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Multiresidual gas chromatography-tandem mass spectrometry method for determination of plant protection product residues in jam and jams market survey

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Multiresidual gas chromatography-tandem mass spectrometry method for determination of plant protection product residues in jam and jams market survey

Abstract: A multiresidual method for determination of 40 active substances in jam was introduced and validated. Acetone, petroleum ether and dichloromethane were used for extraction and gas chromatograph coupled with tandem mass spectrometer for determination. A survey was conducted to test method in practice. 25 jam samples from stores were analysed. 14 of them contained pesticide residues (56 %). Active substances found in samples were fungicides: azoxystrobin, boscalid, cyprodinil, fenhexamid, fludioxonil, fluopyram, pyrimethanil, tebuconazole and one was insecticide: lambda-cyhalothrin.

Key words: jam, pesticide residues, GC-MS/MS, fungicides, insecticides

Multirezidualna metoda s plinsko kromatografijo sklopljeno s tandemsko masno spektrometrijo za določanje ostankov fitofarmacevtskih sredstev v marmeladi in tržna raziskava marmelad

Izvleček: Vpeljali in validirali smo multirezidualno metodo za določanje 40 aktivnih substanc v marmeladi. Za ekstrakcijo smo uporabljali aceton, petroleter in diklorometan, za določitev pa plinski kromatograf sklopljen s tandemskim masnim spektrometrom. Za testiranje metode v praksi smo izvedli raziskavo. Analizirali smo 25 vzorcev marmelade iz trgovin. 14 vzorcev je vsebovalo ostanke fitofarmacevtskih sredstev (56 %). V vzorcih smo določili fungicide: azoksistrobin, boskalid, ciprodinil, fenheksamid, fludioksonil, fluopiram, pirimetanil, tebukonazol in en insekticid: lambda-cihalotrin.

Ključne besede: marmelada, ostanki pesticidov, GC-MS/MS, fungicidi, insekticidi

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1 INTRODUCTION

Fruit is part of healthy daily diet. To produce it in quantities large enough for human population, farmers are using plant protection products (PPPs) during its growth. It was reported (Baša Česnik et al., 2011) that fruit in comparison to vegetables contained more active substances per sample (up to nine). In off-fruit season fruit is often consumed preserved as jam (Reichert et al., 2015, Castillo et al., 2019). Jam is a semi-solid food product, prepared by cooking sugar with fruits pulp, pectin, acid and other ingredients to a sensibly consistency (Awulachew, 2021). Preparation of jam includes processing steps such as washing and cooking (Li et al., 2021). During fruit processing pesticide residues are often degraded (Alister et al., 2018, Li et al., 2021, Munir et al., 2024). Nevertheless, processed products also in form of jam still contain pesticide residues (Reichert et al., 2015, Makni et al., 2023, EFSA, 2024). Therefore efficient, sensitive and selective analytical methods are required for determination of pesticide residues in jam.

Jam is classified as high sugar and low water content commodity (SANTE, 2021). Nowadays extraction procedure for jam described in literature is mainly QuEChERS (Quick Easy Cheap Effective Rugged and Safe) method, where acetonitrile is used as solvent (Valera-Tarifa et al., 2020; Li et al., 2021; Makni et al., 2023; Oliveira et al., 2024), but also non-solvent SPME (Solid Phase Micro Extraction) method is described (Castillo et al., 2019). Our laboratory used acetone method in past, to which dichloromethane and petroleum ether was added, so that active substances of a wide range of polarity were extracted (Baša Česnik and Gregorčič, 2003; Baša Česnik et al., 2006). This method was modernized by reducing solvents quantities four times (Baša Česnik, 2025) and using buffering similarly like in QuEChERS method.

For determination of active substances in jam: a) gas chromatograph coupled with flame ionization detector (GC-FID) (Castillo et al., 2019), b) gas chromatograph coupled with mass spectrometer (GC-MS) (Castillo et al., 2019, Oliveira et al., 2024), c) liquid chromatograph coupled with tandem mass spectrometer (LC-MS/MS) (Reichert et al., 2015, Valera-Tarifa et al., 2020, Li et al., 2021) and d) liquid chromatograph coupled with time of flight detector (LC-TOF) (Makni et al., 2023) were used. The most efficient, sensitive and selective analytical methods are the ones, where tandem mass spectrometers are used. Our laboratory used gas chromatograph coupled with tandem mass spectrometer (GC-MS/MS), which enabled unequivocal identification of substances sought on basis of compounds mass spectra and low limits of quantification (LOQs).

The aim of this paper is to present validation of GC-MS/MS multiresidual method for determination of 40 active substances in jam. Active substances were herbicides (eight), insecticides/acaricides (nine) and/or fungicides (23). They are or were authorized for use in Slovenia for at least last 3 years. The analytical method was applied in practice. 25 jam samples sampled in Slovenian stores were analysed. Results were compared with literature.

2 MATERIALS AND METHODS

2.1 MATERIAL

2.1.1 Chemicals

The certified pesticide standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany). For extraction procedure acetone - p.a. grade, dichloromethane – p.a. grade and petroleum ether – p.a. grade, were purchased from J.T.Baker (Deventer, Netherlands). Also acetone HPLC-grade, which was used for preparation of standards, was purchased from J.T.Baker (Deventer, Netherlands). All other chemicals used were obtained by Sigma-Aldrich (Steinheim, Germany). The water used was MilliQ deionised water.

2.1.2 Preparation of the solutions

Stock solutions of individual active substances were prepared in acetone. Concentration of each active substance was 625 μg ml^{-1}. From 40 stock solutions, three mixed solutions of all 40 active substances were prepared with a concentration of 5 μg ml^{-1}, 1 μg ml^{-1} and 0.1 μg ml^{-1}.

2.1.3 EXTRACTION PROCEDURE

To 20 g of sample in the beaker, 30 ml of acetone: dichloromethane: petroleum ether = 1 (v): 2 (v): 2 (v) and 2 g anhydrous CH_3COONa and 0.4 ml 100 % acetic acid was added. The mixture was homogenized for two minutes with a mixer. 10 g of anhydrous Na_2SO_4 was added. The mixture was homogenized for two minutes with a mixer again. The whole content was filtered through filter paper black ribbon, which contained 20 g of anhydrous Na_2SO_4, into a 500 ml Soxhlet flask. Matrix was returned to the same beaker, 30 ml of acetone: dichloromethane: petroleum ether = 1 (v): 2 (v): 2 (v) was added, mixture was homogenized for two minutes with a mixer and afterwards filtered through the same filter paper as previously. Last step was repeated twice. Then solvent solution in Soxhlet flask was evaporated to approximately 2 ml on

Table 1: Active substances sought, their activity type, MRM transitions, dwell time and collision energy

Active substance	Activity type[a]	MRM transitions (Q1, Q2, Q3)[b]	Dwell (ms)	CE (V)[c]
8-hydroxyquinoline	F	145→117.1,145→89,117→90	77.5	10, 40, 10
azoxystrobin	F	344→329.1,344→171.9,344→155.8	40	10, 40, 40
benthiavalicarb-isopropyl	F	181→180,181→126.9,181→83.1	20.3, 17.6	20, 40, 40
boscalid	F	140→112,140→76,	45.7	10, 30
clomazone	H	204→107,125→99,	87.2	20, 20
cyflufenamid	F	412→118.1,412→89.9,118→90.1,118→63	8.2, 8.6	30, 40, 10, 40
cypermethrin	A, I	181→152.1,181→126.9,181→76.9	24.2, 19.7, 19.1, 22.1	30, 40, 40
cyprodinil	F	225→223.7,224→208.1,	17.3	20, 20
deltamethrin	I	253→171.9,253→93.1,253→77	26.9	10, 20, 40
fenhexamid	F	301→176.9,301→97,301→54.8	13.5	10, 10, 40
flonicamid	I	174→146,174→126,174→69	77.6	10, 20, 40
fluazifop-p-butyl	H	383→282.1,254→146,	8.2	10, 20
fludioxonil	F	248→182.1,248→154.1,248→127.1	9.7	10, 20, 30
flufenacet	H	151→136.1,151→95.1,	30.2	10, 30
fluopicolide	F	347→172,209→182,173→145	14.5	30, 20, 10
fluopyram	F	173→145,173→95.1,	15.3	20, 30
flutolanil	F	172.8→145,172.8→95,172.8→75	12.6	15, 35, 55
indoxacarb	I	264→176,264→147.9,264→112.9	23.7	10, 30, 40
iprovalicarb	F	158→98,158→72.1,158→55.1	8.6, 8.1	10, 10, 20
kresoxim-methyl	F	206→131.1,206→116.1,	12.7	10, 10
lambda-cyhalothrin	I	181→152.1,181→127.1,181→77.1	18.6, 17.6	20, 30, 40
metazachlor	H	209→132.1,209→117.1,133→131.7	14	20, 40, 20
metrafenone	F	408→393,393→378,379→364	29.9	10, 10, 10
metribuzin	H	198→82.1,198→55.1,	29.9	20, 40
myclobutanil	F	179→125,179→90,179→63	8.6	10, 40, 40
napropamide	H	271→72,128→100.1,128→72.1	17.7	20, 10, 10
penconazole	F	248→206.1,248→192.1,248→157.1	12.7	10, 10, 30
pendimethalin	H	252→191.1,252→162.1,252→106.1	12.2	10, 10, 40
pirimicarb	I	238→166.1,166→96.1,	33.4	10, 10
proquinazid	F	288→245,288→217,272→216	13.5	10, 30, 20
prosulfocarb	H	251→128.1,162→91.1,162→65	32.5	10, 10, 40
pyraclostrobin	F	164→132.1,164→104,132→104	34.1	10, 30, 10
pyrimethanil	F	198→183.1,198→118,	63.4	20, 40
pyriproxyfen	I	226→186.1,226→77.1,	21.1	10, 40
spiroxamine	F	100→72.1,100→58.1,	29.9, 38.9	10, 10
tebuconazole	F	250→153,250→125,250→70	10.2	10, 30, 10
tebufenpyrad	A	335→319.9,333→318.2,333→276.1	21.3	10, 10, 10
tefluthrin	I	177→137,177→127,177→87.1	36.6	20, 20, 40
tetraconazole	F	336→218.1,336→164,	24.7	20, 30
trifloxystrobin	F	222→162.1,222→130,131→116	11.1	10, 10, 20

[a] A = acaricide, I = insecticide, F = fungicide, H = herbicide
[b] Q = qualifier ion
[c] CE = collision energy

a rotavapor and dried with nitrogen flow. The dry eluate was dissolved in 2 ml of acetone for HPLC using ultrasound in order to prepare a sample. Extract was filtered with 0.2 µm pore size filter.

The extraction procedure is very similar to the one for vegetables (Baša Česnik and Velikonja Bolta, 2024). The only difference is that samples were buffered similarly like in QuEChERS method (Lehotay and Maštovska, 2005). Buffering resulted in larger peak areas for 4-40 % for 90 % of active substances. Also metribuzin and spiroxamine gave 40 % higher recoveries. The same extraction procedure was used for fruit (Baša Česnik, 2025).

2.2 DETERMINATION

The samples were analysed using a gas chromatograph (Agilent Technologies 8890, Shanghai, China) coupled with tandem mass spectrometer (Agilent Technologies 7010B, Santa Clara, USA), equipped with a Gerstel 20PRE0795 multipurpose sampler (Gerstel, Sursee, Switzerland) and a OV-5MS-SIL Ultra Inert column (Ohio Valley Specialty Company, 30 m, 0.25 mm i.d., 0.25 µm film thickness) with a constant flow of helium at 1.2 ml min^{-1}. The GC oven was programmed as follows: 55 °C for 2 min, from 55 °C to 100 °C at 20 °C min^{-1}, from 100 °C to 280 °C at 4 °C min^{-1}, held at 280 °C for 19.75 min. The temperature of the ion source was 230 °C, the auxiliary temperature was 280 °C and the quadrupoles temperature was 150 °C. For qualitative and quantitative determination, the MRM transitions were used presented in Table 1. For each active substance two to four transitions were scanned. For calibration matrix match standards were used.

Spectrometric parameters for 29 active substances in modernised fruit method (Baša Česnik, 2025) are the same as for the same active substances in jam. Other active substances have different mass transitions, dwell times and collision energies. For sake of completeness they are all presented in Table 1.

2.3 VALIDATION OF METHODS

LOQ and linearity

Limit of quantification (LOQ) and linearity were checked using matrix match standards. For LOQs the minimum S/N ratio had to be 10. For linearity two repetitions for one concentration level, five to eight concentration levels for the calibration curve were analysed. Then F test was used to check linear regression (linearity and range).

Uncertainty

Organically produced peach jam was bought in store and analysed. It contained no pesticide residues sought. For the determination of precision (ISO, 2019), i.e. repeatability and reproducibility, the extracts of spiked blank peach jam at LOQ were analysed. Within a period of 10 days, two parallel extracts were prepared and analysed each day. Then the standard deviation of the repeatability and the standard deviation of reproducibility were both calculated. The uncertainty of repeatability and the uncertainty of reproducibility were calculated by multiplying the standard deviation of repeatability and the standard deviation of reproducibility by the Student's t factor, for nine degrees of freedom and a 95 % confidence level ($t_{95;9} = 2.262$).

$U_r = t_{95;9} \times s_r$; $U_R = t_{95;9} \times s_R$

In SANTE (2021) it is proposed that the measurement uncertainty for PPP residues should be 50 %. Analysts must prove during validation that their measurement uncertainty is below or equal to the proposed measurement uncertainty.

Accuracy

Accuracy was verified by checking the recoveries at LOQ. Average recoveries and RSDs were calculated from analysed extracts used for determination of precision (20 measurements per active substance). According to SANTE (2021) acceptable mean recoveries are those within the range of 70 % to 120 %, with an associated repeatability of RSD ≤ 20 %. According to Alder et al. (2000) acceptable mean recoveries at level > 0.001 mg kg^{-1} and ≤ 0.01 mg kg^{-1} are those within the range of 60 % to 120 %, with an associated repeatability RSD ≤ 30 %. The same requirement as set by Alder et al. (2000) is set in SANTE (2020).

2.4 SAMPLING

25 jam samples were collected in Slovenian stores in November 2024. The sampling distribution is presented in Table 2. No sample was labelled as ecologically produced.

2.5 RISK ASSESSMENT

Long-term (chronic) and short-term (acute) risk assessment for consumer was calculated using Supervised Trial Median Residues (STMRs) and Highest Residues (HRs), respectively. Calculated exposure was compared

Table 2: Jam samples collected from stores in Slovenia in 2024

No. of sample	Description	Produced in
1	strawberry	Austria
2	strawberry	Serbia
3	strawberry	Italy
4	strawberry	Slovenia
5	strawberry	France
6	strawberry	Austria
7	appricot	Austria
8	appricot	Croatia
9	appricot	Slovenia
10	appricot	Italy
11	appricot	Serbia
12	raspberry	Slovenia
13	raspberry	Serbia
14	raspberry	Austria
15	raspberry	Austria
16	blueberry	Italy
17	blueberry	Slovenia
18	blueberry	Serbia
19	peach	Italy
20	cherry	Italy
21	sour cherry	Slovenia
22	mandarin	Italy
23	orange	Serbia
24	plum	Italy
25	plum	Serbia

with Acceptable Daily Intake (ADI) for long-term exposure and with Acute Reference Dose (ARfD) for short-term exposure with EFSA PRIMo model Rev. 3.1. Acceptable exposures are the ones < 100 % of ADI and/or < 100 % of ARfD.

3 RESULTS AND DISCUSSION

3.1 COMPARISON OF METHOD TO ALREADY ESTABLISHED ONES

Previous methods (Baša Česnik and Gregorčič, 2003; Baša Česnik et al., 2006) for determination of pesticide residues in various matrices in our laboratory, used the same mixture of organic solvents for extraction as present method, but in approximately 4-times larger quantities. With this method extraction step with the separatory funnels was omitted, meaning that the method is physically less demanding and less time consuming. With the QuEChERS method, the development of methods for determination of pesticide residues almost stopped, meaning that majority is using acetonitrile as extraction solvent. This method proves opposite – usage of other solvents can be very applicable for the purpose. Selection of GC-MS/MS for scanning of extracts, beside unequivocal identification, means also better sensitivity and selectivity that was achieved with the gas chromatograph coupled with mass spectrometer (GC-MS) in the past. On the other hand selection of active substances is very different as in the past. Focus on presently authorised active substances modernized the method to be suitable for nowadays monitoring of pesticide residues. The method is robust and can be used also for vegetables and fruit. Present method enables determination of 40 active substances which is more as modernised method for fruit with 29 active substances (Baša Česnik, 2025) or modernised method for vegetables with 35 active substances (Baša Česnik and Velikonja Bolta, 2024).

3.2 VALIDATION OF METHOD

3.2.1 LOQ and linearity

For all 40 substances LOQ was 0.005 mg kg^{-1}. For 27 active substances linearity ranged from 0.005–0.035 mg kg^{-1}, for one active substance it ranged from 0.005–0.045 mg kg^{-1} and for 12 active substances it ranged from 0.005–0.05 mg kg^{-1}. R^2 ranged from 0.958 to 0.995. Results are presented in Table 3.

3.2.2 Uncertainty

Uncertainty of repeatability and uncertainty of reproducibility were calculated at LOQ.

Uncertainty of repeatability ranged from 0.0005 to 0.0014 mg kg^{-1} and/or from 9.9 to 27.8 %. Uncertainty of reproducibility ranged from 0.0012 to 0.0020 mg kg^{-1} and/or from 23.3 to 40.3 %.

All uncertainties were <50 % as required by SANTE (2021). Results are presented in Table 3.

3.2.3 Accuracy

Recoveries at LOQ were 90.0 to 103.3 % with RSD 10.5 to 17.2 %. All recoveries are in accordance with all three guidelines (Alder et al., 2000; SANTE, 2020; SANTE, 2021). Results are presented in Table 3.

Table 3: Validation parameters for jam

Active substance	Linearity range (mg kg^{-1})	R^2	LOQ (mg kg^{-1})	Recovery (%)	RSD[a] (%)	U_r[b] (mg kg^{-1})	U_r[c] (%)	U_R[d] (mg kg^{-1})	U_R[e] (%)
8-hydroxyquinoline	0.005-0.035	0.958	0.005	99.9	14.4	0.0006	12.3	0.0007	14.5
azoxystrobin	0.005-0.05	0.986	0.005	97.2	14.0	0.0002	4.4	0.0007	14.0
benthiavalicarb-iso-propyl	0.005-0.05	0.995	0.005	100.0	10.8	0.0003	5.4	0.0005	11.0
boscalid	0.005-0.05	0.992	0.005	99.0	12.1	0.0002	4.7	0.0006	12.3
clomazone	0.005-0.035	0.971	0.005	98.1	11.8	0.0003	6.6	0.0006	11.8
cyflufenamid	0.005-0.035	0.984	0.005	96.1	14.5	0.0004	8.5	0.0007	14.2
cypermethrin	0.005-0.05	0.986	0.005	98.4	11.1	0.0003	5.6	0.0006	11.2
cyprodinil	0.005-0.035	0.977	0.005	99.3	12.4	0.0004	7.2	0.0006	12.5
deltamethrin	0.005-0.05	0.988	0.005	97.8	12.0	0.0003	5.4	0.0006	12.0
fenhexamid	0.005-0.05	0.98	0.005	101.7	17.2	0.0004	8.4	0.0009	17.8
flonicamid	0.005-0.035	0.978	0.005	98.6	12.0	0.0003	7.0	0.0006	12.0
fluazifop-p-butyl	0.005-0.035	0.983	0.005	99.5	13.0	0.0004	7.1	0.0007	13.2
fludioxonil	0.005-0.05	0.982	0.005	98.7	15.1	0.0004	7.1	0.0008	15.2
flufenacet	0.005-0.045	0.979	0.005	100.4	14.3	0.0005	9.4	0.0007	14.6
fluopicolide	0.005-0.035	0.980	0.005	97.1	10.9	0.0003	6.4	0.0005	10.7
fluopyram	0.005-0.035	0.984	0.005	99.7	12.1	0.0004	8.1	0.0006	12.2
flutolanil	0.005-0.035	0.984	0.005	99.4	14.8	0.0004	8.3	0.0008	15.0
indoxacarb	0.005-0.05	0.987	0.005	99.8	13.8	0.0004	8.1	0.0007	14.0
iprovalicarb	0.005-0.035	0.976	0.005	100.2	15.4	0.0005	9.1	0.0008	15.7
kresoxim-methyl	0.005-0.035	0.984	0.005	97.3	12.4	0.0004	7.9	0.0006	12.3
lambda-cyhalothrin	0.005-0.035	0.976	0.005	98.0	11.5	0.0003	6.2	0.0006	11.5
metazachlor	0.005-0.035	0.975	0.005	97.9	11.7	0.0004	7.1	0.0006	11.7
metrafenone	0.005-0.035	0.974	0.005	99.1	11.3	0.0003	5.3	0.0006	11.5
metribuzin	0.005-0.035	0.973	0.005	90.0	15.5	0.0005	11.0	0.0007	14.1
myclobutanil	0.005-0.035	0.979	0.005	97.8	12.0	0.0004	7.1	0.0006	11.9
napropamide	0.005-0.035	0.981	0.005	99.0	12.4	0.0004	7.5	0.0006	12.5
penconazole	0.005-0.035	0.980	0.005	99.3	11.4	0.0003	6.8	0.0006	11.5
pendimethalin	0.005-0.035	0.979	0.005	97.3	12.8	0.0005	9.4	0.0006	12.6
pirimicarb	0.005-0.035	0.977	0.005	99.4	12.3	0.0003	6.9	0.0006	12.4
proquinazid	0.005-0.035	0.979	0.005	97.5	11.3	0.0003	6.0	0.0006	11.2
prosulfocarb	0.005-0.035	0.978	0.005	99.5	12.1	0.0003	6.9	0.0006	12.3
pyraclostrobin	0.005-0.05	0.971	0.005	103.3	14.7	0.0003	5.1	0.0008	15.5
pyrimethanil	0.005-0.035	0.975	0.005	98.6	11.6	0.0004	7.3	0.0006	11.6
pyriproxyfen	0.005-0.05	0.994	0.005	98.5	12.6	0.0003	6.5	0.0006	12.6
spiroxamine	0.005-0.035	0.978	0.005	97.9	12.2	0.0004	7.7	0.0006	12.1

tebuconazole	0.005-0.05	0.993	0.005	97.6	11.5	0.0003	5.5	0.0006	11.5
tebufenpyrad	0.005-0.05	0.992	0.005	98.0	10.8	0.0003	6.0	0.0005	10.8
tefluthrin	0.005-0.035	0.977	0.005	99.0	11.7	0.0003	6.9	0.0006	11.8
tetraconazole	0.005-0.035	0.979	0.005	98.6	11.9	0.0004	7.7	0.0006	11.9
trifloxystrobin	0.005-0.035	0.983	0.005	96.0	10.5	0.0003	6.2	0.0005	10.3

[a] RSD was obtained during recovery analyses
[b,c] U_r = uncertainty of repeatability
[d,e] U_R = uncertainty of reproducibility

3.3 SURVEY OF PESTICIDE RESIDUES IN JAM SAMPLES

14 samples of 25 analysed (56.0 %) contained pesticide residues. 11 samples of 25 analysed (44.0 %) were pesticides free. Pesticide residues were found in strawberry, apricot, raspberry, cherry, sour-cherry and orange jam. Residues content was 0.005 to 0.031 mg kg^{-1}. Blueberry, peach, mandarin and plum jam contained no ac-

Table 4: Contents (mg kg^{-1}) of pesticide residues found in strawberry jam

Active substance / No of sample	boscalid	cyprodinil	fenhexamid	fludioxonil	fluopyram	pyrimethanil
sample no. 2			0.021			0.007
sample no. 3	0.005					
sample no. 4		0.009		0.006		
sample no. 6		0.009		0.005	0.005	

Table 5: Contents (mg kg^{-1}) of pesticide residues found in apricot jam

Active substance / No of sample	boscalid	fluopyram	pyrimethanil
sample no. 7			0.010
sample no. 8	0.005	0.009	
sample no. 9	0.017	0.008	
sample no. 11	0.031		

Table 6: Contents (mg kg^{-1}) of pesticide residues found in raspberry jam

Active substance / No of sample	azoxystrobin	boscalid	cyprodinil	fenhexamid	fludioxonil	pyrimethanil
sample no. 12	0.015	0.012	0.006	0.015		0.017
sample no. 13		0.014	0.013		0.011	
sample no. 15		0.012			0.005	0.015

Table 7: Contents (mg kg^{-1}) of pesticide residues found in cherry, sour-cherry and orange jam

Active substance / No of sample	fludioxonil	lambda-cyhalothrin	pyrimethanil	tebuconazole
Sample no. 20: cherry	0.005			
Sample no. 21: sour cherry		0.021		0.018
Sample no. 23: orange			0.006	

tive substances sought. Results are presented in Tables 4-7.

The highest number of active substances (six) was found in strawberry and raspberry samples. The highest number of active substances per sample was found in one raspberry jam, which contained five active substances sought.

Nine active substances were found in all 25 samples. Eight of them were fungicides: azoxystrobin, boscalid, cyprodinil, fenhexamid, fludioxonil, fluopyram, pyrimethanil, tebuconazole and one was insecticide: lambda-cyhalothrin. The most frequently found was boscalid in seven samples. All active substances found are authorised in EU.

In jam like in other processed fruit, no Maximum Residue Levels (MRLs) are set like for fruit. Therefore re-

Table 8: Contents (mg kg^{-1}) of pesticide residues calculated in strawberry and MRLs for strawberry

Active substance / No of sample	boscalid	cyprodinil	fenhexamid	fludioxonil	fluopyram	pyrimethanil
sample no. 2			0.039			0.012
sample no. 3	0.022					
sample no. 4		0.037		0.043		
sample no. 6		0.023		0.024	0.011	
MRL	6	5	10	4	2	5

Table 9: Contents (mg kg^{-1}) of pesticide residues calculated in apricot and MRLs for apricot

Active substance / No of sample	boscalid	fluopyram	pyrimethanil
sample no. 7			0.014
sample no. 8	0.026	0.039	
sample no. 9	0.176	0.066	
sample no. 11	0.107		
MRL	5	1.5	10

Table 10: Contents (mg kg^{-1}) of pesticide residues calculated in raspberry and MRLs for raspberry

Active substance / No of sample	azoxystrobin	boscalid	cyprodinil	fenhexamid	fludioxonil	pyrimethanil
sample no. 12	0.035	0.028	0.011	0.015		0.017
sample no. 13		0.054	0.044		0.063	
sample no. 15		0.039			0.020	0.021
MRL	5	10	3	15	5	15

Table 11: Contents (mg kg^{-1}) of pesticide residues calculated in cherry, sour-cherry and orange and MRLs for cherry, sour-cherry and orange

Active substance / No of sample	fludioxonil	lambda-cyhalothrin	pyrimethanil	tebuconazole
Sample no. 20: cherry	0.030			
MRL (cherry)	5	0.3		1
Sample no. 21: sour cherry		0.163		0.091
Sample no. 23: orange			0.009	
MRL (orange)			8	

calculation was conducted from residues in jam, using fruit portion in jam and processing factors for the active substances during jam preparation, to calculate residues in fruit. Processing factors for jam are available in EU database (https://zenodo.org/record/1488653#.YHBgL44z-ZaQ). For fenhexamid and pyrimethanil no processing factors were available, therefore processing factor of 1 was used in calculations. Calculated residue content in fruit was 0.009 to 0.176 mg kg^{-1}. Results of residues in fruit with valid MRLs are presented in Tables 8-11.

No active substance had calculated residues in fruit above valid MRLs. Nevertheless, risk assessment was conducted. EFSA PRIMo model, used also during authorisation of plant protection products and active substances in EU and Slovenia, does not have residues in jam included as possible inputs. Therefore risk assessment was conducted only with calculated residues for fruit. Calculated STMRs and HRs used as input values are presented in Table 12. ADI, ARfD values along with calculated exposure are presented in Table 13. Theoretical Maximum Daily Intake (TMDI) ranged from 0.003 to 2 % of ADI. International Estimated Short Term Intake (IESTI) ranged from 0.2 to 40 % of ARfD. The highest exposure was observed for lambda-cyhalothrin, the most

Table 12: STMRs and HRs (mg kg^{-1}) for active substances found in different jams

	raspberry							
	STMR	HR						
Azoxystrobin	0.035	0.035						
	appricot		raspberry		strawberry			
	STMR	HR	STMR	HR	STMR	HR		
Boscalid	0.107	0.176	0.039	0.054	0.022	0.022		
	raspberry		strawberry					
	STMR	HR	STMR	HR				
Cyprodinil	0.028	0.044	0.030	0.037				
	raspberry		strawberry					
	STMR	HR	STMR	HR				
Fenhexamid	0.015	0.015	0.039	0.039				
	cherry		raspberry		strawberry			
	STMR	HR	STMR	HR	STMR	HR		
Fludioxonil	0.030	0.030	0.042	0.063	0.034	0.043		
	appricot		strawberry					
	STMR	HR	STMR	HR				
Fluopyram	0.053	0.066	0.011	0.011				
	cherry							
	STMR	HR						
Lambda-cyhalothrin	0.163	0.163						
	appricot		orange		raspberry		strawberry	
	STMR	HR	STMR	HR	STMR	HR	STMR	HR
Pyrimethanil	0.014	0.014	0.009	0.009	0.019	0.021	0.012	0.012
	cherry							
	STMR	HR						
Tebuconazole	0.091	0.091						

STMR = Supervised Trial Median Residue
HR = highest residue

Table 13: ADIs (mg kg^{-1} bw day^{-1}), ARfDs (mg kg^{-1} bw) and chronic (TMDI) and acute (IESTI) exposure of consumers for active substances found in jam

	ADI	ARfD	TMDI (% ADI)	IESTI(% ARfD)
Azoxystrobin	0.2	/	0.003	0.2
Boscalid	0.04	/	0.1	15
Cyprodinil	0.03	/	0.06	2
Fenhexamid	0.2	/	0.01	0.3
Fludioxonil	0.37	/	0.008	0.2
Fluopyram	0.012	0.5	0.2	0.5
Lambda-cyhalothrin	0.0025	0.005	2	40
Pyrimethanil	0.17	/	0.03	0.7
Tebuconazole	0.03	0.03	0.1	4

ARfD = Acute Reference Dose
TMDI = Theoretical Maximum Daily Intake
IESTI = International Estimated Short Term Intake
ADI = Acceptable daily intake

toxic active compound found in jam. Nevertheless short- and long- term exposure were acceptable for consumers.

Among active substances sought by our laboratory, Makni et al. (2023) found azoxystrobin, cyprodinil, fludioxonil, fluopyram, penconazole, pyrimethanil, tetraconazole and trifloxystrobin in strawberry jam; cyprodinil and fludioxonil in apricot jam; azoxystrobin, boscalid, cyprodinil, fenhexamid, fludioxonil and trifloxystrobin in raspberry jam; fluopyram and tebuconazole in cherry jam. Contents of active substances ranged from 0.001 to 0.066 mg kg^{-1} (Makni et al., 2023). Reichert et al. (2015) found among active substances sought by our laboratory: azoxystrobin, boscalid, fenhexamid, kresoxim-methyl, myclobutanil, penconazole, pyrimethanil and tebuconazole in strawberry jam; myclobutanil and tebuconazole in apricot jam; tebuconazole in peach jam. Contents ranged from 0.01 to 0.033 mg kg^{-1} (Reichert et al., 2015). All active substances found by our laboratory, except lambda-cyhalothrin, were found by Reichert et al. (2015) and/or Makni et al. (2023). The reason is probably that these authors did not analyse lambda-cyhalothrin in their samples. The highest concentration determined by Makni et al. (2023) is approximately twice higher as maximum content found by our laboratory. On contrary the highest content found by Reichert et al. (2015) is approximately as high as the one found by our laboratory.

4 CONCLUSIONS

Multiresidual method for determination of pesticide residues in jam was introduced and validated on blank peach matrix. The method is suitable for determination of 40 active substances. The LOQ for all active substances was 0.005 mg kg^{-1}. Calibration curves gave linear responses with R^2 0.958 to 0.995. Recoveries ranged from 90.0 to 103.3 % with RSD 10.5–17.2 % at LOQ. Uncertainties of repeatability ranged from 9.9 to 27.8 % and uncertainties of reproducibility ranged from 23.3 to 40.3 % at LOQ. The method is in accordance with valid guidelines (Alder et al., 2000; SANTE, 2020; SANTE, 2021).

25 jam samples from Slovenian stores were analyzed with this method. Nine active substances were found in jam: azoxystrobin, boscalid, cyprodinil, fenhexamid, fludioxonil, fluopyram, lambda-cyhalothrin, pyrimethanil and tebuconazole. Their content range was 0.005 to 0.031 mg kg^{-1}.

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The author declares that all original research data are contained in the article.

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