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Application of liquid chromatography with electrospray tandem mass spectrometry to the determination of a new generation of pesticides in processed fruits and vegetables

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Abstract

This paper describes a method for the sensitive and selective determination of 24 new pesticide residues (azoxystrobin, trifloxystrobin, kresoxim-methyl, fenazaquin, indoxacarb, fenothiocarb, furathiocarb, benfuracarb, imidachloprid, dimethomorph, fenpyroximate, hexythiazox, tebufenpyrad, tebufenozide, difeconazole, fenbuconazole, flusilazole, paclobutrazol, tebuconazole, tetraconazole, bromuconazole, etofenprox, fenhexamid, pyridaben) in apple puree, concentrated lemon juice and tomato puree. A miniaturized extraction–partition procedure requiring small amounts of non-chlorinated solvents was used. The extracts are analyzed by liquid chromatography–electrospray ionization tandem mass spectrometry (LC–ESI–MS–MS) without any further clean-up step. The pesticides are separated on a reversed-phase polar column using a gradient elution. Fifty-five simultaneous MS–MS transitions of precursor ions were monitored (two or three for each pesticide). Studies at fortification levels of 0.001–0.020 and 0.010–0.200 mg/kg gave mean recoveries ranging from 76 to 106% for all compounds, except for imidacloprid, with (R.S.D.s) ≤15%. The excellent sensitivity and selectivity of LC–MS–MS method allowed quantitation and identification at low levels also in difficult matrices with a run time of 20 min. With the developed method almost 100 samples of commercial fruit products (nectars, juices, purees) were analyzed. None of samples contained residues higher than 0.010 mg/kg.
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Keywords: Fruits; Vegetables; Food analysis; Pesticides

1. Introduction

Use of agrochemicals at various stages of cultivation and during post-harvest storage play an important role in food protection and quality preservation.

Therefore, thorough monitoring of pesticide residues is crucial for proper assessment of human exposure to pesticides through foods. Maximum residue limits in foodstuffs have been set by Government agencies and European Union Commission to guarantee consumer safety and to regulate international trade [1,2].

Analytical methodologies employed must be capable of residue measurement at very low levels and must be also provide unambiguous evidence to confirm both the identity and the quantity of any residues detected.

Most pesticides are volatile and thermally stable and therefore the most frequently used methods rely on gas chromatographic (GC) separation [3–5] and detection with selective and sensitive detectors such as electron-capture detection (ECD), nitrogen–phosphorus detection (NPD) and mass spectrometry (MS).

However, the number of compounds that cannot be determined by GC because of their poor volatility, high polarity and thermal instability has grown dramatically in the last few years. Agrochemicals belonging to carboxamide, quinazolin, phenoxypyrazol, strobilurin, pyrimidine, triazol, carbamate, neonicotinoid, morpholine classes are representative of the newly introduced molecules.

Nowadays, liquid chromatography coupled with mass spectrometry (LC–MS) is becoming one of most powerful techniques for the residue analysis of polar, ionic or low volatility pesticides in fruits and vegetables [6,7]. Modern LC–MS instruments employing atmospheric pressure ionization (API) provide excellent sensitivity and selectivity that enables analysis of target analytes at trace levels.

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Moreover, LC in combination with the use of tandem MS (MS–MS) is capable of discriminating more efficiently than LC–MS between the analyte and matrix signal [8].

Recently, several applications have described the use of MS–MS with both triple quadrupole and ion trap analyzers in multi-residue analysis of pesticide [9–13]. Most of methods achieve satisfactory results even without making use of clean-up treatments. Perret et al. [10] described a method based on LC–MS–MS for the determination of multiclass pesticide residues in fruit juices. A sensitive LC–MS–MS method capable of the analysis of a range of pesticide residues in crude extracts from a variety of fruits and vegetables was developed by Taylor et al. [11]. Klein and Alder [12] used electrospray ionization tandem MS (ESI–MS–MS) for the simultaneous determination of about 100 pesticides in crops at concentrations below than 0.010 mg/kg; Zrostlikova et al. [13] determined 17 polar/thermolabile pesticides in apple and apricot by ion trap MS–MS detection.

In this paper we developed a sensitive LC–MS–MS approach for the determination of representatives of several groups of newly introduced molecules. The possibility of analyzing extracts from processed fruits and vegetables using triple quadrupole instrument with an ESI interface without any type of sample pre-treatment except for extraction–partition was evaluated.

The aim was the rapid residue determination of 24 pesticides in processed fruits and vegetables at the low mg/kg levels (<0.010 mg/kg). For vegetables and fruits intended for production of baby food, a maximum residue level (MRL) of 0.010 mg/kg is applicable for all pesticides [14]. This threshold level is also frequently applied for testing compliance with guidelines for organic production [15].

Because of widespread use and insufficient residue data there is an increasing need to monitor pesticides of new generation in processed foods and in particular fruit and vegetable products. In this study a total of 102 samples of fruit nectars, purees and juices purchased from the markets were analyzed.

2. Experimental

2.1. Chemicals and materials

Certified pesticide standards (purity ≥97.0%) were obtained from Dr. Ehrenstorfer (Ausburg, Germany). Pesticide residue grade solvents (acetone, cyclohexane, ethyl acetate) were obtained from Merck (Darmstadt, Germany). HPLC-grade solvents (acetonitrile and methanol) were obtained from Carlo Erba (Milan, Italy). LC-grade water was produced by a Waters purification system (Smeg, Parma,

Table 1
Analyte MS–MS transitions, retention time and instrument conditions

Compound	Retention Time (min)	First transition mass (*m*/*z*)[a]	DP (V)[b]	CE (V)[c]	Second transition mass (*m*/*z*)	DP (V)[b]	CE (V)[c]	Third transition mass (*m*/*z*)	DP (V)[b]	CE (V)[c]
Azoxystrobin	8.13	404 → 372	19	20	404 → 344	19	30	404 → 329	19	40
Benfuracarb	9.11	411 → 195	13	32	411 → 252	13	18	411 → 190	13	17
Bromuconazole	7.91	378 → 159	25	40	376 → 159	25	40	380 → 161	25	40
Difeconazole	8.60	406 → 251	49	34	408 → 253	47	32			
Dimethomorph	7.23	388 → 301	26	26	390 → 303	32	27			
Etofenprox	9.96	359 → 183	52	31	394 → 177	9	20			
Fenazaquin	9.62	307 → 161	22	21	307 → 147	22	26	307 → 57	22	45
Fenbuconazole	8.17	337 → 125	27	40	337 → 70	27	44			
Fenhexamide	7.40	302 → 97	64	34	304 → 97	62	33			
Fenothiocarb	8.26	254 → 72	20	30	254 → 160	20	13			
Fenpyroximate	9.32	422 → 366	50	23	422 → 135	50	46			
Flusilazole	8.08	316 → 247	21	26	316 → 165	21	37			
Furathiocarb	9.11	383 → 195	20	25	383 → 252	20	23			
Hexythiazox	9.41	353 → 228	15	23	353 → 168	15	35			
Kresoxim-methyl	8.64	314 → 206	10	10	314 → 116	10	19	314 → 267	10	9
Imidachloprid	3.04	256 → 209	26	19	256 → 175	26	22			
Indoxacarb	9.02	528 → 249	15	23	528 → 293	15	20	528 → 218	15	31
Paclobutrazol	6.97	294 → 70	30	41	296 → 70	35	40			
Pyridaben	9.58	365 → 309	40	18	367 → 311	40	18			
Tebuconazole	7.57	308 → 70	27	47	310 → 70	27	49	308 → 151	27	35
Tebufenozide	8.21	297 → 133	16	20	353 → 139	46	24			
Tebufenpyrad	8.72	334 → 117	60	55	334 → 145	60	45			
Tetraconazole	7.87	372 → 159	27	37	374 → 161	27	45			
Trifloxystrobin	8.94	409 → 186	15	24	409 → 206	15	20			

[a] MS–MS transition used for quantitation.
[b] Declustering potential (similar to the cone voltage of other manufacturers).
[c] Collision energy.

Italy). Formic acid (98%) was supplied from Baker (Deventer, The Netherlands). Sodium chloride and sodium sulfate anhydrous were ≥99.0% (Carlo Erba). The sodium sulfate anhydrous was heated at 550 °C at least for 4 h, cooled in a dessicator and stored in sealed bottle. A total of 102 processed fruits (nectars, juices and purees) were purchased from local markets in Parma. They included products derived from apple (20.6%), pear (15.7%), apricot (20.6%), peach (11.8%), plum (5.9%), orange (17.6%) and lemon (8.7%). Concentrated lemon juice of 50° Brix was semiprocessed product directly supplied from manufactures. Samples for recovery studies were tested to be free from pesticides.

2.2. Standard preparation

Individual stock solutions (ca. 500 μg/ml) were prepared by dissolving neat pesticides in methanol. Appropriate aliquots of individual stock solutions were diluted with methanol to make a standard mixed solution at concentrations ranging between 2.5 and 25 μg/ml depending on LC–MS–MS sensitivity (2.5 μg/ml axoxystrobin, trifloxystrobin, fenothiocarb, furathiocarb, fenpyroximate, difeconazole, flusilazole, fenbuconazole; 5.0 μg/ml fenazaquin, benfuracarb, hexythiazox, tebufenpyrad, tebufenozide, paclobutrazol, tebuconazole, tetraconazole, bromuconazole; 10.0 μg/ml indoxacarb, pyridaben; 12.5 μg/ml dimethomorph; 25.0 μg/ml kresoxim-methyl, imidachloprid, etofenprox, fenhexamid). An intermediate solution at concentrations ranging between 0.250 and 2.5 μg/ml was prepared in acetonitrile–water (40:60, v/v) and used for recovery tests. Working standard solutions were prepared by diluting intermediate mixed solution. Matrix-matched standards were prepared by drying sample extracts in acetone–hexane (15:85, v/v) under a stream of nitrogen and reconstituting with the volume of working standard solutions.

2.3. Sample preparation

Samples were extracted according to the procedure previously reported [3,4].

Prior to extraction, the pH of a 20.0 g sample was adjusted to 6.0. For this purpose, an aliquot (20 g) of previously homogenized sample was weighed into a 25 ml becker and a magnetic stir bar was added. The pH was adjusted to 6.0 by adding 10 M NaOH to sample stirred at high speed. Then the homogenate was quantitatively transferred to a 250 ml centrifuge bottle. A 10.0 g amount of sample was weighed for the analysis of concentrated lemon juice. In this case, in order to adjust the pH to 6.0, NaOH pellets were added. Acetone (exactly 40 ml) and sodium chloride (7 g) were added and the mixture was homogenised for 2 min using an Ultra-Turrax T25 mixer at 5000 rpm. Ethyl acetate–cyclohexane (50:50, v/v) (exactly 20 ml) was added and the sample blended again for 1 min at 9000 rpm. The homogenate was centrifuged for 15 min at 5000 rpm. The volume of organic phase, measured out in a graduated cylinder, was 55 ml. A 50 ml aliquot (18.2 g) was filtered through a glass microfibre filter previously washed with 15 ml ethyl acetate–cyclohexane (50:50, v/v) and containing a bed of anhydrous sodium sulfate (20 g). The filter was rinsed with 20 ml ethyl acetate–cyclohexane (50:50, v/v). The effluents were collected in a 100 ml round-bottom flask, evaporated under vacuum to a small volume (ca. 0.5 ml) at a bath temperature of 30 °C and the last solvent traces were then removed with a gentle stream of nitrogen. The sample was finally taken up with acetone–hexane (15:85, v/v) to a volume of 9 ml. An aliquot of extract (0.5 ml) was evaporated with a stream of nitrogen and the residue taken up with 1 ml acetonitrile–water (40:60, v/v). To remove solid particles, extract was filtered into an autosampler vial through a poly(vinylidene difluoride) (PVDF) syringe filter unit (0.45 μm pore size, Millipore, Bedford, MA, USA).

2.4. High performance liquid chromatography

HPLC was performed using an 1100 series liquid chromatograph system equipped with G1322A degaser, G1312A pump, G1313A autosampler (Agilent Technologies Italia, Milan, Italy).

A 4 μm Synergy Polar-RP column (150 mm × 2.0 mm) (Phenomenex, Aschaffenburg, Germany) was operated at a

Table 2
Common name, activity and chemical class of the pesticides under investigation

Common name	Activity	Chemical class
Azoxystrobin	Fungicide	Strobilurin
Trifloxystrobin		
Kresoxim-methyl		
Tebuconazole	Fungicide	Triazol
Tetraconazole		
Flusilazole		
Fenbuconazole	Plant growth regulator	
Paclobutrazol		
Bromuconazole		
Difeconazole		
Furathiocarb	Insecticide	Carbamate
Fenothiocarb		
Benfuracarb		
Indoxacarb		
Imidacloprid	Insecticide	Neonicotinoid
Fenpyroximate	Acaricide	Phenoxypyrazol
Fenhexamid	Fungicide	Hydroxyanilide
Tebufenozide	Insecticide	Benzohydrazide
Hexitiazox	Acaricide	Carboxamide
Tebufenpyrad		
Pyridaben	Acaricide	Pyridazinone
Dimetomorph	Fungicide	Morpholine
Fenazaquin	Acaricide	Quinazolin
Etofenprox	Insecticide	Phenoxybenzyl ether

flow rate of 0.250 ml/min. The following elution program was used: at the start 60% solvent A (0.1% aqueous formic acid) and 40% solvent B (acetonitrile); after 0.5 min the percentage of solvent B was linearly increased to 95% in 4.0 min; kept constant for 5.5 min; ramped to original composition in 1 min; and then equilibrated for 9.0 min. Prior to use, the solvents were filtered through 0.22 μm filter with applied vacuum.

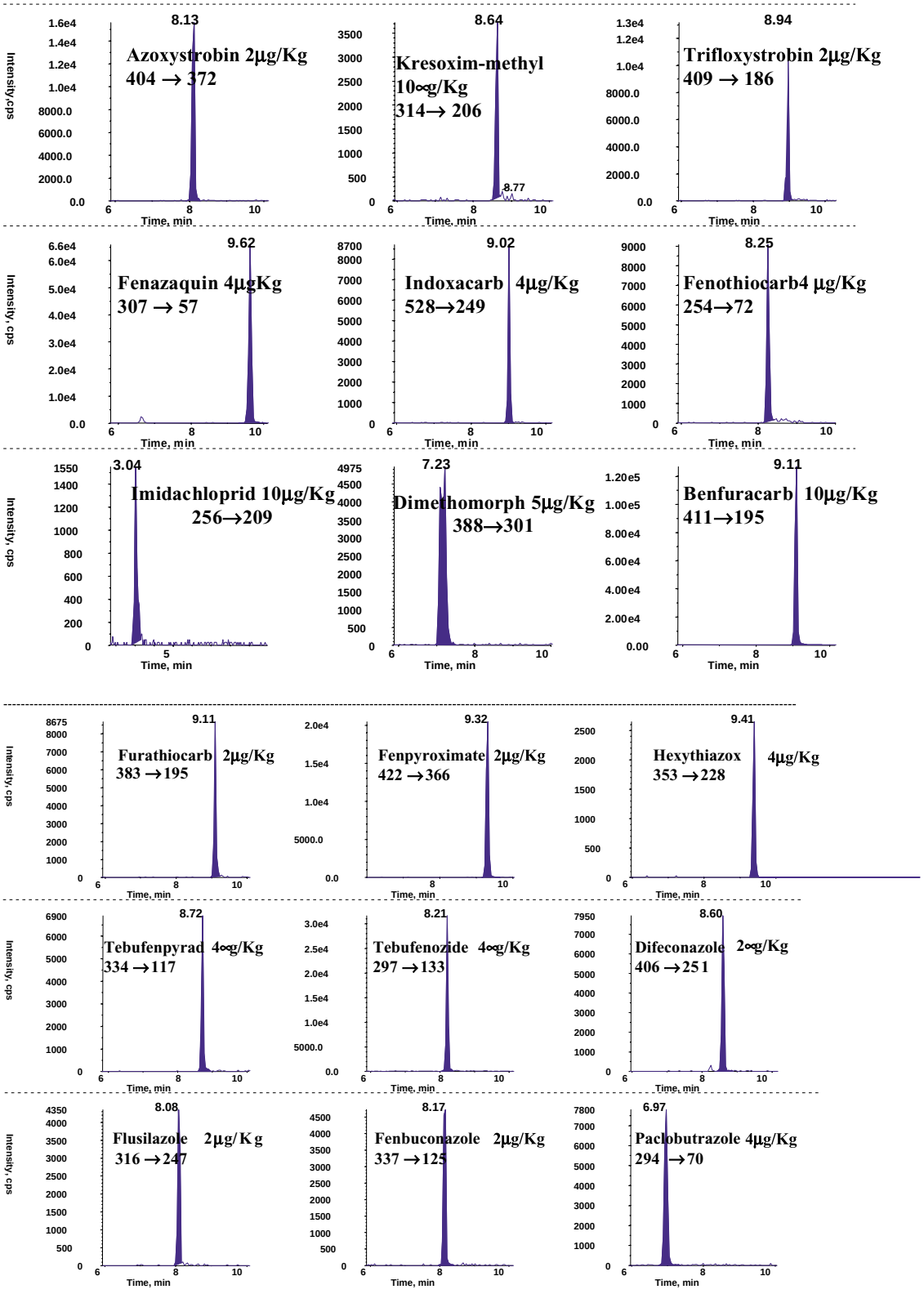

Fig. 1. Typical MRM profiles of a fortified apple puree at 2–10 μg/kg. Injection volume, 40 μl of 1 g/ml sample.

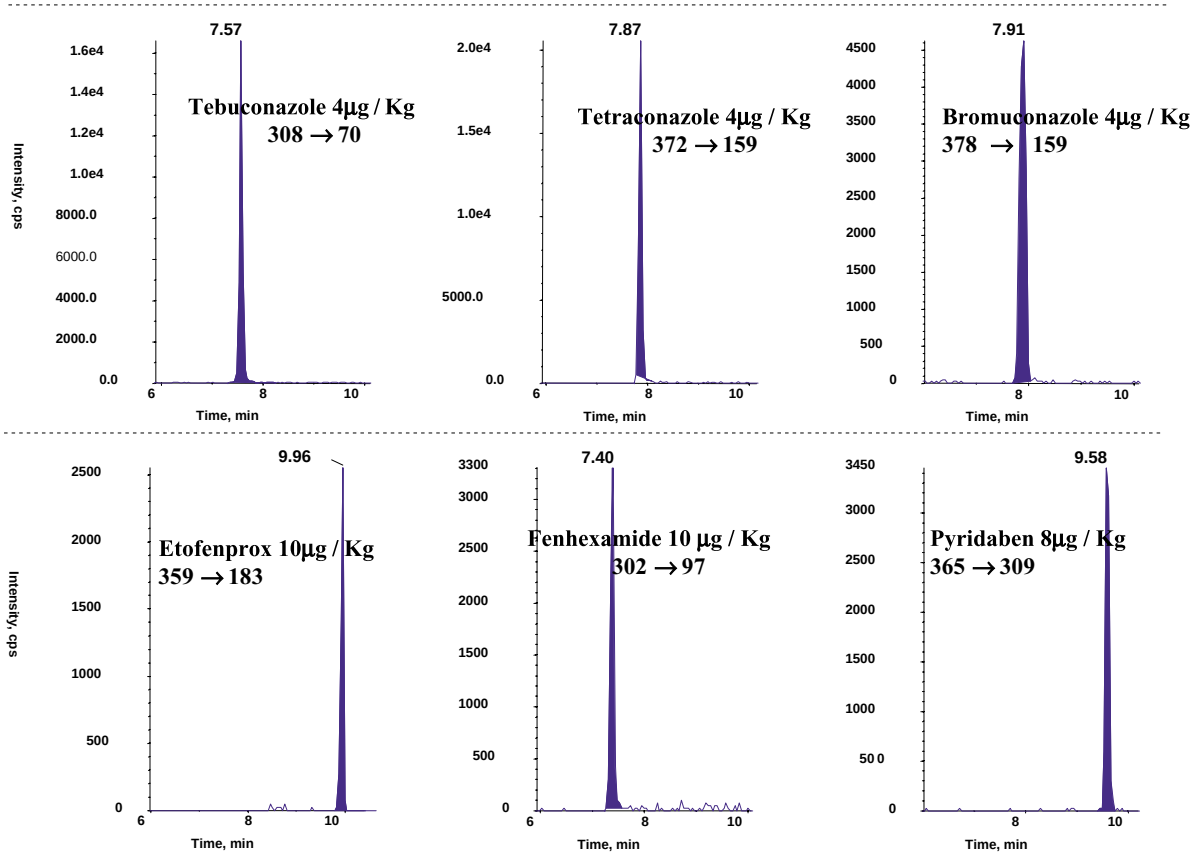

Fig. 1. (*Continued*).

A portion (40 µl) of extract containing 1.0 g/ml sample (juices, nectars and purees) or 0.5 g/ml sample (concentrated lemon juice) was injected.

2.5. Mass spectrometry operating conditions

API–MS detection was achieved using PE Sciex API 2000 triple quadrupole mass spectrometer (Applera Italia, Milan, Italy) equipped with a Turboionspray interface (ESI).

The instrument was operated in positive ion electrospray mode with 55 MS–MS transitions monitored during LC separation in the multiple reaction monitoring (MRM) mode. Selection and tuning of transitions as well as analyte-dependent parameters DP (declustering potential) and CE (collision energy) were performed by direct

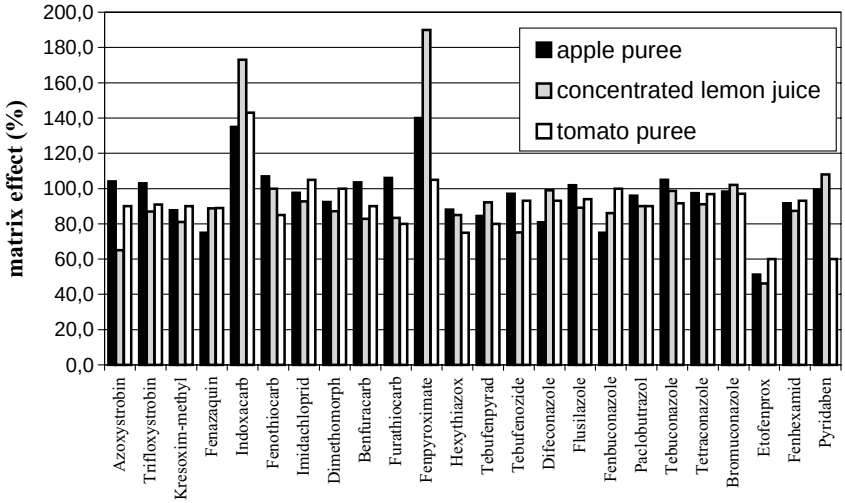

Fig. 2. Matrix effects of tested pesticides. Matrix effect (%) = peak area of matrix-matched standard/ peak area of solvent standard × 100. Sample aliquot 1 g/ml (tomato and apple puree), 0.5 g/ml (concentrated lemon juice); concentration levels correspond to highest fortification levels of Table 3.

Table 3
Recoveries of pesticides from fortified processed fruits and vegetables

Pesticide	Recovery % (R.S.D. %)[a]					
	Added (mg/kg)	Apple puree	Added (mg/kg)	Concentrated lemon juice	Added (mg/kg)	Tomato puree
Azoxystrobin	0.001	92 (7)	0.002	87 (9)	0.001	94 (6)
	0.010	89 (9)	0.020	92 (10)	0.010	95 (9)
Benfuracarb	0.002	86 (9)	0.004	99 (10)	0.002	90 (11)
	0.020	93 (10)	0.040	91 (10)	0.020	95 (14)
Bromuconazole	0.002	85 (9)	0.004	85 (8)	0.002	98 (8)
	0.020	90 (14)	0.040	91 (5)	0.020	91 (10)
Difeconazolo	0.001	85 (12)	0.002	86 (10)	0.001	101 (3)
	0.010	84 (14)	0.020	87 (9)	0.010	91 (7)
Dimethomorph	0.005	79 (15)	0.010	92 (9)	0.005	77 (9)
	0.050	79 (8)	0.100	84 (10)	0.050	97 (3)
Etofenprox	0.010	90 (8)	0.020	76 (11)	0.010	76 (13)
	0.100	89 (10)	0.200	81 (10)	0.100	89 (12)
Fenazaquin	0.002	86 (12)	0.004	92 (10)	0.002	89 (10)
	0.020	86 (10)	0.040	89 (11)	0.020	87 (7)
Fenbuconazole	0.001	82 (11)	0.002	98 (7)	0.001	94 (8)
	0.010	83 (9)	0.020	86 (9)	0.010	78 (7)
Fenhexamid	0.010	92 (10)	0.020	82 (12)	0.010	84 (11)
	0.100	90 (7)	0.200	86 (11)	0.100	89 (13)
Fenothiocarb	0.001	85 (9)	0.002	90 (10)	0.001	95 (9)
	0.010	94 (7)	0.020	81 (5)	0.010	89 (6)
Fenpyroximate	0.001	89 (4)	0.002	91 (8)	0.001	81 (11)
	0.010	92 (5)	0.020	94 (10)	0.010	87 (12)
Flusilazole	0.001	84 (11)	0.002	91 (10)	0.001	103 (5)
	0.010	90 (11)	0.020	87 (10)	0.010	97 (6)
Furathiocarb	0.001	89 (13)	0.002	97 (7)	0.001	93 (9)
	0.010	89 (10)	0.020	90 (10)	0.010	92 (8)
Hexythiazox	0.002	91 (10)	0.004	85 (10)	0.002	79 (10)
	0.020	88 (13)	0.040	88 (9)	0.020	105 (8)
Kresoxim-methyl	0.010	89 (10)	0.020	95 (9)	0.010	96 (6)
	0.100	93 (8)	0.200	88 (9)	0.100	94 (8)
Imidachloprid	0.010	77 (12)	0.020	69 (10)	0.010	69 (9)
	0.100	83 (10)	0.200	62 (15)	0.100	83 (11)
Indoxacarb	0.004	89 (8)	0.008	92 (11)	0.004	96 (9)
	0.040	87 (11)	0.080	92 (10)	0.040	98 (9)
Paclobutrazol	0.002	86 (9)	0.004	89 (8)	0.002	87 (8)
	0.020	90 (7)	0.040	87 (10)	0.020	90 (8)
Pyridaben	0.004	88 (11)	0.008	92 (9)	0.004	91 (9)
	0.040	89 (7)	0.080	99 (7)	0.040	91 (14)
Tebuconazole	0.002	89 (10)	0.004	87 (9)	0.002	96 (7)
	0.020	92 (12)	0.040	88 (12)	0.020	98 (6)
Tebufenozide	0.002	96 (8)	0.004	86 (9)	0.002	94 (11)
	0.020	92 (13)	0.040	88 (8)	0.020	93 (9)
Tebufenpyrad	0.002	90 (7)	0.004	99 (9)	0.002	94 (5)
	0.020	91 (13)	0.040	78 (11)	0.020	95 (5)
Tetraconazole	0.002	91 (7)	0.004	89 (5)	0.002	95 (8)
	0.020	93 (6)	0.040	89 (9)	0.020	89 (6)
Trifloxystrobin	0.001	83 (10)	0.002	86 (10)	0.001	106 (2)
	0.010	89 (10)	0.020	93 (10)	0.010	91 (7)

[a] Each value is the mean of six determinations, R.S.D.: relative standard deviation.

infusion of individual pesticide solutions in methanol at a concentration of 1 mg/l (Table 1). A dwell time of 25 ms per transition was used.

ESI source parameters were optimized for all compounds by flow injection experiments. For this purpose, HPLC pumps were set-up with acetonitrile–0.1% formic acid (40:60, v/v), then the autosampler and HPLC system were connected to the MS with no column in-line (flow rate 0.250 ml/min, 10 μl injection volume, analyte concentration 0.1 mg/l). The capillary voltage was 5500 V. Nitrogen was used as nebulizer gas (60 psi; 1 psi = 6894.76 Pa), curtain gas (30 psi), heater gas (50 psi) and collision gas (3 psi). The TurboIonSpray probe temperature was maintained at 400 °C.

2.6. Recovery study

For recovery experiments two different volumes (0.080 and 0.800 ml) of intermediate standard solution (2.5–0.250 μg/ml) were added to 20 g of apple and tomato purees and 10 g of concentrated lemon juice in a centrifuge bottle. Resulting samples were mixed and allowed to stand for 15 min before extractions. Six replicates at each fortification level were prepared. Concentrations were calculated by measuring peak areas from extracted-ion current profiles and comparing them with those obtained from matrix-matched standards of a concentration similar to that of sample. Sample data were processed by external standard technique and a single point calibration.

3. Results and discussion

The compounds selected in this study belong to different chemical classes that are representative of newly introduced pesticides. Table 2 lists the their common names, main activity and chemical classes.

A previous procedure for determination of different pesticide classes in processed fruits and vegetables was used [3,4]. With this method, extraction with acetone and partition with cyclohexane/ethyl acetate was performed in one step. It requires only small volumes of solvent per sample,

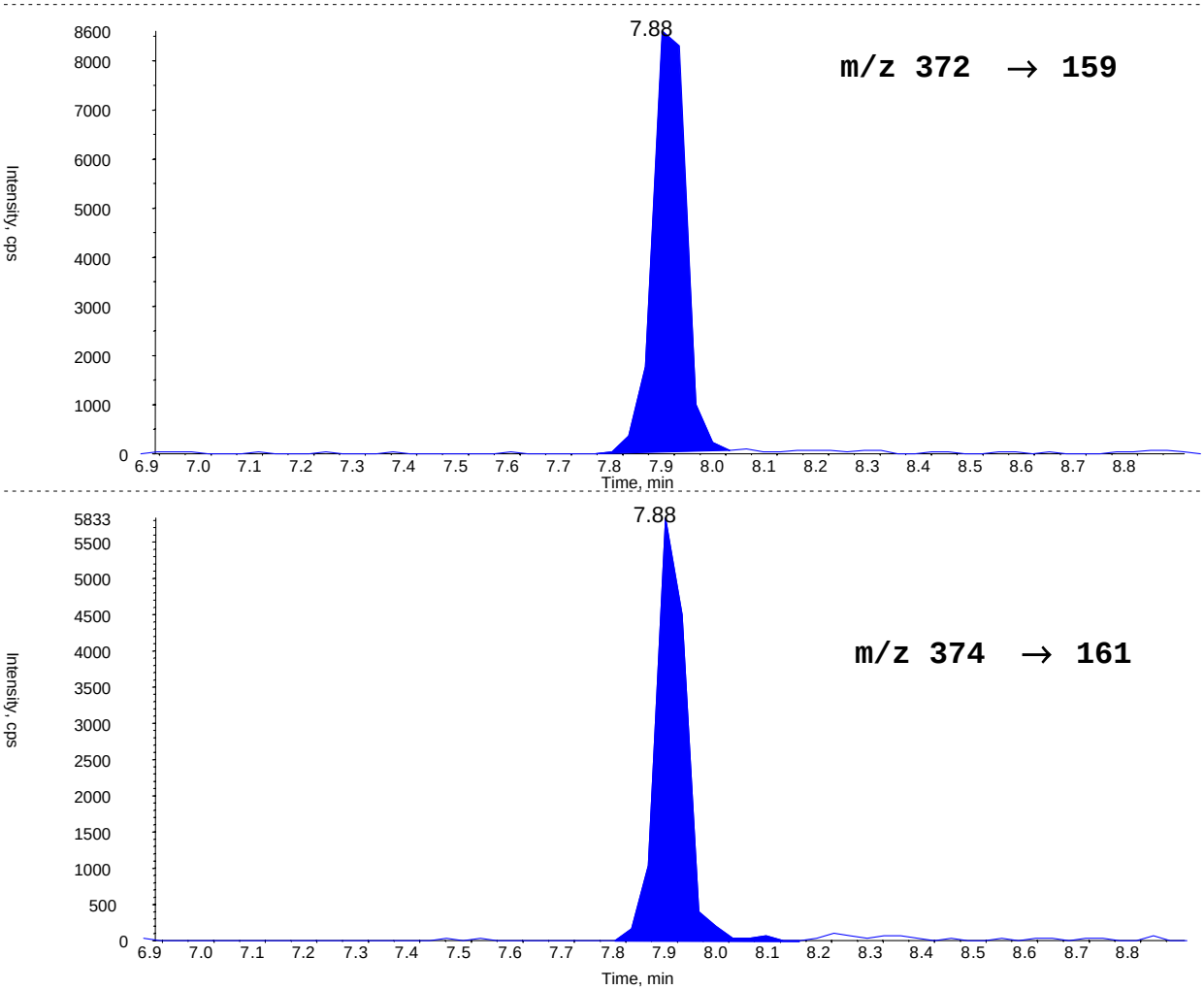

Fig. 3. LC–MS–MS chromatograms of a positive apricot nectar containing tetraconazole at 2.2 μg/kg).

short analysis time and does not use any chlorinated solvents. Prior to extraction, the sample pH was adjusted to value 6.0. Benfuracarb was not recovered at pH below 6.0 in all matrices under investigation. Imidachloprid was partially recovered (<50%).

In the present study extracts were analyzed by LC–MS–MS without any further clean-up step. Suitable transitions from precursor to product ions (MRM transitions) were identified for each compound as described in Section 2. For confirmation of results a second and, for azoxystrobin, kresoxim-methyl, fenazaquin, benfuracarb, tebuconazole, bromuconazole, a third fragmentation of the selected parent ions can be used. The simultaneous measurement of 55 MRM transitions was carried out (Table 1). Thus, 24 pesticides can be screened in a single injection using only one retention time window (period).

The LC column was an ether-linked phenyl phase and provided good retention and peak shapes for all analytes. Typical chromatograms of individual MRM transitions for 24 pesticides in apple puree extract at concentrations ranging from 2 to 10 μg/kg are shown in Fig. 1. Similar profiles were obtained from concentrated lemon juice and tomato puree. In the case of dimethomorph, it being present as two isomers, the peak was split.

Under the LC gradient conditions described in Section 2 the pesticides elute within the 10 min. Run time was 20 min including column conditioning. These chromatograms demonstrate how the enhanced selectivity afforded by MS–MS detection allowed discrimination between target pesticides that were marginally separated by LC. No peaks were detected in unfortified samples for any of the pesticide/matrix combinations.

Although interferences are not visible in the LC–MS–MS chromatograms, coeluting matrix components could inhibit or enhance the analyte signal. This phenomenon is referred to as matrix effects [13] and can be expressed as a ratio of

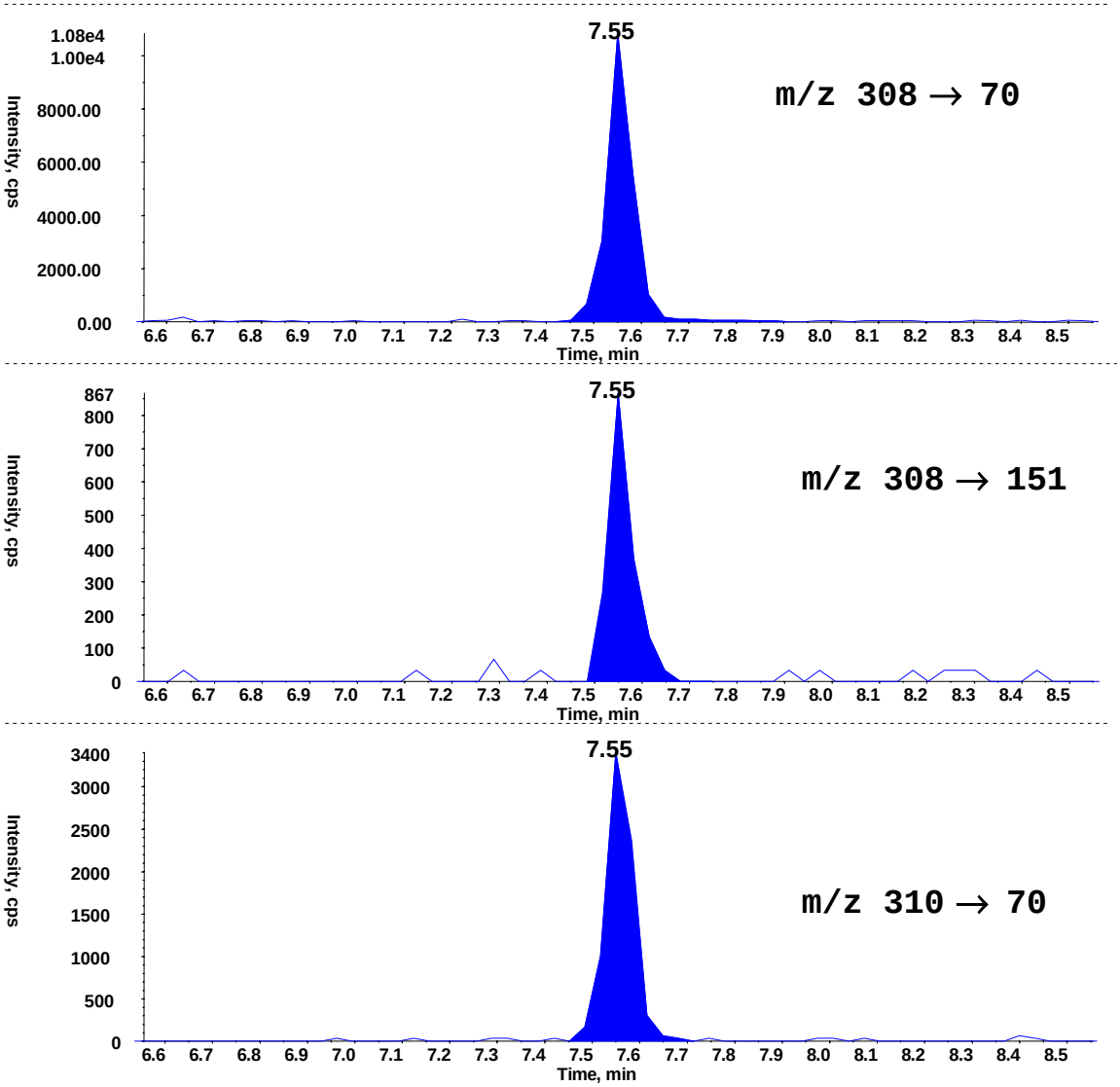

Fig. 4. LC–MS–MS chromatograms of a positive apricot nectar containing tebuconazole at 3.3 μg/kg).

analyte response in matrix-matched standard to its response in solvent standard. The matrix effects measured in fruit and vegetable products selected for the method validation at the highest levels of fortification are reported in Fig. 2. As can be seen from this histogram no considerable signal reduction in matrix extracts was detected for the most compounds except for etofenprox. Matrix effects of 46.2, 51.2 and 60.0% were observed for this pesticide in concentrated lemon juice, apple and tomato purees, respectively. LC–MS–MS response suppression caused by sample matrix component has been widely discussed in the literature [12,13]. Less common behaviour was observed for fenpyroximate and indoxacarb where the detector response was enhanced by matrix (matrix effect ≥135%).

The best way to compensate for matrix effects is the use of isotope internal standards, however for the most pesticides these compounds are not available. In this study, calibration was performed by external matrix-matched standards to eliminate the matrix effect and to obtain a more realistic determination.

The recovery results and the relative standard deviations (R.S.D.s) obtained from analysis of processed fruits and vegetables at two fortification levels are shown in Table 3. The recoveries of the pesticides are very good (>75%) in most cases and are independent of sample matrix and the fortification level. A good repeatability from six repetitive determinations of recovery has been achieved (R.S.D. ≤15%) for all analytes. Slightly low recoveries (<70%) were observed for imidachloprid in concentrated lemon juice at the both spiking levels and in tomato puree at the lowest level. In apple puree, however, recoveries (>76%) were satisfactory.

Lowest calibrated levels (LCLs) corresponded to lowest fortification levels of Table 3. These levels were based on a 40 μl injection of the final extract containing 1 g sample/ml (for juices and purees) and 0.5 g sample/ml (for concentrated lemon juice). LCLs ranged from 1 to 10 μg/kg for juices and purees, from 2 to 20 μg/kg for concentrated lemon juice with a soluble solid content of 50° Brix.

The optimized analytical procedure was used to analyze processed fruit products obtained from local markets. A total of 102 samples were examined for residues of the 24 pesticides. Processed products derived from different commodity groups were chosen. They included nectars, purees and juices of citrus, stone and pome fruits. Baby foods (20 samples) and products from organic (33 samples) and conventional (49 samples) agriculture were analyzed. Results show that only two samples contained detectable residues. Fig. 3 reports LC–MS–MS chromatograms for the apricot nectar in which tetraconazole was found at 2.2 μg/kg. MRM chromatograms of the apricot nectar contaminated by tebuconazole at 3.3 μg/kg are shown in Fig. 4. The three ion transitions are shown.

4. Conclusions

This work shows that LC–MS–MS is a powerful analytical technique for the rapid determination of 24 pesticides in crude extracts of processed fruits and vegetables.

The excellent selectivity and sensitivity allows quantification and identification of low levels of pesticides in tomato and apple juice purees (LCLs 1–10 μg/kg) and in concentrated lemon juice (LCLs 2–20 μg/kg). These low levels allow application of the presented method even at the concentration required by current regulator laws for baby and organic foods.

The optimized method was used to analyze 102 fruit processed products. None of samples contained residues higher than 10 μg/kg. Only two apricot nectars contained detectable residues of tebuconazole (3.3 μg/kg) and tetraconazole (2.2 μg/kg).

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