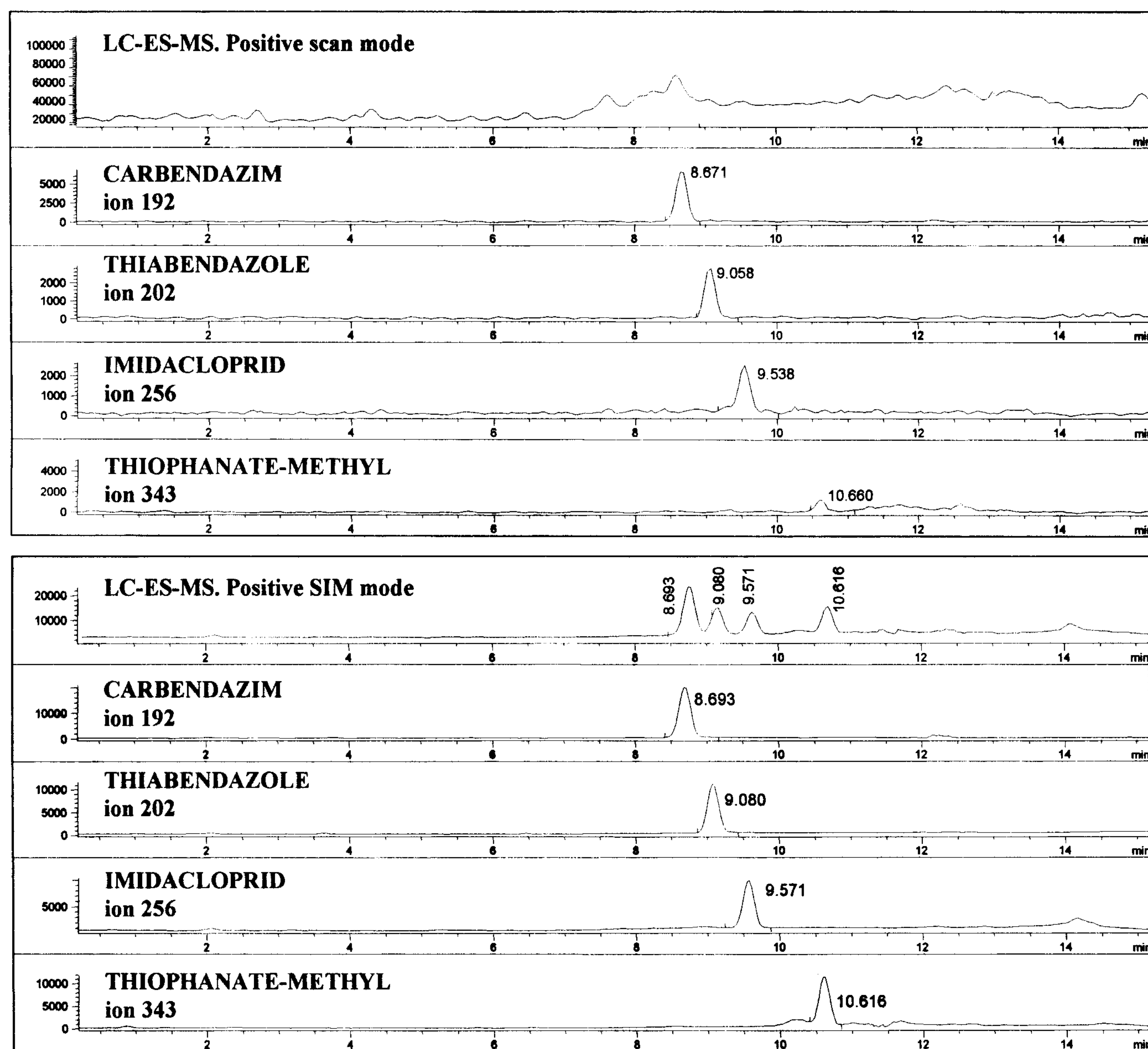

Figure 2. LC–ES–MS chromatograms for a tomato sample fortified with carbendazim, thiabendazole, thiophanate-methyl, and imidacloprid at 0.5 mg/kg after ethyl acetate extraction. Retention times (min): carbendazim, 8.6; thiabendazole, 9.0; imidacloprid, 9.5; and thiophanate-methyl, 10.6; and imidacloprid, 9.5.

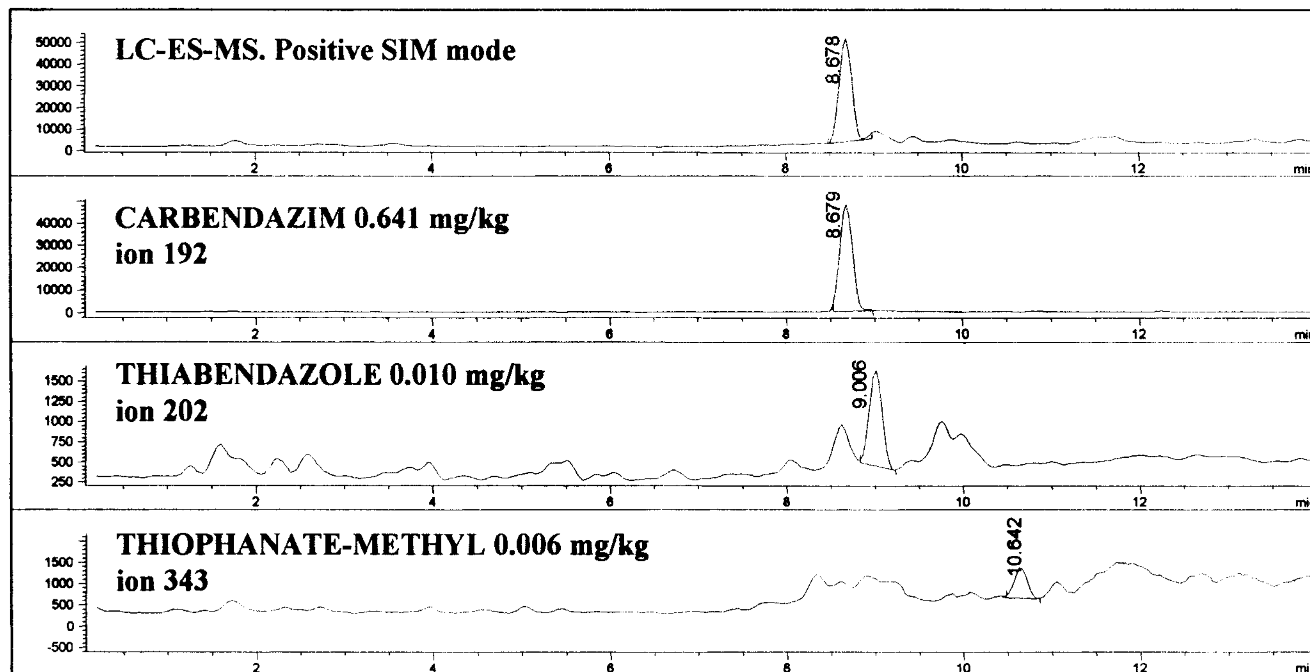

Figure 3. Typical LC–ES–MS chromatograms in the SIM mode for a nectarine extract.

202, 256, 343, and 291 for carbendazim, thiabendazole, imidacloprid, thiophanate-methyl, and benomyl, respectively. It is important to note the high sensitivity achieved by using the SIM mode (<5 μg/L) in all cases. Repeated injections ($n = 10$) of each analyte at 0.1 μg/mL demonstrated that the method showed good precision for all analytes; the coefficients of variation (CVs) were <5%.

Linearity and Limits of Detection (LODs)

Calibration graphs for pear and tomato samples were constructed for carbendazim, thiabendazole, thiophanate-methyl, and imidacloprid in the range of 5–500 ng (0.05–5.0 mg/kg) absolute amounts injected.Correlation coefficients were >0.996 in all cases. LODs were calculated by using a signal-to-noise ratio of 3. The LODs for carbendazim, thiabendazole, thiophanate-methyl, and imidacloprid were ≤10 μg/kg in the SCAN mode and 1.0 μg/kg in the SIM mode.

Recoveries and Repeatability

The multiresidue method applied was based on published methods that used ethyl acetate extraction. Benomyl and thiophanate-methyl, respectively, were totally and partially converted to carbendazim. Therefore, the recovery experiments for these 2 fungicides were carried out separately, and recoveries were calculated as carbendazim after quantitative conversion, or as the sum of carbendazim and thiophanate-methyl (20). Table 2 shows the recoveries and precision for the pesticides added at 0.05 and 0.5 mg/kg to untreated pear and tomato samples. Fortification levels were representative of the tolerance limits of the European Union (EU). Recoveries were calculated by using an external standard. Injections were made for each concentration level in the SCAN and SIM modes. Overall average recoveries for carbendazim, thiabendazole, and imidacloprid were >88% at both fortification levels and in both matrixes. The CVs for carbendazim, thiabendazole, and imidacloprid were <15% and quite similar for the SCAN and SIM modes. Typical chromatograms in the SIM and SCAN modes for a spiked tomato sample are shown in Figure 2. A major advantage of the method described here is the use of a single extraction method that is also used in our laboratories for the determination of *N*-methyl carbamate, organophosphorus, and organochlorine pesticides.

Degradation of benomyl and thiophanate-methyl to carbendazim is a well-known phenomenon. Several samples fortified with these 2 fungicides were extracted and monitored at different times to evaluate the conversion rate. Degradation was complete within 25 min after the extraction procedure. Overall mean recoveries ($n = 10$) of benomyl as carbendazim were >91% for pears and tomato samples. Thiophanate-methyl was converted to about 20% carbendazim. Therefore, the residues in these analyses were calculated as the sum of carbendazim and intact thiophanate-methyl, and the overall mean recoveries also were >90%.

Application

As an application, we evaluated concentrations of 4 pesticides in 200 samples from the 1998 monitoring program of COEXPHAL (Association of Growers and Exporters of Hor-

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Table 3. Imidacloprid and benzimidazole pesticide residues found in fruits and vegetables from January to December 1998

Product	No. of samples analyzed	No. of residue findings				No. of residues exceeding tolerance[a]
		Carbendazim	Thiabendazole	Imidacloprid	Thiophanate-methyl	
Tomato	50	21	7	23	—	2
Bean	8	3	—	—	—	—
Green bean	5	—	—	—	—	—
Lettuce	16	2	—	—	—	—
Pepper	15	3	1	8	—	—
Cucumber	12	5	—	—	—	—
Potato	8	1	1	2	—	—
Carrot	7	2	—	2	—	—
Courgette	6	—	—	—	—	—
Eggplant	5	2	—	2	—	—
Cauliflower	3	—	3	—	—	—
Cabbage	6	—	—	—	—	—
Apple	10	5	3	—	—	—
Pear	8	5	2	2	—	—
Melon	9	—	—	3	—	—
Watermelon	7	3	—	—	—	—
Nectarine	10	7	6	—	5	1
Grape	6	3	—	—	—	—
Plum	4	2	—	—	—	—
Peach	5	3	—	—	—	—
Total	200	67	23	42	5	3

[a] European Union directive for carbendazim and thiabendazole. Spanish regulation for imidacloprid.

ticultural Products of Almería). A 5 kg sample was sent to COEXPHAL's laboratory for analysis; 0.5 kg was frozen for later analysis, if needed, and the rest was homogenized for analysis by the proposed method. Typical chromatograms for a nectarine sample containing carbendazim, thiabendazole, and thiophanate-methyl are shown in Figure 3.

The results are shown in Table 3. A high percentage >50% of the analyzed samples contained ≥1 of the target pesticides, and ≥15% contained ≥2. However, only very few findings (2%) exceeded the EU or Spanish tolerances.

Conclusions

A simple and robust LC–MS method has been developed for the determination of imidacloprid and benzimidazole pesticides at μg/kg levels in various crops. Residues of benomyl were calculated as carbendazim. The use of MS–API makes this method suitable after ethyl acetate extraction of the pesticides without extra cleanup procedures. During the 1998 monitoring of various crops, the number of findings that exceeded the tolerance were insignificant. However, the number of positive findings was >65%, demonstrating the method's usefulness in enforcing maximum residue limits according to current criteria, as well as providing an extensive evaluation for assessing possible risks to humans.

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