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Complete List of Authors:	Li, Honge; School of Chemistry and Chemical Engineering, Shandong University Wang, Chenchen; School of Chemistry and Chemical Engineering, Shandong University Zhu, Qian; Central Laboratory of Shandong Academy of Agricultural Sciences, Key Laboratory of Test Technology on Food Quality and Safety of Shandong Province, The Base of Public Service on Pesticide Residues of Shandong Province Du, Hongxia; Central Laboratory of Shandong Academy of Agricultural Sciences, Key Laboratory of Test Technology on Food Quality and Safety of Shandong Province, The Base of Public Service on Pesticide Residues of Shandong Province Guan, Shuai; Central Laboratory of Shandong Academy of Agricultural Sciences, Key Laboratory of Test Technology on Food Quality and Safety of Shandong Province, The Base of Public Service on Pesticide Residues of Shandong Province Wang, Fengen; Central Laboratory of Shandong Academy of Agricultural Sciences, Key Laboratory of Test Technology on Food Quality and Safety of Shandong Province, The Base of Public Service on Pesticide Residues of Shandong Province Zhang, Wenjun; Central Laboratory of Shandong Academy of Agricultural Sciences, Key Laboratory of Test Technology on Food Quality and Safety of Shandong Province, The Base of Public Service on Pesticide Residues of Shandong Province Fan, Wenjing; Central Laboratory of Shandong Academy of Agricultural Sciences, Key Laboratory of Test Technology on Food Quality and Safety of Shandong Province, The Base of Public Service on Pesticide Residues of Shandong Province Chen, Zilei; Central Laboratory of Shandong Academy of Agricultural Sciences, Key Laboratory of Test Technology on Food Quality and Safety of Shandong Province, The Base of Public Service on Pesticide Residues of Shandong Province Yang, Guosheng; Shandong University, Chemistry and Chemical Engineering Aboul-Enein, Hassan; National Research Centre, Egypt, Pharmaceutical and

	Medicinal Chemistry Department

Reduction of matrix effects through a simplified QuEChERS method and small injection volumes in a LC-MS/MS system for the determination of 28 pesticides in fruits and vegetables

Honge Li[a], Chenchen Wang[a], Qian Zhu[b], Hongxia Du[b], Shuai Guan[b], Fengen Wang[b], Wenjun Zhang[b], Wenjing Fan[b], Zilei Chen[b,*] Guosheng Yang[a,*], Hassan Y. Aboul-Enein[c]

[a] School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China

[b] Central Laboratory of Shandong Academy of Agricultural Sciences, Key Laboratory of Test Technology on Food Quality and Safety of Shandong Province, The Base of Public Service on Pesticide Residues of Shandong Province, Jinan 250100, People's Republic of China

[c] Pharmaceutical and Medicinal Chemistry Department, Pharmaceutical and Drug Industries Research Division, National Research Centre, Dokki, Giza 12622, Egypt

corresponding author:

Guosheng Yang: e-mail: gsyang@sdu.edu.cn

Tel.: +86-531-88364464

Fax: +86-531-88564464

Zilei Chen: e-mail: czl7274@163.com

ABSTRACT

A simplified QuEChERS method coupled with a small injection volume was developed for the simultaneous determination of 28 pesticides in 6 matrices (apple, cucumber, tomato, luffa, cabbage, and eggplant) using LC-MS/MS. The sample preparation consists of acetonitrile with 0.1% (v/v) formic acid extraction solvent and without any depurative powder was used. Three fortified levels (10, 50, and 100 μg kg^{-1}) were determined and recoveries of 168 analyte/matrix combinations were in the range of 60% to 120% except for cyromazin, pendimethalin, and fenpropathrin. Half of the 168 LOQs were below 0.1 μg kg^{-1}, and 29 LOQs were above 1 μg kg^{-1}. Moreover, Four relationships between signal suppression and injection volume was observed ranging from 0.5 μL to 15 μL. For many analyte/matrix combinations, the matrix effects could be reduced to less than 20% if the injection volume was less than a critical value (named critical volume). Critical volume depends on initial extent of matrix effects was explored and the conclusion was: for weak or medium MEs, usually ≤ 2 μL injection volume was needed and for several weak MEs, injection volume ≤ 5 μL can reduce matrix effect to negligible level.

1. Introduction

Liquid chromatography-tandem mass spectrometry (LC-MS/MS) and QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) sample preparation methods have been widely used in pesticide analysis for more than 10 years. This approach is fast and provides high sensitivity. However, it is well known that ion suppression is a critical limitation for quantitative analysis using LC-MS/MS.[1-3]

Matrix effect (ME) can be classified into two categories: suppress the response of the analyte and enhance the response. The latter case is hardly observed in LC-MS/MS systems, while ion suppression exists in nearly every analyte/matrix combination, and several mechanisms have been proposed to explain this phenomenon.[4-6] Once matrix components have coeluted with the analyte, competition may occur between the matrix and analyte during the electrospray process. The interferents not only compete for the limited amount of elementary charge (about 10^{-5} mol L^{-1}), but also for the surface of the droplet.[6] Moreover, matrix compounds also increase the viscosity of the droplet, thus preventing evaporation of the reagent and analyte from transferring to the surface for ionization. Finally, the matrix may consist of nonvolatile substances that can form adducts with the analyte.[7-9]

Remarkable approaches to eliminate and compensate for Matrix effects (MEs) have been discussed and summarized by Lehotay et al., who also enumerate the advantages and shortcomings of each method.[10] Moreover, several approaches to decrease MEs and improve recoveries have also been described, including: (1) several modified QuEChERS sample preparation methods;[11-20] (2) the internal standard method;[21] (3) dilution of matrix extraction;[4,8] (4) the microflow approach[22] and (5) post-column infusion.[23] Many previous studies have focused on sample preparation to reduce MEs and improve recoveries, but few approaches except for the post-column infusion and microflow methods have focused on the injection process. Although the microflow LC-MS/MS approach has several advantages, it concentrates on using a narrow tip emitter in the electrospray ionization (ESI) source, which is not always available in common laboratories. Additionally, several studies have also reported that a smaller sample injection not only optimizes the peak shape and sensitivity but also reduces MEs.[4, 24-26] However, it remains unclear how injection volumes influence the MEs in various fruits and vegetables, and rare previous study has focused on the elimination of MEs through the use of a small injection volume.

The aim of this study is to explore a simplified sample preparation coupled with small injection volume method to decrease MEs and confirm the relationship between injection volume and MEs for the most commonly used 28 pesticides in 6 commodities (apple, cucumber, tomato, luffa, cabbage, and eggplant). Finally, the optimized injection volume and sample preparation process were successfully used for the determination of pesticide residues in vegetables and fruit obtained from local markets.

2. Experimental

2.1. Reagents and materials

Twenty-eight pesticide standards (≥ 98.0% purity) were purchased from Ehrenstorfer GmbH (Augsburg, Germany). HPLC grade acetonitrile (ACN), MeOH and water obtained from Thermo Fisher Scientific (USA) were used as extraction solvents and the mobile phase. AR grade magnesium sulfate anhydrous ($MgSO_4$) and sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. HPLC grade formic acid (FA) was obtained from Kermel (Tianjin China). Primary-secondary amine (PSA) sorbent was purchased from Agilent.

Anhydrous $MgSO_4$ was heated in vacuum drying oven at 220 °C for 12 hours and cooled in

desiccators before being used. Water used as the mobile phase was replaced every day to prevent bacterial contamination.

2.2. HPLC–MS/MS parameters and software

The 6460 Series triple quadrupole mass spectrometer with an ESI source coupled with high performance liquid chromatograph (Agilent Technologies, Palo Alto, CA) was used throughout the study. High performance liquid chromatograph was equipped with syringe (G4226A, Agilent Technologies) with the range of 0-20 µL and the loop (5067-4703, Agilent Technologies) with the range of 0-40 µL.

A ZORBAX SB-C18 (50 mm × 2.1 mm i.d., 1.8-micron particle size, Agilent Technologies, USA) was used for the separation of all pesticides. The mobile phases were water (A) and MeOH (B) with the following linear gradient: 0 min, 90% A; 0.2 min, 90% A; 5 min, 10% A; 6 min, 10% A; 6.1 min, 90% A. The flow rate was 0.3 mL min^{-1} and the total chromatography running time was 8 min. The column temperature was maintained at 35 °C and the injection volume was 1 µL.

Mass spectrometry was equipped with an electrospray ionization (ESI) source operated in positive ion mode, which provides high signal intensities for all of the compounds in MRM scan type. The operating parameters were as follows: polarity, positive; cell acceleration voltage, 4 V; dwell time, 20 ms; drying gas temperature, 325 °C; drying gas flow, 8 L min^{-1}; nebulizer pressure, 35 psi; sheath gas temperature, 375 °C; sheath gas flow, 11 L min^{-1}; capillary voltage, 4000 V; delta EMV(+), 300 V. The Agilent Mass Hunter 7.0 software was used for acquiring data and for qualitative and quantitative analysis.

2.3. Preparation of stock solutions and calibration curves

Individual stock solutions of pesticides were prepared at 100 mg L^{-1} in MeOH and stored at -18 °C in the dark for a maximum of 1 year. The working solutions (1, 5, 10, 50, 100, and 500 µg L^{-1}) were prepared by mixing stock solutions and performing serial dilutions with fresh MeOH daily. The matrix-matched standards (1, 5, 10, 50, 100, and 500 µg L^{-1}) were prepared similarly by serial dilutions with blank sample extract (cucumber, apple, eggplant, cabbage, luffa, and tomato).

2.4. Sample preparation procedure

Different samples of apple, eggplant, tomato, cucumber, luffa, and cabbage were purchased from a local market and stored at -18 °C in polyethylene bags before homogenization. Before analysis, 5.0 g samples were weighed out and transferred to a polypropylene centrifuge tube. Then, 5 mL of ACN with 0.1% (v/v) formic acid was added to the tube, and the samples were homogenized at 7000 rpm for 2 min. Afterwards, 0.8 g NaCl and 3.0 g $MgSO_4$ were added, and the tube was transferred into ice water immediately to prevent agglomeration. The tube was then vortexed using an IKA® MS 3 digital (1 min at 3000 rpm) and centrifuged at 10000 rpm for 10 min at 0 °C. To explore a better purification process supernatant was divided into two parts: 1) 1 mL was directly transferred into a glass vial and evaporated to near dryness with a nitrogen stream while being immersed in a 30 ◦C water bath; then one milliliter of H_2O : MeOH solution (50:50, v/v) was added to the glass tube which was vortexed for 1 min to re-dissolve multi-residues 2) 1 mL was transferred into polypropylene centrifuge tube containing 50 mg PSA , then was vortexed 1 min at 3000 rpm and centrifuged at 10000 rpm for 10 min at 0 °C. Finally, 1) and 2) solution was filtered through a 0.22 µm nylon filter (Whatman, U.K.) and collected in a sample vial for injection.

2.5. Optimization of LC-MS/MS parameters and conditions

All instrumental parameters were optimized to obtain the maximum signal response for each analyte by injecting 1 mg L^{-1} individual standard solutions into the LC-MS/MS at a flow rate of 0.3 mL min^{-1}. For each compound, the most and second most intense ions were used for quantification and confirmation, respectively. All of the optimized parameters for the 28 pesticides are summarized in Table 1.

3. Results and Discussion

3.1. A simplified QuEChERS method

As a clean-up technique, one sorbent or a mixture of sorbents including PSA, which is used to remove polar compounds, and C_{18}, which is used for nonpolar analytes was often used to remove the interferents. However, the polarity of the 28 target compounds, ranging from non-polar (cyromazin) to strong-polar (fenpropathrin), several analytes may be removed regardless of which sorbent or sorbent mixture is used, so to improve the recoveries of all the target compounds, we tried to contrast the sample preparation procedure without any depurative powder. In the procedure, anhydrous $MgSO_4$ was used to eliminate superfluous water and NaCl were used to separate the organic phase from the water phase and control ion separation. The results are shown in Figure 1. It is clear that for all analytes, recoveries can be noticeably improved to the range of 70%-120%, except for cyromazin (36%) and pendimethalin (22%).

The simplified QuEChERS method was also applied to the other five matrices at three spiked concentration levels (10, 50, and 100 μg kg^{-1}) and mean recoveries of all the analytes ranged from 60% to 117%, except for the cyromazin (fenpropathrin, pendimethalin)/tomato, cyromazin (fenpropathrin)/eggplant and fenpropathrin/cabbage combinations, which were determined with low recoveries (< 60%).

3.2. Determination of matrix effects

The conventional and precise determination of MEs were determined by comparing the ratio of slopes between the solvent-matched and matrix-matched calibration curves. The MEs were calculated using the following equation:[27]

$$ME = \frac{slop(fortified\ \text{curve}) - slop(solvent\ \text{curve})}{slop(solvent\ \text{curve})} \times 100\% \qquad (1)$$

The MEs of 168 analyte/matrix combinations were calculated using equation (1) and classified to three categories according to the extent of MEs for most of the pesticides: weak (apple and tomato); medium (cucumber, luffa, and eggplant) and strong ME (cabbage).[28,29] The MEs of the six fruits and vegetables studied are shown in Table 2.

3.3. Influence of the injection volume on matrix effects

To reduce the workload, 84 pesticides/matrix combinations (28 pesticides × 3 representative matrices) were used to study the relationships between MEs and the injection volume, the representative matrices were apple (with weakest MEs), cucumber (with medium MEs) and cabbage (with strongest ME). To conduct the study, identical concentrations and injection volumes of fortified extracts and standards in MeOH were used. In this section, a more straightforward calculation of MEs was used as

the following equation:[30]

$$ME = \frac{peak \text{ areas(fortified extract)- peak areas(solvent)}}{\text{peak areas(solvent)}} \times 100\% \quad (2)$$

Afterwards, the calculated mean (from 3 replicates) MEs were plotted against the injection volume (0.5, 1, 2, 5, 10, and 15 μL). The results are shown in Figure 2, which reveals the main four relationships bettween MEs and the injection volume. We summarized the relationships as follows:

(A) A logarithmic relation between the injection volume and ME was obtained (this case is plotted as curve A in fig.2) and in total, more than 80% pesticide/matrix combinations (28 pesticides × 3 matrixes) followed the same regulation (here, cyromazin in cabbage extract). The coefficients of determination (R^2) ranged from 0.9239 to 0.9977. Moreover, we also can observe that the injection volume has a large influence on MEs and when injection volume is reduced to a certain threshold volume, which we call the critical injection volume, the ME (≤ 20%) becomes negligible.

(B) When the injection volume was small (typically ≤ 2 μL or ≤ 5 μL), MEs (< 20%) were at an identical level, then sharply increased (MEs ⩾ 60%) with injection volume increasing and remained constant even when larger injection volumes were used. For example, the data from cyromazin in apple extract is shown in curve B and 9 combinations followed this regulation.

(C) The third relationship in Figure 2 was curve C, which indicated injection volume had no influence on MEs (-8% to -14%). This situation only existed in 3 combinations (here, emamectin benzoate in cucumber extract). This is most likely because physical and chemical properties of target compounds were not changed by matrix compounds, there was less competition and affect on the ionization in the electrospray-ionization(ESI) droplets.

(D) Finally, the last case is described as curve D in Figure 2. From curve D, we can see matrix effect increased linearly with injection volume increasing, However only two pesticides/matrix combinations followed this trend and the coefficients of determination (R^2) both were more than 0.99 (here, diazinon in apple extract). Critical injection volumes were both discovered in this two pesticides/matrix combinations. This is most likely when a larger amount of sample was injected, competition between interferents and analyte for the ionization linearly increased.

From above analysis, we can see that critical injection volumes existed in almost all analyte/matrix combinations (weak and medium MEs), which can reduce the MEs to an insignificant level (≤ 20%). However, the MEs for cabbage (strongest ME) are still non-ignorable even when a 0.5 μL injection volume was used. To explore the analogous regulations, a dilution factor of 10 was used to lower the ME.[8] After dilution, critical injection volume was observed to reduce the MEs to below 20% in almost all combinations. Table 3 presents the critical injection volume that was needed in dependence on the degree of matrix effect. From Table 3, we can see that a small injection volume (usually ≤ 2 μL for weak or medium MEs and ≤ 5 μL for several weak MEs) can decrease ion suppression to ignorable level. This phenomenon may be: when a smaller amount of sample was injected, there was less competition for the ionization in the electrospray-ionization(ESI) process. Moreover, we also found large injection volume not only reduce sensitivity but also lead to peak tailing in LC-MS/MS system which different from traditional chromatographs,[24,25,31,32] the phenomenon are shown in Figure 3. This is most likely when a larger amount of sample was injected, ionization for analytes was unable to accomplish instantly and completely, so peak tailing and non-linear relation between peak area and injection volume were gained. In this study, to eliminate MEs for most pesticides/matrix combinations and to reduce injection error, a 1 μL injection volume was used and a dilution factor of 10 was used for cabbage sample.

To the best of our knowledge, normal injection volume usually 5 μL or 10 μL was used to enhance the sensitivity by many researchers in traditional chromatographs and LC-MS/MS system.[10-12,14] However，in this study, we find normal injection volume can not only increase MEs, but also can lead to bad peak shapes in LC-MS/MS system for some compounds. In order to reduce the matrix effects by normal injection volume, matrix-matching method was used which is onerous due to the need for many blank extracts. Moreover, when a large amount of sample was injected to apparatus, serious pollution and expensive maintenance may be produced. In other researches[4,8,33(文献)], matrix dilution was used to reduce matrix effects, however, this method is onerous, more organic solvent and even can increase the detection limits simultaneously when a large dilution extent was used.[8]

3.4. Method validation

3.4.1. Linearity. Linearity was investigated by plotting signal responses vs. concentration of the analytes with 1 μL injection volume. Six concentrations levels (1, 5, 10, 50, 100, and 500 μg L^{-1}) were prepared with pure solvent and six matrices, and good linearity for all twenty-eight analytes, i.e., linear regression coefficients (R^2) greater than 0.99, was achieved. Linearity was observed in the range 1-500 μg L^{-1} for most analyte/matrix combinations.

3.4.2. LODs and LOQs. The calculated LODs and LOQs are shown in Table 2, from which we can see that half of the LOQs (84 of the total 6×28) were below 0.1 μg kg^{-1} and 29 LOQs were above 1 μg kg^{-1}. The maximum LOQ is 13.6 μg kg^{-1} (aldicarb-sulfone in eggplant) and the minimum LOQ is 0.002 μg kg^{-1} (dimethomorph in cucumber). There is no observed relationship between MEs and LOQ. For cabbage (strong MEs), LOQs and LODs have no noticeable change upon ten-fold matrix dilution. This indicates that for cabbage with a strong ME, LODs and LOQs were not changed by a certain degree of matrix dilution. Furthermore, the LOQ values were always lower than the MRLs established by EU.

3.4.3. Recovery (trueness) and precision (repeatability). Recovery and precision were studied in six selected matrices (apple, cucumber, tomato, luffa, cabbage, and eggplant) at three fortified levels (10, 50, and 100 μg kg^{-1}) for all of the analytes. The recoveries were all in the range of 60%-120% at three spiked levels, except for cyromazin (ca. 30% in 1/3 spiked matrices), pendimethalin (ca. 30% in tomato), and fenpropathrin (ca. 40% in half-spiked matrices). Moreover, the intra- and inter-day RSDs were below 10% and 15%, respectively. All of the recovery results are shown in Table 4 and the precision data is summarized in Table 1. Finally, 28 compounds in cucumber matrix at 10 μg kg^{-1}concentration was used to validate the precision of 1 μL injection volume, 10 continuous injections experiment was carried out and the RSDs (n=10) for syringe and loop were all less than 5%.

3.5. Application to real sample

The multi-residue analysis of 28 analytes in apple (3 samples), cucumber (3 samples), tomato (3 samples), luffa (3 samples), cabbage (3 samples) and eggplant (3 samples) obtained from a local market was used to validate the effectiveness of this system. The samples were prepared as the section 2.4 and solvent-marched method was used to quantify the compounds. In 18 samples, omethoate, 3-ketocarbofuran, carbofuran, flumorph, paclobutrazol, dimethomorph, phoxim, prochloraz, buprofezin were detected in apple samples; carbendazim, flumorph, myclobutanil, pyraclostrobin, prochloraz, buprofezin and fenpropathrin were detected in cucumber samples; omethoate, phoxim, buprofezin, chlorfluazuron, fenpropathrin were detected in tomato; omethoate, azoxystrobin, phoxim, pyraclostrobin, pendimethalin, fenpropathrin were detected in luffa; omethoate, carbendazim, acetamiprid, rotenone, hexaflumuron, emamectin benzoate, chlorfluazuron, fenpropathrin were detected in cabbage;

carbendazim, azoxystrobin, dimethomorph, chlorfluazuron were detected in eggplant at levels which all below the MRLs. In conclusion, satisfactory precision and accuracy can be attained by the method proposed in this work.

4. Conclusions

In this study, a simplified QuEChERS method coupled with small injection volume (1 μL) were explored and validated for the simultaneous determination of 28 pesticides in fruits and vegetables using an LC-MS/MS apparatus. Good analytical results including linearity, sensitivity, LOD, LOQ and recovery were obtained with the method.

MEs stem from the sample matrix co-eluting with target analytes, and the extent of ion suppression depends on the logarithm of the injection volume. MEs can be reduced to negligible level (≤ 20%) when the injection volume is small (≤ 2 μL for weak to medium MEs or ≤ 5 μL for several weak MEs) for most analyte/matrix combinations. Decreasing the injection volumes did not reduce the sensitivity. If strong MEs are present initially, then a matching dilution can be used to optimize the injection volume. For cabbage with a strong ME, the limits of qualification and quantification were changed less by a certain degree of matrix dilution.

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The authors declare no conflict of interest.

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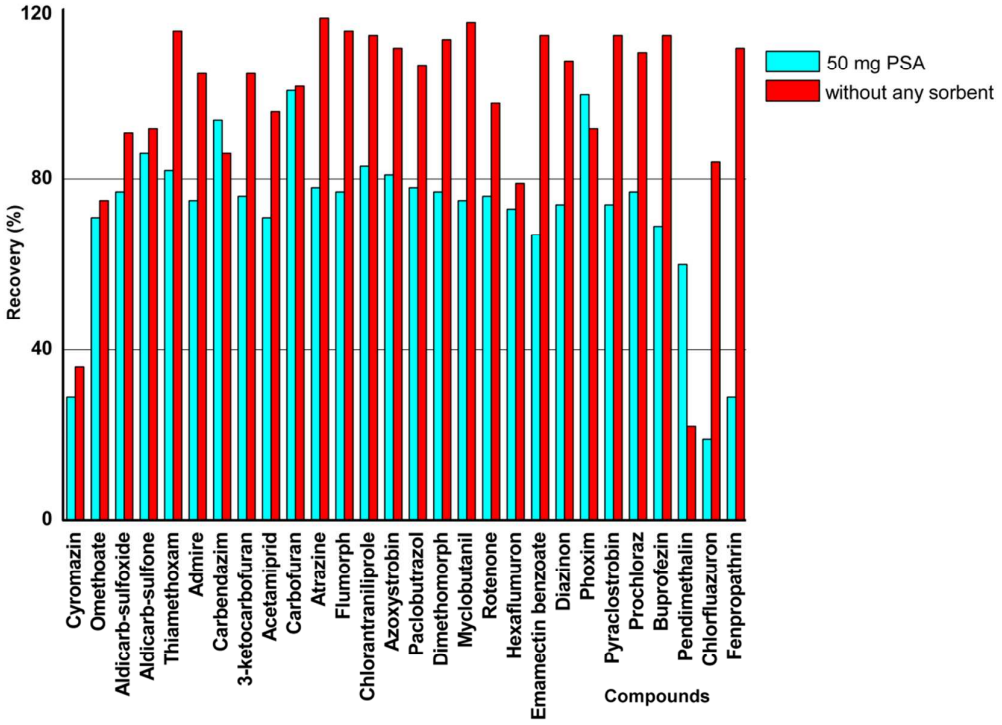


Figure 1. Comparison of the PSA sorbent with no sorbent on the recoveries of 28 pesticides in tomato extract with a concentration of 10 μg kg^{-1}.

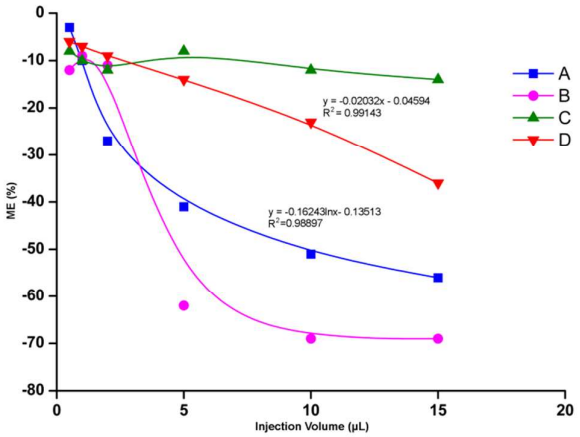


Figure 2. Four different relationships observed between the injection volume and matrix effects. (A) Logarithmic relationship shown for cyromazin in cabbage extract at a concentration of 10 μg kg^{-1} by 10 times diluted. (B) Sharp change in the matrix effect observed (from -18% to -60%) when the injection volume is more than 5 μL. Shown here is cyromazin in apple extract at a concentration of 20 μg kg^{-1}. (C) No relation between injection volume and ion suppression. Shown here is emamectin benzoate in cucumber extract at a concentration of 10 μg kg^{-1}. (D) Good linearity with R^2>0.99 shown for diazinon in apple extract at a concentration of 20 μg kg^{-1}.

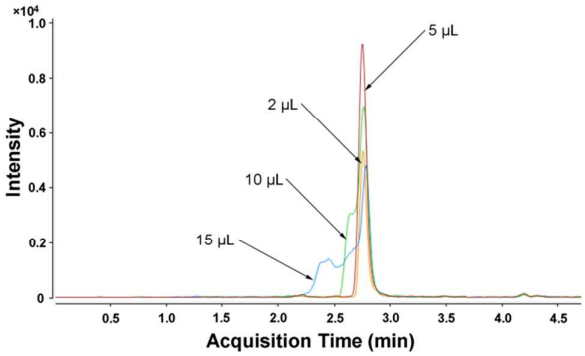


Figure 3. Chromatograms corresponding to three injection volumes (5 µL, 10 µL, and 15 µL) obtained for the analysis of admire in cucumber extract at a 10 µg kg^{-1} concentration.

Table 1 Optimized conditions of the LC-MS/MS for all analytes and the intra- and inter-day RSDs of the analysis method.

Analyst	RT (min)	Precursors	Product ion	Frag. (V)	CE (eV)	intra-day RSDs % (n=5)						inter-day RSDs % (n=5)					
						apple	cucumber	tomato	luffa	cabbage*	eggplant	apple	cucumber	tomato	luffa	cabbage*	eggplant
cyromazin	0.671	167.1	85.2*; 108.0	120	15[a]; 20	7.73	6.97	4.32	7.41	6.92	5.73	9.72	10.31	10.49	10.58	10.99	11.03
omethoate	1.063	214	182.8*; 55.0	85	5[a]; 10	3.72	3.51	3.25	3.23	2.01	4.83	6.45	5.98	7.02	5.93	6.87	9.95
aldicarb-sulfoxide	1.808	229	166 *; 109.0	80	5[a]; 12	3.68	4.01	3.99	3.58	4.38	3.05	7.43	8.51	7.48	6.54	7.97	8.86
aldicarb-sulfone	1.933	223.0	86.2*; 147.9	80	10[a]; 5	4.79	5.21	5.02	4.96	6.71	4.76	9.04	9.67	8.78	10.23	10.23	9.03
thiamethoxam	2.326	292	211.0*; 181.0	80	5[a]; 20	2.74	2.96	3.02	2.94	3.99	3.56	8.02	9.34	9.67	9.53	10.34	9.02
admire	2.757	256.1	209.0*; 75.0	100	8[a]; 8	6.41	6.70	6.03	3.04	5.02	6.53	10.02	9.47	9.78	10.08	11.23	10.32
carbendazim	2.777	192.1	160.0*; 132.0	90	15[a]; 30	9.03	9.21	8.99	9.12	4.75	7.76	10.67	10.34	11.03	10.92	9.99	10.78
3-ketocarbofuran	2.972	238.1	180.9*; 163.0	80	5[a]; 8	3.94	4.02	4.18	4.21	6.89	4.27	7.92	7.64	8.04	8.42	7.54	6.92
acetamiprid	3.081	223	126.0*; 90.1	90	20[a]; 35	6.05	5.86	4.97	5.99	6.03	5.38	9.92	9.05	10.87	11.02	10.93	10.45
carbofuran	3.942	222.1	165.0*; 123.0	85	5[a]; 20	8.78	8.94	8.83	2.57	2.04	8.93	11.45	10.87	9.04	10.48	10.32	10.98
atrazine	4.372	216	174.0*; 146.0	120	15[a]; 25	7.24	7.53	6.23	7.46	2.58	6.02	8.04	9.92	10.21	8.49	9.58	10.42
flumorph	4.573	372	284.9*; 164.9	160	15[a]; 30	9.01	9.92	8.92	8.83	8.39	6.27	11.93	11.85	12.00	12.04	10.83	9.04
chlorantraniliprole	4.580	483.9	285.8*; 452.6	100	10[a]; 10	5.74	5.72	5.93	2.04	2.35	5.87	7.73	8.02	7.95	7.60	7.42	8.09
azoxystrobin	4.733	403.9	371.8*; 343.9	100	10[a]; 20	3.92	3.42	3.76	5.78	4.29	3.61	6.05	7.09	6.84	6.52	6.01	7.72
paclobutrazol	4.862	293.8	70.0*; 124.8	120	15[a]; 35	2.65	3.01	3.02	3.92	4.02	3.05	7.43	7.06	6.84	7.35	7.28	7.93
dimethomorph	4.913	388.1	300.9*; 65.0	140	15[a]; 30	6.27	6.03	6.43	6.03	5.71	5.76	9.03	9.10	9.83	10.03	10.54	10.6
myclobutanil	4.943	289.1	70.2*; 125.1	120	15[a]; 35	5.28	5.35	5.78	3.97	2.95	6.89	8.14	8.15	7.73	7.92	6.04	9.87
rotenone	5.217	395.1	213.0*; 40.9	160	20[a]; 15	4.93	5.04	4.83	3.82	4.02	4.03	7.93	7.04	6.99	6.42	8.05	8.58
hexaflumuron	5.237	309	156.0*; 139.0	100	10[a]; 30	4.09	4.00	3.98	1.04	9.36	5.93	6.59	6.78	6.77	7.98	9.83	9.03
emamectin	5.314	886.4	158.2*; 26.0	210	40[a]; 40	3.78	3.92	4.21	2.95	2.91	5.46	7.93	6.58	7.93	8.52	7.71	9.03
diazinon	5.372	305.1	169.0*; 53.1	120	20[a]; 15	2.09	1.98	2.04	3.01	2.54	1.85	5.21	5.34	5.00	6.23	6.41	5.09
phoxim	5.390	299	77.3*; 129.0	110	25[a]; 5	1.92	2.04	2.98	4.05	3.33	4.98	5.72	5.09	6.42	5.10	5.37	6.81
pyraclostrobin	5.415	388	162.8*; 295.6	110	20[a]; 10	3.55	3.78	3.01	3.95	4.53	2.99	5.02	5.61	4.87	6.20	5.82	6.78
prochloraz	5.433	376.1	307.9*; 65.6	90	5[a]; 10	4.12	3.96	4.21	4.44	4.09	4.68	7.98	8.94	8.53	9.17	7.83	6.04
buprofezin	5.739	306.4	200.7*; 15.7	100	8[a]; 8	2.84	2.99	3.05	2.95	3.04	2.74	5.76	5.04	4.38	5.93	5.49	6.04
pendimethalin	5.911	282.3	212.0*; 194.0	95	8[a]; 13	4.66	4.78	4.59	3.58	5.43	3.56	9.32	8.57	10.03	9.38	8.92	7.09
chlorfluazuron	5.996	539.9	383.0*; 58.0	130	15[a]; 15	1.88	2.05	3.42	4.02	5.34	3.75	7.89	6.09	6.14	6.45	5.34	6.02
fenpropathrin	6.016	350.2	125.0*; 97.1	100	10[a]; 30	9.39	8.88	7.45	5.31	6.73	4.36	10.01	9.09	10.80	11.34	10.57	11.95

*Quantification ion. [a]The collision energy of quantification ion.

Table 2 Matrix effects obtained from the calibration curves, critical volumes, and LOQs of all (28×7) analyte/matrix combinations.

	Matrix Effects (ME) %						LOQ(μg kg^{-1})						
Analyst	apple	cucumber	tomato	luffa	cabbage	eggplant	apple	cucumber	tomato	luffa	cabbage	cabbage*	eggplant
cyromazin	-8	-31	-10	-42	-47	-44	1.05	0.24	0.09	0.015	2.03	2.14	3.15
omethoate	-8	-2	-10	-6	-22	-6	0.03	0.06	0.03	0.06	0.27	0.2	0.45
aldicarb-sulfoxide	4	-10	-8	-7	-8	2	0.072	0.06	0.06	0.09	0.20	0.15	0.6
aldicarb-sulfone	-3	-20	-20	0	-21	-3	2.01	2.49	1.95	1.8	4.71	4.00	13.6
thiamethoxam	6	10	13	-20	-59	-22	0.015	0.03	0.06	0.06	0.12	0.08	0.66
admire	10	0	6	-1	-45	-2	0.105	0.09	0.027	0.09	0.13	0.05	1.8
carbendazim	-9	-1	-7	-7	-17	6	0.009	0.06	0.06	0.18	1.62	1.0	0.39
3-ketocarbofuran	-5	-6	-15	-5	-58	-10	0.24	0.12	1.28	0.18	1.01	0.62	4.05
acetamiprid	11	6	-9	-39	-38	-33	0.051	0.012	0.003	0.09	0.5	0.4	10.1
carbofuran	9	-14	0	-18	-30	-13	0.03	0.06	0.03	0.06	0.05	0.04	0.24
atrazine	-3	-9	-5	-12	-19	-10	0.03	0.03	0.03	0.12	0.11	0.09	0.3
flumorph	-8	-41	-14	-42	-46	-45	0.051	0.03	0.03	0.009	0.09	0.07	0.63
chlorantraniliprole	-5	-19	-9	-24	-53	-25	0.12	0.06	0.27	0.18	0.14	0.11	0.45
azoxystrobin	-7	-14	-10	-16	-38	-22	0.06	0.06	0.012	0.12	0.05	0.03	0.45
paclobutrazol	-8	-38	-7	-35	-50	-40	0.048	0.09	0.15	0.09	1.98	1.94	0.75
dimethomorph	-10	-24	-23	-25	-57	-46	0.021	0.002	0.006	0.03	0.07	0.05	0.39
myclobutanil	-9	-58	-26	-57	-58	-52	0.09	0.09	0.06	0.15	0.32	0.28	0.81
rotenone	-10	-36	-23	-38	-64	-44	0.21	0.24	0.27	0.6	0.25	0.23	3.3
hexaflumuron	9	-43	-26	-48	-77	-46	0.18	0.39	0.03	0.69	1.72	1.71	2.4
emamectin	-1	-4	-4	6	-10	-8	0.09	0.03	0.018	0.03	0.012	0.008	0.24
diazinon	-4	-10	-6	-18	-26	-17	0.012	0.03	0.027	0.06	0.13	0.1	0.3
phoxim	32	-30	-10	-28	-52	-36	0.19	0.27	0.81	0.69	1.01	0.93	9.09
pyraclostrobin	-6	-7	-7	-6	-25	-10	0.06	0.06	0.06	0.03	0.10	0.08	0.21
prochloraz	20	18	20	-5	-13	-16	0.021	0.03	0.03	0.021	0.01	0.009	0.33
buprofezin	-6	-21	-7	-21	-24	-15	0.039	0.06	0.06	0.03	0.08	0.08	0.51
pendimethalin	-3	-14	-7	-15	-19	-17	3.75	1.74	0.081	0.03	0.09	0.07	0.54
chlorfluazuron	-13	-11	-8	-17	-25	14	1.92	0.06	2.7	1.2	0.17	0.2	5.01
fenpropathrin	-9	-23	-6	-15	-27	-34	1.01	0.99	10.44	0.99	2.5	2.03	3.12

* ten times dilution by H_2O:MeOH solution (50:50, v/v)

Table 3 Required critical injection volume for reduction of matrix effects depending on the initial level of matrix effects (summary of table 2)

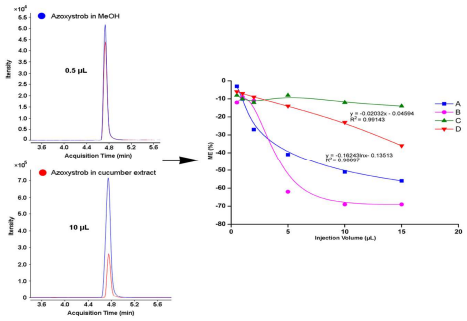
	required critical injection volume for	
Initial level of matrix effect (%)	ME ≤ −20%	n
Weak (≤ 20)	0.5-5.8	47
Medium (20-50)	0.5-1.9	16
Strong (≥50)	No critical volume	7
Strong matrix with 10 fold-dilution	1.0-1.7	7

n: number of pesticide-matrix combinations

Table 4 Recoveries of three spiked analytes (10, 50, and 100 μg kg^{-1}) in six fruit and vegetable matrices.

Analyst	10 μg kg^{-1}						50 μg kg^{-1}						100 μg kg^{-1}					
	apple	cucumber	tomato	luffa	cabbage*	eggplant	apple	cucumbe	tomato	luffa	cabbage*	eggplant	apple	cucumber	tomato	luffa	cabbage*	eggplant
cyromazin	27	101	36	64	91	31	33	98	29	65	77	35	42	88	29	69	85	30
omethoate	94	89	75	96	79	77	67	92	71	102	79	81	75	96	71	80	82	88
aldicarb-sulfoxide	104	89	91	64	88	70	79	97	77	74	82	89	72	94	77	71	79	84
aldicarb-sulfone	89	99	92	97	94	93	101	106	86	94	105	92	94	89	86	86	85	102
thiamethoxam	63	87	116	77	81	110	75	93	82	82	87	71	78	76	82	70	74	105
admire	96	96	105	83	116	83	85	109	75	91	91	112	87	97	75	89	95	91
carbendazim	70	97	86	60	97	70	86	89	94	75	86	65	93	87	94	71	90	81
3-ketocarbofuran	108	79	105	66	103	87	94	85	76	87	76	104	96	83	76	78	98	87
acetamiprid	75	108	96	105	110	94	81	99	71	112	69	89	75	101	71	95	102	87
carbofuran	82	94	102	110	84	86	92	97	101	100	83	80	96	87	101	106	87	94
atrazine	110	105	118	98	95	94	98	108	78	105	91	97	105	99	78	89	98	97
flumorph	95	108	113	94	103	107	113	98	87	99	106	103	101	97	77	97	96	94
chlorantraniliprole	76	73	114	106	106	86	76	64	83	110	78	79	71	81	83	99	101	72
azoxystrobin	120	79	110	88	109	95	84	96	81	94	114	87	90	86	81	79	96	87
paclobutrazol	72	95	106	85	105	92	73	97	78	89	94	78	103	103	78	79	98	95
dimethomorph	102	99	113	76	109	90	109	100	97	80	87	85	94	87	77	85	94	103
myclobutanil	105	76	117	91	106	104	81	84	75	88	64	97	89	82	75	89	99	100
rotenone	61	67	98	97	77	108	111	84	96	100	99	96	102	72	76	88	81	96
hexaflumuron	93	79	79	88	69	103	74	81	73	93	80	85	64	85	73	95	75	94
Emamectinbenzoate	97	106	114	105	99	109	115	97	67	108	117	98	108	104	67	98	106	87
diazinon	111	91	108	78	81	104	105	89	74	83	75	109	84	84	74	82	96	97
phoxim	105	105	92	98	95	95	99	75	100	103	81	97	109	97	100	102	84	84
pyraclostrobin	69	83	114	94	81	112	77	94	104	99	93	11	83	78	74	99	86	89
prochloraz	81	101	110	78	111	112	86	109	67	87	110	91	91	89	77	86	103	102
buprofezin	101	101	115	67	99	101	102	108	69	73	102	87	95	100	69	74	84	89
pendimethalin	103	98	22	88	78	120	69	104	32	92	107	115	71	105	50	95	31	108
chlorfluazuron	109	87	84	65	75	73	95	104	79	75	91	80	87	94	19	74	81	69
fenpropathrin	71	51	110	65	41	51	83	39	29	78	46	44	92	43	29	73	32	32

* ten times dilution by H_2O:MeOH solution (50:50, v/v)



One sentence of text: Reduction matrix effects to negligible level by small injection volume.