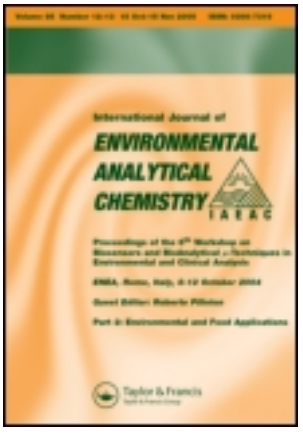

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Multiresidue determination of pesticides by solid-phase extraction and GC-MS for control of peach production in Bulgaria

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Multiresidue determination of pesticides by solid-phase extraction and GC-MS for control of peach production in Bulgaria

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A multiresidue analytical method based on acetone extraction and clean-up/pre-concentration on polymeric sorbents was validated for 42 pesticides in peach matrix in order to control safety of fresh production on the Bulgarian market. Matrix-matched calibration was used by addition of pesticides just before SPE. In this way the standards and the samples undergo exactly the same procedure and an improvement of recoveries for the target analytes was observed. The identification and quantification were done by gas chromatographic technique with mass-spectrometric detection (GC-MS). The limits of detection obtained were 0.005 mg kg^{-1} or lower for the most of analytes, and the recovery data were in range 73–109% at three spiked levels 0.01, 0.1 and 0.2 mg kg^{-1}. The validated method was used for monitoring of selected pesticides in fresh peach fruits home production. Approximately 30% of the analysed lots (total 33 samples) contained residues mainly of cypermethrin and procymidone, but did not exceed EU MRLs.

Keywords: pesticides; multiresidue method; monitoring; peach fruits

1. Introduction

The chemical approach for pest control is still the most popular method for plant protection for many countries in the world. In order to provide protection of consumer health and environment, a permissible limit for each combination pesticide/product has to be observed. According to EU legislation [1], pesticide residues ought to be controlled through the whole food chain in order to stop the foodstuffs containing unallowable contamination to enter in the manufacturing process. National Service for Plant Protection in Bulgaria is an organisation in charge of controlling pests and chemical contaminants in plant foodstuffs before they are placed on the market. An operative programme was elaborated for monitoring of pesticide residues in crops after harvesting. This programme aims to provide adequate control of proper application of plant protection products, observing the quarantine dates during crop production and possible misuses with banned formulations. At the same time, the implementation of the programme enables control of the first stage of the food chain for pesticide residues being exceeded. The number of monitored pesticides as well as the type of inspected crops was chosen on the basis of available data for residues identified in previous years and dietary intake of native consumers. Peaches are important fruits for the country as the

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home production equated to more than 21 thousand tons in 2006 [2]. They are cultivated mainly under conventional agricultural conditions and because of this, possible pesticide residues represent a potential risk for consumers and have to be investigated.

Most of the multiresidue procedures proposed for determination of volatile pesticides in fruits use gas chromatography (GC) instrumentation and different kinds of detectors – electron capture, nitrogen-phosphorus, flame ionisation, etc. [3–5]. Nevertheless, mass spectrometry (MS) is preferred as a time-saving and labour-saving approach [6]. The number of classes of pesticides that can be detected simultaneously by this technique is much higher than with conventional residue analysis methods.

Different approaches are used currently for sample preparation. Among them, the solid phase extraction (SPE) technique using various types of sorbents has been increasingly applied in more recent multiresidue methods as an alternative to the classical method for clean-up and pre-concentration of raw plant extracts [7–9]. In our previous investigations, the efficiency of sorbent with different retention mechanisms was compared for clean-up of grains, fruits and vegetables samples [10]. The obtained limits of quantitation for 25 pesticides were found below $0.01\,mg\,kg^{-1}$. Recently, polymeric sorbents, which consist of highly-crosslinked polystyrene-divinyl benzene material, arouses interest because of their improved properties. The main advantage of these sorbents is the high adsorption capacity for more polar pesticide substances due to their large specific surface. This feature proves to be very important during extension of laboratory methods to increasing the number of analytes and to more polar compounds.

This paper describes a procedure and adaptation of analytical method for simultaneous determination of more than 40 pesticides through clean-up of acetone extracts on polymeric sorbent. Improvement of recovery values for pyrethroids was found by using matrix-matched standard solutions made through addition of pesticides just before SPE. In this way, the standards and the samples undergo exactly the same procedure. The pesticide residues were detected identified and quantified using the GC-MS technique. The validated analytical procedure was applied for monitoring of pesticide residues in home-produced fresh peaches.

2. Experimental

2.1 *Reagents and materials*

Certified analytical standards of pesticides and internal standard ethion were of 99% or higher certified purity and purchased from Dr Ehrenstorfer (Augsburg, Germany) or Sigma-Aldrich (Seelze, Germany). Acetone, ethyl acetate and methanol (gas chromatography grade) were purchased from Merck KGaA (Darmstadt, Germany). A stock standard solution of each pesticide was prepared at $1000\,\mu g\,mL^{-1}$ in acetone or ethyl acetate depending on their solubility and was stored in a glass-stopped flask in a freezer at $-18^{\circ}C$. A mixed standard of pesticides was prepared from the individual stock solutions at $10\,\mu g\,mL^{-1}$ in acetone and stored at $4^{\circ}C$ in the dark. This standard solution was used for fortification of blank peach matrix in recovery experiments and for preparation of working standards in acetone at a concentration range of $0.01\,\mu g\,mL^{-1}$ to $1.0\,\mu g\,mL^{-1}$. Matrix matched standards were prepared by adding appropriate amounts of standard solutions to control blank peach extract in the range $0.01\,mg\,kg^{-1}$ to $1.0\,mg\,kg^{-1}$. The internal standard solution of ethion was prepared at $100\,\mu g\,mL^{-1}$ in acetone and $50\,\mu L$ of it was added to the final extract before injection.

Commercial pre-packed cartridges LiChrolut EN® (Merck KGaA, Germany) were used for solid-phase extraction. Each cartridge contains 6 mL free volume and 500 mg of highly-crosslinked polystyrene-divinyl benzene sorbent material with a surface area $1200\,m^2\,g^{-1}$ and particle size 40–120 μm.

High quality water was obtained from water distiller GFL 2004 (GFL, Germany) following polishing procedure on a system Water pro PS (Labconco, USA). The carrier gas helium used in gas chromatographic system was of purity greater than 99.9995% (Siad, Bulgaria) and gas flow rate was $1.0\,mL\,min^{-1}$. Vortex mixer V-1 plus (Boeco, Germany) and centrifuge Rotofix 32A (Hettich GmbH&CoKG, Germany) were used in the sample preparation process. Vacuum manifold Vac-Elut (Varian Inc., The Netherlands) coupled to vacuum pump 2012C–02 (Welch Rietschle Thomas) was used for SPE.

2.2 *Samples handling*

Samples of peaches (33 lots) originated from various fruit growers in the country. Representative samples of 2 kg were collected randomly in lots after harvesting and before placing on the market. They were transported quickly to the laboratory in ice-boxes. After homogenisation with a food processor (Moulinex, SEB group, France) samples were stored at −18°C until analysis. A pesticide-free sample was checked by chromatographic analysis and was used as blank matrix in preparation of matrix matched standards for calibration.

2.3 *Extraction procedure*

For pesticide extraction previously described by Stajnbaher and Zupancic-Kralj [11], the method was used with some modifications. Ten grams of homogenised peach samples were weighed into 50 mL centrifuge polypropylene tubes with screw caps, 20 mL of acetone were added, caps were tightened and the mixtures were vigorously shaken by Vortex for 5 min. Then centrifugation was performed at 3000 rpm for 5 min and the supernatant was transferred in a glass cylinder in order to measure the volume. The exact half of the raw extract was diluted with water to 70 mL and was allowed to pass through the SPE cartridge with maximum flow rate $8\,mL\,min^{-1}$. Before loading of raw extract the cartridge was conditioned with 6 mL ethyl acetate, 6 mL methanol and 8 mL ultra pure water. After loading the water-acetone extract, the cartridge was washed with 10 mL water and the sorbent was dried under reduced pressure (vacuum about 20 mmHg) for approximately 30 min. Then the retained pesticides were eluted with 2 mL ethyl acetate followed by 7 mL mixture of ethyl acetate : acetone (9:1). All fractions were brought together and solvents were evaporated to 5 mL final volume, so that the matrix concentration was the same in all samples – $1\,g\,mL^{-1}$. After that 50 μL of IS were added and 1 μL was injected into chromatographic system.

2.4 *Instrumental analysis by GC-MS*

A Thermo Finnigan Trace GC Ultra (Milan, Italy) gas chromatograph coupled to Finnigan Trace DSQ (Austin, Texas, USA) mass spectrometer, equipped with split/splitless injector, autoinjector model AI 3000 and capillary column Factor Four VF 5ms,

30 m × 0.25 mm ID × 0.25 μm film thickness (Varian Inc, Middelburg, The Netherlands), was applied. The temperature conditions in the chromatographic system were as follows: injector 230°C and splitless time 1 min; oven starting temperature was 70°C and was held for 1 min, then increased at rate 30°C min^{-1} to 190°C (held for 1min) increased to 235°C with rate 5°C min^{-1} and finally increased at rate 15°C min^{-1} to 280°C, held for 8 min. Mass spectrometer was operated in electron ionisation mode (ionisation energy 70 eV) while the transfer line and ion source temperatures were set at 250°C and 220°C, respectively. Selected ion monitoring (SIM) mode with minimum 3 ions for each analyte was used for detection and quantification of analytes. Dwell time for each fragment ($m z^{-1}$) was set from 60 to 10 ms, depending on the number of monitored ions in one segment. Xcalibur 1.3 Data System software was used for data acquisition and processing.

3. Results and discussion

In the early method development stage different SPE conditions were examined in order to find the procedure that suits all studied analytes. According to Stajnbaher and Zupancic-Kralj [11], triethylamine (TEA) was used in the elution step of the procedure to improve the extraction recovery of basic pesticides. At the initial step, the necessity of using TEA for the selected pesticide compounds was tested. A comparison was made between two elution systems – first, 2 mL of ethyl acetate containing 1% TEA followed by 6 mL of ethyl acetate – acetone (9 : 1) and – second – the same system but without TEA. No significant difference was observed between the two elution schemes concerning recoveries of analytes. In both cases, the pyrethroids were not sufficiently recovered. The problem could be referred to the possible π–π interactions between the aromatic moieties of the sorbents and molecules of pyrethroids [12]. Overcoming this problem could be achieved by use of more non-polar solvent in the elution scheme. Thus, 2 mL n-hexane was examined as a final elution step. This resulted in increasing of recovery for pyrethroids but at the same time increasing the amount of non-polar matrix co-extractives in the final extracts. One possible solution was found making matrix-matched standard solutions by addition of pesticides prior to SPE. In this way, the standards and the samples undergo exactly the same procedure. This approach led to satisfactory recoveries and repeatability for all target compounds.

During optimisation of mass spectrometric detection in SIM mode, the parameter dwell time has a key role. It denotes how long the quadrupole takes to scan across the range of the SIM width. By increasing its value, dwell time becomes longer and gets a better signal to noise ratio for a chromatographic peak. As a result, the detector response is increased and sensitivity can be improved. On the other hand, if more than 2 analytes are monitored in the same time window, several characteristic ions have to be measured. Thus, the dwell time has to take lower values in order to save data points per peak required for satisfactory detector response. According to Hu *et al.* [13], if the number of scanning cycles per second in the same time window decreases below 2 it leads to a drastic drop in ion intensity, so a value higher than 2 should be maintained. At the beginning of our instrumental method development, the influence of scan time on the peak shape and analyte response was investigated for a segment where two analytes (vinclozolin and chlorpyrifos-methyl) were simultaneously eluted and a total of 6 ions were monitored. The optimum peak shape and intensity, e.g for chlorpyrifos-methyl were obtained when dwell time was set to 30 ms (Figure 1). In our further investigations the recommendations

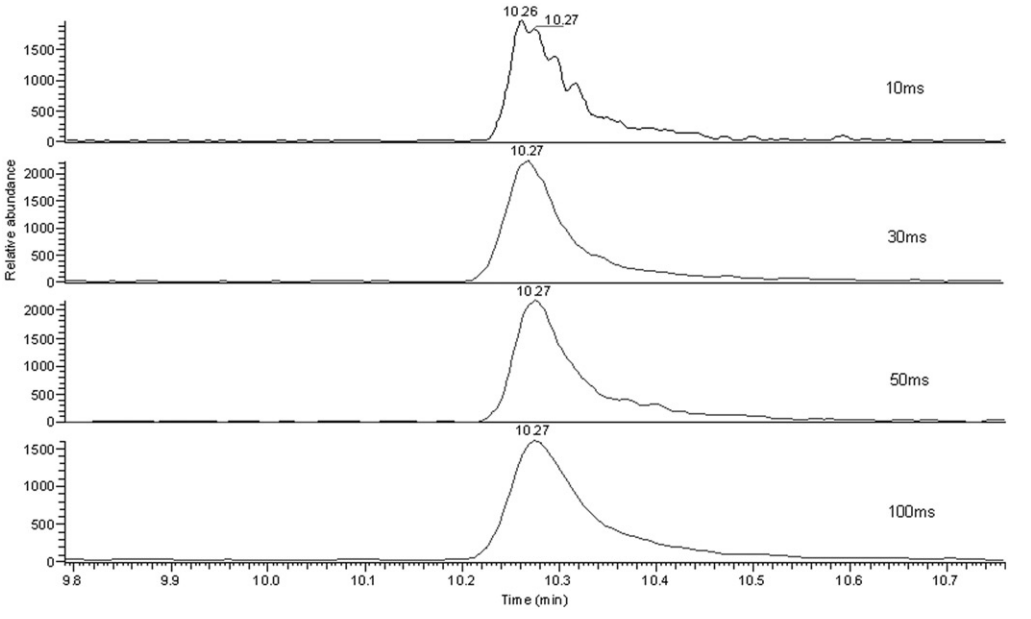

Figure 1. Influence of dwell time of mass spectrometer on the peak shape and response for chlorpyriphos-methyl.

of Hu *et al*. [13] were kept and scanning cycles per second were adjusted to be more than 2 in each segment depending on number of control ions (Table 1).

The developed method of sample preparation and GC-MS analysis was validated for peach matrix. The investigation covered the following validation parameters: linearity range, correlation coefficient (R^2), accuracy expressed by recovery, precision as relative standard deviation (RSD), limit of detection (LOD) and limit of quantification (LOQ). The obtained data are presented in Table 2.

A good linearity for all analytes is achieved in the range 0.01–1 mg kg^{-1} and values of R^2 are higher than 0.98. The accuracy of the procedure is evaluated by estimation of recovery at three levels in 3 replications. Recoveries at level 0.01 mg kg^{-1} vary from 72.6% (for permethrin) to 109.4% (for endosulfan beta), obtained recoveries at level 0.1 mg kg^{-1} vary from 81.3% (for folpet) to 104.03% (for fenpropatrin) and at level 0.2 mg kg^{-1} recovery values are from 78.2% (for folpet) to 107.3% (for fenpropathrin). The obtained values meet the European requirements on quality control procedures for pesticide residues analysis [14]. Limits of detection (LOD) and quantification (LOQ) are determined as the lowest concentrations of the pesticides that yield signal-to-noise (S/N) ratios of 3 and 10, respectively. For this, signal to noise ratio for all target pesticides are examined for peach samples spiked in the range 0.002–0.010 mg kg^{-1}. The calculated values for LOQ are very low, in some cases even below 0.005 mg kg^{-1} (e.g. chlorpirifos-methyl, pirimiphos-methyl, penconazole, bifenthrin). However, as the lowest level at which recovery experiments were performed is 0.01 mg kg^{-1}, the reporting level of the method for each pesticide is 0.01 mg kg^{-1}.

The routine efficacy of this method was verified by analysis of 33 lots of peach production intended for placing on the market. Each lot was analysed once and

Table 1. Characteristics of the time segments of mass spectrometer operating in SIM mode for the studied analytes.

Segment	Pesticide	Monitored ion fragments ($m\,z^{-1}$)	Total number of ion fragments	Dwell time for each fragment (ms)	Cycles number per second
1	Diazinon	179, 137, 199	3	60	4.2
2	Chlorothalonyl	264, 266, 268	3	60	4.2
3	Pirimicarb	166, 167, 238	3	60	4.2
4	Chloropyrifos-methyl	125, 286, 288	6	30	3.7
	Vinclozolin	187, 198, 212			
5	Metalaxyl	206, 160, 249	3	60	4.2
6	Pirimiphos-methyl	276, 290, 305	3	60	4.2
7	Fenitrothion	125, 260, 277	3	60	4.2
8	Dichlofluanid	123, 167, 224	6	30	3.7
	Malathion	125, 127, 173			
9	Chlorpyrifos	197, 199, 314	3	60	4.2
10	Parathion-ethyl	97, 109, 291	6	30	3.7
	Triadimefon	128, 181, 210			
11	Penconazole	159, 248, 250	3	60	4.2
12	Captan	77, 79, 264	6	30	3.7
	Procymidone	96, 283, 285			
13	Folpet	104, 260, 262	9	15	3.7
	Triadimenol	112, 128, 168			
	Methidathion	85, 125, 145			
14	Endosulfan alpha	195, 237, 241	3	60	4.2
15	Hexaconazole	214, 216, 231	3	60	4.2
16	Myclobutanil	150, 179, 245	6	30	3.7
	Krezoxim-methyl	116, 131, 132			
17	Cyproconazole	139, 222, 224	3	60	4.2
18	Endosulfan beta	195, 237, 241	6	30	3.7
	Ethion (IS*)	153, 231, 233			
19	Propiconazole	173, 259, 261	3	60	4.2
20	Tebuconazole	125, 250, 252	3	60	4.2
21	Epoxyconazol	165, 192, 194	3	60	4.2
22	Iprodione	187, 314, 316	12	10	2.9
	Bifenthrin	165, 167, 181			
	Bromopropylate	185, 339, 341			
	Fenpropathrin	97, 181, 265			
23	Metconazol	125, 250, 319	3	60	4.2
24	Phosalone	182, 184, 367	3	60	4.2
25	Lambda-cyhalothrin	141, 181, 197	3	60	4.2
26	Pyrazophos	221, 232, 373	6	30	3.7
	Fenarimol	107, 139, 251			
27	Permethrin	163,165,183,184	3	60	4.2
28	Beta-cyfluthrin	165, 199, 226	3	60	4.2
29	Cypermethrin	163, 165, 181	3	60	4.2
30	Fenvalerate	125, 167, 225, 419	4	50	3.7
31	Difenoconazol	265, 267, 323, 325	4	50	3.7
32	Deltamethrin	181, 253, 255	3	60	4.2

Note: *IS: internal standard.

Table 2. Validation parameters for studied pesticides in peach matrix.

	Pesticides	Mean recovery ± RSD ($n = 9$) 0.01 mg kg^{-1}	0.1 mg kg^{-1}	0.2 mg kg^{-1}	R^2	LOD [mg kg^{-1}] (S/N 3)	LOQ [mg kg^{-1}] (S/N 10)
1	Diazinon	105.80 ± 20.50	90.02 ± 11.40	85.78 ± 2.40	0.9838	0.0027	0.0091
2	Chlorothalonyl	78.04 ± 8.19	82.12 ± 10.41	84.55 ± 4.21	0.9877	0.0030	0.0099
3	Pirimicarb	94.23 ± 15.59	91.07 ± 14.39	94.13 ± 5.24	0.9955	0.0014	0.0047
4	Chlorpyrifos-methyl	89.66 ± 21.87	87.62 ± 11.13	87.26 ± 2.69	0.9889	0.0003	0.0009
5	Vinclozolin	95.98 ± 9.38	85.26 ± 9.80	84.97 ± 0.87	0.9961	0.0016	0.0052
6	Metalaxyl	91.99 ± 20.97	87.81 ± 14.26	88.93 ± 5.03	0.9859	0.0012	0.0039
7	Pirimiphos-methyl	93.75 ± 12.46	89.14 ± 9.25	88.20 ± 1.36	0.9899	0.0008	0.0026
8	Fenithrotion	96.29 ± 13.92	85.67 ± 8.13	87.08 ± 2.57	0.9852	0.0021	0.0070
9	Dichloflunid	83.81 ± 11.28	86.83 ± 7.85	85.92 ± 2.98	0.996	0.0027	0.0091
10	Malathion	99.58 ± 5.49	92.75 ± 9.37	95.54 ± 4.36	0.9832	0.0029	0.0097
11	Chlorpirifos	90.78 ± 15.23	87.68 ± 11.53	85.00 ± 1.41	0.982	0.0024	0.0079
12	Parathion-ethyl	103.99 ± 5.55	85.15 ± 10.27	85.39 ± 1.58	0.9855	0.0027	0.0089
13	Triadimefon	107.19 ± 22.65	89.54 ± 13.08	83.57 ± 7.50	0.9818	0.0024	0.0080
14	Penconazole	99.66 ± 19.00	93.14 ± 15.16	90.72 ± 4.85	0.9871	0.0005	0.0016
15	Captan	98.99 ± 6.71	86.99 ± 13.04	80.69 ± 3.26	0.9914	0.0031	0.0103
16	Procymidone	98.28 ± 13.74	85.55 ± 12.29	86.57 ± 4.05	0.988	0.0025	0.0084
17	Folpet	105.94 ± 3.88	81.30 ± 22.04	78.16 ± 9.48	0.9945	0.0029	0.0095
18	Triadimenol	97.64 ± 20.91	108.23 ± 5.45	103.5 ± 11.2	0.9801	0.0026	0.0087
19	Methidathion	101.75 ± 14.45	94.35 ± 11.25	90.41 ± 2.86	0.9946	0.0022	0.0072
20	Endosulfan-alpha	105.41 ± 14.51	84.34 ± 8.86	80.85 ± 8.27	0.9877	0.0021	0.0070
21	Hexaconazole	102.35 ± 11.21	91.66 ± 14.86	96.18 ± 4.08	0.9832	0.0023	0.0077
22	Myclobutanil	104.76 ± 15.47	90.12 ± 17.42	88.51 ± 6.00	0.9918	0.0023	0.0078
23	Krezoxim-methyl	94.34 ± 20.30	93.91 ± 15.63	88.03 ± 2.20	0.9956	0.0017	0.0056
24	Cyproconazole	96.10 ± 15.62	94.78 ± 15.45	94.93 ± 5.36	0.983	0.0025	0.0082
	Endosulfan-beta	109.44 ± 4.82	86.46 ± 7.72	87.11 ± 4.71	0.9875	0.0030	0.0099
25	Propiconazole	98.68 ± 7.87	92.24 ± 16.82	89.08 ± 6.11	0.9879	0.0013	0.0044
26	Tebuconazole	87.94 ± 15.93	91.59 ± 17.82	91.71 ± 6.21	0.9902	0.0014	0.0045
27	Epoxyconazole	94.65 ± 24.08	93.49 ± 13.75	90.66 ± 6.19	0.9978	0.0014	0.0046
28	Iprodione	102.07 ± 10.05	90.41 ± 13.86	88.65 ± 3.30	0.9983	0.0014	0.0047
29	Bifenthrin	89.52 ± 20.22	91.81 ± 20.32	87.38 ± 24.35	0.9819	0.0008	0.0026
30	Bromopropylate	85.88 ± 23.88	87.99 ± 13.58	83.05 ± 7.50	0.9813	0.0025	0.0084
31	Fenpropathrin	100.75 ± 13.27	104.03 ± 10.30	107.31 ± 14.79	0.9865	0.0027	0.0090
32	Metconazol	104.09 ± 12.76	96.65 ± 11.72	95.77 ± 7.57	0.9891	0.0025	0.0082
33	Phosalone	90.16 ± 16.46	96.02 ± 12.72	89.33 ± 3.06	0.9913	0.0016	0.0052
34	Lambda-Cyhalothrin	89.14 ± 18.54	95.00 ± 11.63	87.04 ± 2.81	0.9864	0.0013	0.0042
35	Pyrazophos	86.37 ± 19.40	95.99 ± 10.78	91.27 ± 4.57	0.9861	0.0013	0.0043
36	Fenarimol	88.82 ± 17.62	92.95 ± 12.99	96.30 ± 4.02	0.9976	0.0023	0.0078
37	Permethrin	72.62 ± 4.49	92.08 ± 3.56	90.99 ± 4.16	0.9853	0.0019	0.0062
38	Beta-Cyflutrhrin	83.80 ± 16.05	87.37 ± 6.10	88.49 ± 4.16	0.9895	0.0019	0.0062
39	Cypermethrin	90.32 ± 12.27	89.43 ± 12.43	86.56 ± 5.82	0.9816	0.0028	0.0093
40	Fenvalerate	84.50 ± 14.66	87.90 ± 9.75	87.22 ± 5.13	0.9841	0.0021	0.0069
41	Difenoconazol	86.77 ± 22.45	96.12 ± 12.06	97.63 ± 5.33	0.9861	0.0023	0.0076
42	Deltamethrin	90.64 ± 13.83	93.77 ± 11.58	88.37 ± 5.22	0.9818	0.0029	0.0102

confirmation of the positive results was mandatory for suspected MRL excesses only. The quantification was done with internal standard calibration (IS – ethion). Our results showed a presence of single pesticide residue in 10 samples (30% of the total number). Residues of a total of five active substances were detected in the positive samples (Table 3). Cypermethrin residues were found in 5 tested samples in the range of 0.01–0.018 mg kg^{-1}

Table 3. Monitoring data for pesticide residues in conventional home produced peaches.

Sample code	Pesticide residue	Amount, mg kg^{-1}	MRL*, mg kg^{-1}
MM06-20	triadimenol	0.023	0.1
MM06-32	hexaconazole	0.014	0.02
MM06-33	folpet	0.013	2.0
MM06-34	cypemethrin	0.018	2.0
MM06-36	cypemethrin	0.017	2.0
MM06-37	procymidone	0.027	2.0
MM06-38	procymidone	0.085	2.0
MM06-39	cypermethirn	0.014	2.0
MM06-40	cypermethirn	0.01	2.0
MM06-48	cypermethirn	0.01	2.0

Note: *According to national legislation [15].

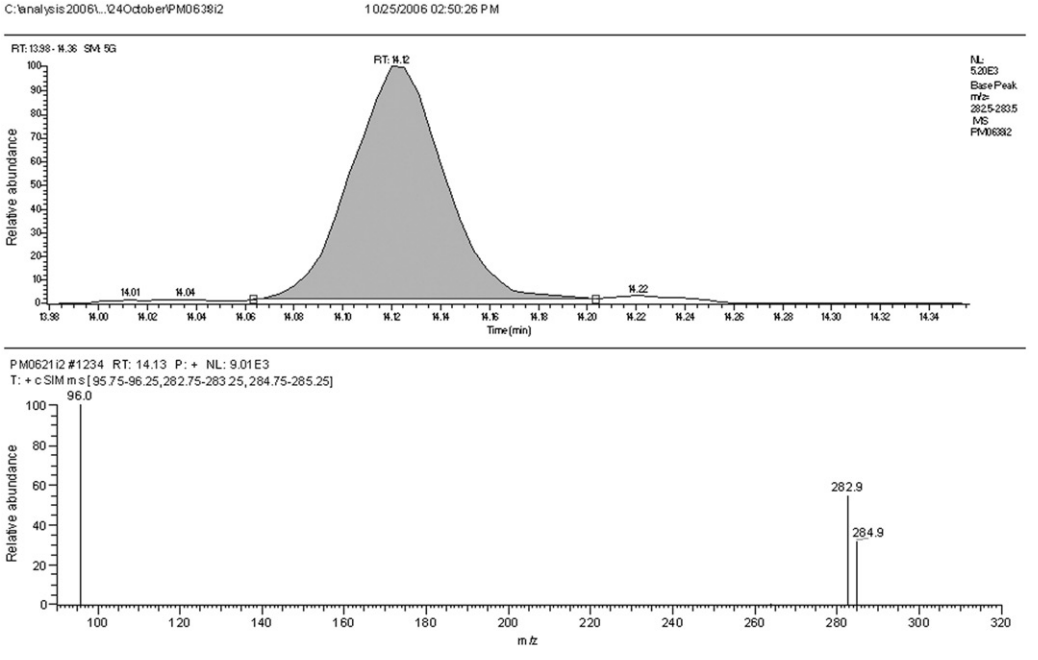

Figure 2. Chromatogram (up) and mass spectra (down) in SIM mode of real peach sample (MM06-38) containing procymidone at concentration level 0.085 mg kg^{-1}, retention time 14.12 min. For instrumental conditions of data acquiring, see the section entitled 'Methods and Materials'.

which is more than 100 times lower than European MRLs for this substance in peach fruits (2.0 mg kg^{-1}). Procymidone residues were found in 2 peach lots in amounts 0.027 mg kg^{-1} and 0.085 mg kg^{-1}, respectively, and these values are about 50 times lower than the permitted MRL of peach/procymidone combination. Figure 2 shows the chromatogram and spectrum for one positive peach sample in which procymidone was found. In three other samples of peaches, single residues of triadimenol, hexaconazole, and folpet were

found at levels 0.023 mg kg^{-1}, 0.014 mg kg^{-1} and 0.013 mg kg^{-1}, respectively. Determined residues are still lower than fixed MRLs.

4. Conclusions

A highly accurate and repeatable multiresidue analytical method based on acetone extraction and clean-up/pre-concentration on polymeric sorbents was validated for the determination of 42 pesticides in peach matrix. Matrix-matched calibration was used by addition of pesticides just before SPE. Since the standards and the samples undergo exactly the same procedure, an improvement of recoveries for the target analytes was obtained. In the working range 0.01–1 mg kg^{-1} satisfactory recoveries were obtained – from 72.6% to 109.4%. The calculated values for LOQ were very low, in some cases even below 0.005 mg kg^{-1}. Routine use demonstrated that the proposed method is suitable for the analysis of residual amounts of pesticides in peach production down or below MRLs. The analysed peach lots (33 samples) intended for placing on the market were safe and met all requirements concerning pesticide content as rather low residue levels of pesticides after application of plant protection products were found – from 0.01 to 0.085 mg kg^{-1}.

Acknowledgements

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