Journal of Chromatography B 1060 (2017) 281–290

Contents lists available at ScienceDirect

Journal of Chromatography B

journal homepage: www.elsevier.com/locate/jchromb

The optimization and establishment of QuEChERS-UPLC–MS/MS method for simultaneously detecting various kinds of pesticides residues in fruits and vegetables

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ARTICLE INFO

Keywords:
Ultra-high performance liquid chromatography-tandem mass spectrometric (UPLC–MS/MS)
Fruit
Vegetable
Pesticide residue

ABSTRACT

Objectives: The quality safety supervision and test of agricultural products urgently need a very excellent analytical method with simultaneously detecting many components in order to assess, prevent and control pesticide residues.

Methods: In this research, three fruits and three vegetables produced in Shanghai were selected as the materials, 54 pesticide residues were detected with the ultra-high performance liquid chromatography-tandem mass spectrometric (UPLC–MS/MS) method on the basis of optimized QuEChERS method according to different materials properties.

Results: The results showed that: all samples were directly extracted by acetonitrile containing 1% (v/v) acetic acid; complex matrix samples were purified by a mixed sorbent of 300 mg $MgSO_4$ + 100 mg PSA + 100 mg C18 + 0.01 g Carb, general matrix samples didn't add Carb, simple matrix samples such as watermelon directly filmed; Chromatographic column was ZORBAX Eclipse Plus-C18 column (3.0 mm × 150 mm, 3.5 μm) at 40 °C, the methanol-water of mobile phase at a flow rate of 0.45 mL/min by a gradient elution contained 0.1% formic acid and 5 mmol/L ammonium acetate and the injection volume was 1 μL. With switching electrospray ion source polarity, $[M-H]^-$ and high sensitive $[M+Na]^+$ were respectively the precursor ions of eight pesticides and avermectin, $[M+H]^+$ was those of the else 45 pesticides. The detection parameters of multi-reactions monitoring (MRM) with simultaneously positive and negative ions (electron multiplier voltage was 200 V) scanning were set as follows: the 310.3 kPa of nebulizer pressure, the 300 °C of drying gas temperature, the 7 L/min of drying gas flow, the 3000 V and 3500 V of respectively capillary positive and negative voltage. With the optimized method, the calibration curves of 54 pesticides were better linear in 15–500 μg/kg ($r \geq 0.988$), the average adding standard recovery rates of 54 pesticides were 73.2%–134.3% except pymetrozine and cyromazine with the relative standard deviations (RSD) of 1.0%–13.8%; the limit of detection (LOD) under three times signal-to-noise ratio (S/N) and limit of quantitative (LOQ) under 10 times S/N were respectively confirmed 0.003–2.000 μg/kg and 0.01–6.67 μg/kg.

Conclusions: The results demonstrated that the optimized "QuEChERS-UPLC–MS/MS method" was a simple, rapid, sensitive, accurate, efficient, economical and safe method that simultaneously detected multiple pesticide residues through one time sample treatment; It had some advantages such as more pesticides per detection, simple and convenient pretreatment and less solvent dosage to be suitable for the quick high-throughput quantitative screening and confirmation of pesticide residues in fruits and vegetables.

1. Introduction

The yearly resident consumption rate of fresh fruits and vegetables in China was more than 90% and ranked the first in the world [1]. Excessive pesticides uses or banned and severely restricted pesticides uses are happened occasionally when planters prevent insects or diseases and increase yields [2]. Illegal pesticides uses not only cause residues over the standards and but also pollute and destroy the environment, which seriously affect survival and health of plants, animals and humans [3]. In recent years, widely use, high detection rate or recessive existence of pesticides are mainly high toxic carbamate pesticides, high efficient and low toxic pesticides, the alternate use of old

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http://dx.doi.org/10.1016/j.jchromb.2017.06.008
Received 25 April 2017; Received in revised form 26 May 2017; Accepted 4 June 2017
Available online 10 June 2017
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Table 1
The qualitative and quantitative ions (*m/z*) of fifty- four pesticides.

Analyte	Precursor ion	Product ion	Analyte	Precursor ion	Product ion
Aldicarb_sulfoxide	207.0	(+)132.0; (+)89.0*	Avermectin	895.4	(+)751.5; (+)449.2*
Aldicarb_sulfone	223.0	(+)148.0; (+)86.0*	Spinosad D	746.5	(+)142.1; (+)98.0
Carbendazim	192.1	(+)160.0*; (+)132.1	Spinosad A	732.5	(+)142.1; (+)98.0
Methomyl	163.0	(+)106.0; (+)88.0*	Flubendiamide	681.0	(−)272.0; (−)254.0
Hiamethoxam	292.0	(+)211.0*; (+)181.0	Chlorfluazuron	540.0	(+)383.0; (+)158.0
Imidacloprid	256.1	(+)209.0*; (+)175.0	Thifluzamide	524.8	(−)166.0; (−)125.0
Chlorantraniloprole	484.0	(+)453.0*; (+)286.0	Lufenuron	511.0	(+)158.0; (+)141.0
Acetamiprid	223.1	(+)126.0*; (+)56.0	Cyantraniliprole	470.9	(−)202.0; (−)145.0
Aldicarb	208.0	(+)116.0*; (+)89.0	Spirodiclofen	411.0	(+)313.0; (+)71.2
Carbofuran	222.1	(+)165.0*; (+)123.0	Prochloraz	376.0	(+)308.0; (+)266.0
Thidiazuron	219.0	(−)100.0*; (−)72.0	Propargite	368.1	(+)231.1; (+)175.1
Forchlorfenuron	246.1	(−)127.0*; (−)91.2	Picoxystrobin	368.1	(+)205.0; (+)145.0
Carbofuran-3-hydroxy	238.2	(+)135.1; (+)107.2*	Thiophanate methyl	343	(+)151.0; (+)93.0
Pyrimethanil	200.1	(+)183.0; (+)107.0*	Flusilazole	316.1	(+)247.0; (+)165.0
Mandipropamid	412.1	(+)356.0; (+)328.0*	Kresoxim-methyl	314.1	(+)267.0; (+)206.0
Boscalid	343.0	(+)307.0*; (+)271.0	Azoxystrobin	404.1	(+)372.0; (+)344.0
Fluopicolide	382.9	(+)364.8; (+)172.9*	Methoxyfenozide	313.0	(+)149.0; (+)91.0
Dimethomorph	388.1	(+)301.0*; (+)165.0	Bifenazate	301.0	(+)198.0; (+)170.0
Fipronil	434.9	(−)330.0*; (−)250.0	Metalaxyl	280.2	(+)220.0; (+)192.0
Diflubenzuron	311	(+)158.0*; (+)141.0	Nitenpyram	271.0	(+)99.2; (+)56.3
Emamectin benzoate	886.2	(+)158.2*; (+)126.1	Flonicamid	230.0	(+)203.0; (+)174.0
Chlorobenzuron	307.0	(−)126.0; (−)154.1*	Cyprodinil	226.1	(+)108.0; (+)93.0
Phoxim	299.1	(+)129.0*; (+)77.0	Pymetrozine	218.3	(+)105.2; (+)79.0
Pyraclostrobin	388.1	(+)194.0*; (+)163.0	Carbaryl	202.0	(+)145.0; (+)117.0
indoxacarb	528.0	(+)249.0; (+)218.0*	Cymoxanil	199.1	(+)128.0; (+)111.0
Difenoconazole	406.1	(+)337.0; (+)251.0*	Cyromazine	167.1	(+)125.0; (+)85.0
Pyridaben	365.1	(+)309.0*; (+)147.0	Metaflumizone	505.2	(−)302.0; (−)285.0

Note: * stands for quantification ion.

Table 2
The collision energies (CE) and fragment voltages of fifty- four pesticides.

Analyte	CE(eV)	Fragment (V)	Analyte	CE(eV)	Fragment (V)
Aldicarb_sulfoxide	5; 10	70	Avermectin	42; 54	200
Aldicarb_sulfone	5; 10	70	Spinosad D	35; 55	140
Carbendazim	20; 25	90	Spinosad A	35; 55	140
Methomyl	5; 5	80	Flubendiamide	30; 25	155
Hiamethoxam	12; 20	80	Chlorfluazuron	15; 15	120
Imidacloprid	10; 10	80	Thifluzamide	25; 35	130
Carbofuran-3-hydroxy	20; 30	60	Lufenuron	10; 20	80
Acetamiprid	15; 15	80	Cyantraniliprole	15; 15	120
Aldicarb	5; 10	70	Spirodiclofen	5; 15	110
Carbofuran	10; 20	120	Prochloraz	10; 10	80
Thidiazuron	5; 25	70	Propargite	10; 10	80
Forchlorfenuron	5; 20	80	Picoxystrobin	5; 20	80
Chlorantraniloprole	17; 23	120	Thiophanate methyl	20; 30	100
Pyrimethanil	25; 25	120	Flusilazole	15; 20	120
Mandipropamid	5; 11	120	Kresoxim-methyl	5; 5	80
Boscalid	12; 28	160	Azoxystrobin	10; 15	120
Fluopicolide	15; 20	120	Methoxyfenozide	5; 25	100
Dimethomorph	20; 25	120	Bifenazate	5; 20	80
Fipronil	15; 30	120	Metalaxyl	10; 15	120
Diflubenzuron	10; 15	80	Nitenpyram	20; 30	80
Emamectin benzoate	40; 50	200	Flonicamid	15; 15	70
Chlorobenzuron	24; 11	100	Cyprodinil	30; 40	120
Phoxim	10; 20	80	Pymetrozine	23; 23	80
Pyraclostrobin	10; 20	120	Carbaryl	5; 10	80
indoxacarb	15; 20	120	Cymoxanil	5; 15	80
Difenoconazole	15; 20	160	Cyromazine	20; 25	120
Pyridaben	10; 20	80	Metaflumizone	15; 45	135

and new fungicides and plant growth regulators [4]. So many countries and regions have formulated the strict limits standards of pesticide residues, “National food safety standard-maximum residue limits for pesticides in food (GB 2763 - 2014)” in China ruled 3650 detection items of the maximum pesticide residue limits [5]. The amounts of pesticide residues in fruits and vegetables have become the important indicators of quality security, all countries in the world are increasingly seeking to develop a quick detection technology to effectively control more pesticide residues.

Pesticide residue analysis is an analytical technology of the trace components in complex mixture; it needs both fine trace operation and high sensitivity of trace detection method. Now, the sample pretreatment techniques of pesticide residue detection mainly include the traditional liquid–liquid extraction (LLE), solid phase extraction (SPE),

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