JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Simultaneous Determination of Five Plant Growth Regulators in Fruits by Modified Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) Extraction and Liquid Chromatography−Tandem Mass Spectrometry

Xiaomei Shi,[†] Fen Jin,*[,†] Yuting Huang,[†] Xinwei Du,[†] Chunmei Li,[‡] Miao Wang,[†] Hua Shao,[†] Maojun Jin,[†] and Jing Wang*[,†]

[†]Key Lab of Agro-product Quality and Safety, Institute of Quality Standards and Testing Technology for Agro-products, Chinese Academy of Agricultural Sciences, Beijing 100081, People's Republic of China

[‡]Northwest A&F University, Yangling 712100, People's Republic of China

Supporting Information

ABSTRACT: An effective method using liquid chromatography−tandem mass spectrometry (LC−MS/MS) was developed and optimized to obtain a complete separation of five representative plant growth regulators (PGRs) [gibberellic acid, 2,4-dichlorophenoxyacetic acid (2,4-D), thidiazuron, forchlorfenuron, and paclobutrazol] in fruits. Extraction was performed with acetonitrile containing 0.1% (v/v) acetic acid, applying modified quick, easy, cheap, effective, rugged, and safe (QuEChERS) methodology. LC−MS/MS conditions including composition of mobile phases and mass spectrometry (MS) conditions were evaluated to achieve the highest sensitivity in MS detection. All of the data acquisition was employed in the segmented multiple-reaction monitoring mode for the selected negative and positive transition ions. The octadecylsilyl (C18) dispersive solid-phase extraction (SPE) sorbent was found to provide the more satisfied recoveries than primary secondary amine (PSA) and graphitized carbon black (GCB) for five target PGRs. The optimized method allowed for recoveries of 76−112% for the five PGRs from fruit samples with relative standard deviation (RSD) values less than 10%. Limits of quantification (0.5−16.5 μg/kg) were lower than the maximum limit of residues established for PGRs. The results demonstrated that the developed LC−MS/MS and QuEChERS extraction method is highly effective for analyzing trace amounts of target PGRs in fruit samples. Finally, the method was successfully used to detect residual PGRs in Beijing, China, in 2010. The concentrations of 2,4-D (5.1−1503 μg/kg) and paclobutrazol (1−1381 μg/kg) found in orange and peach, respectively, suggesting that the use of these PGRs in these fruits should be regulated in China in the future.

KEYWORDS: *Plant growth regulators, QuEChERS extraction, liquid chromatography−tandem mass spectrometry, fruits*

1. INTRODUCTION

Plant growth regulators (PGRs) are a class of synthetic pesticides, which have similar physiological activity to their natural pesticides, plant hormones, and can effectively promote, inhibit, or modify growth and development of plants. PGRs are widely used in agricultural production, and the amount is increasing. The global sales of PGRs have reached approximately 740 million dollars in 2007, which was 1.54-fold more than that in 2002.[1] Furthermore, some PGRs have appeared to be extensively used in edible plants in many countries, such as Australia, Japan, China, and India. Therefore, their toxicity and residues in foods and the environment have become of increased concern in recent years. Many countries and organizations have regulated the maximum residue limits (MRLs) for some PGRs in edible foods.[2−5] Examples of forchlorfenuron MRLs for kiwifruit are 10 μg/kg in Australia, 40 μg/kg in the U.S.A., 50 μg/kg in the European Union, and 100 μg/kg in Japan.

In China, food safety incidents are gradually increasing because of the abuse of PGRs in fruits for the past few years. In 2011, the incident of exploding watermelon caused a very adverse impact on the watermelon industry because of the abuse of forchlorfenuron worldwide. The residue level of PGRs in foods, especially in fruits, received more and more attention. According to the properties and features, PGRs can be roughly defined to four groups: gibberellins, auxins, cytokinins, and inhibitors.[6,7] Gibberellic acid (GA_3), 2,4-dichlorophenoxyacetic acid (2,4-D), forchlorfenuron, thidiazuron, and paclobutrazol are the five representatives of the four groups commonly used in fruits. However, to the best of our knowledge, almost no studies were reported to simultaneously analyze multiple classes of PGRs in fruit samples.[8,9]

The quick, easy, cheap, effective, rugged, and safe (QuEChERS) method makes it easier and less expensive to examine chemicals in food than other pretreatment methods and has been successfully used for the extraction and purification of a variety of chemicals, including pesticides,[10−14] polycyclic aromatic hydrocarbons,[15] antibiotics,[16] and veterinary drugs[17,18] in a wide range of matrices. In comparison to

Received: October 14, 2011
Revised: December 1, 2011
Accepted: December 12, 2011
Published: December 12, 2011

solid-phase extraction (SPE) and conventional packed column chromatography, the QuEChERS was a simultaneous extraction and cleanup technique that required less time and solvent. However, this technique has hardly been applied to the study of PGRs in foods, possibly because of the poor recoveries.[19,20]

The aim of the present work was to develop and validate a modified QuEChERS extraction and liquid chromatography–tandem mass spectrometry (LC–MS/MS) method for the simultaneous determination of five commonly used PGRs (GA_3, 2,4-D, thidiazuron, forchlorfenuron, and paclobutrazol) in fruit samples. As far as we know, methodologies have not been reported for the simultaneous determination of multiresidues of target PGRs in fruits, and the applicability and robustness of the proposed method have been verified using spiked and field fruit samples.

2. EXPERIMENTAL SECTION

2.1. Reagents and Chemicals. High-performance liquid chromatography (HPLC)-grade acetonitrile and methanol were obtained from Fisher Scientific (Pittsburgh, PA). Acetic acid (content >99.7%) and ammonium acetate (content >99.5%) of HPLC grade were purchased from DIMA Technology (Richmond Hill, Ontario, Canada). Anhydrous magnesium sulfate, sodium chloride, and sodium acetate of analytical grade were obtained from the Chemical Reagent Company (Beijing, China). Anhydrous magnesium sulfate had been heated at 450 °C for at least 5 h, cooled naturally, and stored in desiccators. Primary secondary amine (PSA), octadecylsilyl (C18), and graphitized carbon black (GCB) sorbents were obtained from Agela Technologies (Beijing, China). Highly purified water (Milli-Q, Millipore, Bedford, MA) was used throughout the preparation of the mobile phase.

2.2. Standard Solution Preparation. Certified standards of GA_3, 2,4-D, thidiazuron, forchlorfenuron, and paclobutrazol (purity higher than 99%) were purchased from Dr. Ehrenstofer GmbH (Augsburg, Germany), and their chemical structures were shown in Figure 1.

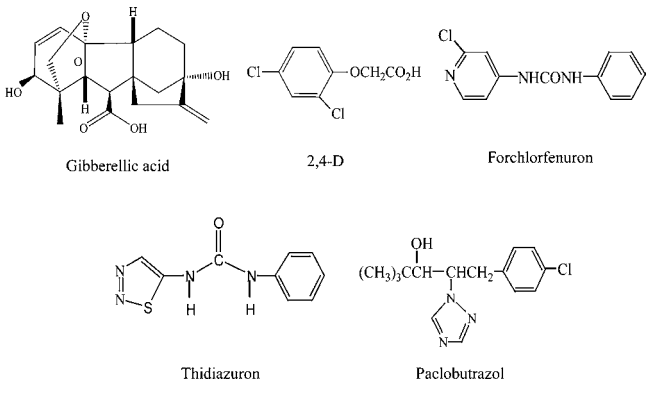

Figure 1. Structures of five target PGRs.

Stock solution was prepared at 2000 mg/L in acetonitrile. Mixed standard solutions were prepared by dilution of the stock solutions with acetonitrile. All of the solutions were stored at −20 °C.

2.3. Instruments and Chromatographic Conditions. Chromatographic analyses were conducted using an Agilent series 1200 HPLC system (Agilent, Santa Clara, CA) equipped with a binary pump, a column oven, and an auto sampler. The five PGRs were separated on an XTerra C18 column (150 × 2.1 mm, with a 5.0 μm particle size, Waters, Milford, MA). The mobile phases consisting of mobile phase A (5 mM/L ammonium acetate and 0.5% acetic acid in methanol) and mobile phase B (5 mM/L ammonium acetate and 0.5% acetic acid in pure water) were used with a gradient elution of A/B from 15:85 to 40:60 (0–1 min, hold for 2.5 min), 50:50 (3.5–6 min), 55:45 (6–10 min), and 95:5 (10–15 min, hold for 5 min) at a flow rate of 0.20 mL/min. The injection volume was 5 μL, and the column temperature was maintained at 40 °C.

Mass spectrometric detection was carried out using an API 5000 tandem quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) in multiple-reaction monitoring (MRM) mode. The instrument was equipped with an electrospray (ESI) ionization source. Typical ESI parameters were used as follows: ion spray voltage (IS), 4500 V; atomization air pressure (GS_1), 40 psi; auxiliary gas (GS_2), 40 psi; curtain gas (CUR), 5 psi; ion source temperature (TEM), 450 °C; entrance potential (EP), 10 V; and collision cell exit potential (CXP), 15 V. The MRM transitions, collision energy (CE), and declustering potential (DP) were summarized in Table 1. Data acquisition was performed under time-segmented conditions based on the chromatographic separation of the target compounds to maximize sensitivity of detection. Segment 1–17 min was detected in the negative-ion mode, and segment 17–25 min was detected in the positive-ion mode. All system control, data acquisition, and data analysis were performed with the AB Sciex Analyst 1.4.2 software (Applied Bioscience).

2.4. Sample Extraction and Cleaning. A fully homogenized sample (10 g) was weighed in a 50 mL plastic centrifuge tube. With the addition of 10 mL of 0.1% acetic acid in acetonitrile, the tube was vigorously shaken for 1 min. Afterward, 4 g of anhydrous magnesium sulfate was added, and the solution was shaken immediately for another 1 min, then homogenized, and centrifuged for 5 min at 5000 rpm. A total of 1 mL of the clarified supernatant was transferred into a clean plastic centrifuge tube containing 50 mg of C18 sorbents. The mixture was then shaken for 1 min, centrifuged for 5 min at 5000 rpm, and finally, filtered through a 0.22 μm membrane prior to HPLC–MS/MS analysis.

3. RESULTS AND DISCUSSION

3.1. Optimization of LC–MS/MS Conditions. Using a Q1 scan in infusion experiments, $[M + H]^+$ was selected as the precursor ion for forchlorfenuron (m/z 248) and paclobutrazol (m/z 294), which was the same as the previous reports.[21–24] For GA_3 (m/z 345), 2,4-D (m/z 219), and thidiazuron (m/z 219), $[M - H]^-$ was chosen as the precursor ion. Figure 2 shows the ESI–MS/MS spectra for the five PGRs in the full-scan product ion experiments at the corresponding collision energy. For the five PGRs, the first precursor ion product transition in Table 1, which was with highest intensity, was selected for quantitation. It should be noted that, for GA_3, the transition from $[M - H]^-$ to $[M - H-(COO)_2-H_2O]^-$ (m/z 345 → 239) was previously reported with the highest intensity[25,26] compared to the transition from $[M - H]^-$ to $[M - H-(COO)_3-C_5H_{10}]^-$ (m/z 345 → 143). We found that the intensity of the transition m/z 345 → 143 was 2 times higher than that of m/z 345 → 239 and, thus, was chosen as the quantitation transition in the present study.

As we know, the pH and additives of mobile phases can affect the LC resolution and MS response of chemicals. For the target PGRs in the present study, the addition of acetic acid can significantly influence their retention behaviors on the separation column, especially for GA_3 and 2,4-D, which have carboxyl groups in their structures. As shown in Figure 3, the peak shape was greatly improved and the retention time was prolonged for GA_3 and 2,4-D with the increase of the acetic acid concentration from 0 to 0.5%. The addition of acetic acid also helped to increase the MS signal response of PGRs, and the highest responses of the five PGRs occur at a percentage of 0.5% acetic acid (Figure 3c). In addition, the effect of the addition of ammonium acetate in the mobile phase was also evaluated. As shown in Figure 3d, the chromatographic separation of thidiazuron and 2,4-D was greatly improved by adding 5 mM/L ammonium acetate in the mobile phase.

dx.doi.org/10.1021/jf204183d | J. Agric.Food Chem. 2012, 60, 60–65

Table 1. Molecular Weights, Retention Times, and Optimized MS/MS Parameters for the Five Target PGRs

ESI mode	analyte	MW	RT (min)	MRM transition	DP (V)	CE (V)
negative	GA_3	346.38	9.66	345.2 → 143.1	90	40
				345.2 → 239.2	90	35
				345.2 → 221.2	90	30
	2,4-D	221.04	15.80	219.0 → 161.0	46	20
				219.0 → 125.0	46	40
	thidiazuron	220.24	13.94	219.1 → 100.0	60	15
				219.1 → 71.0	60	46
positive	forchlorfenuron	247.68	17.42	248.2 → 129.0	100	25
				248.2 → 93.0	100	53
	paclobutrazol	293.79	18.97	294.2 → 70.0	100	37
				294.2 → 125.0	110	50

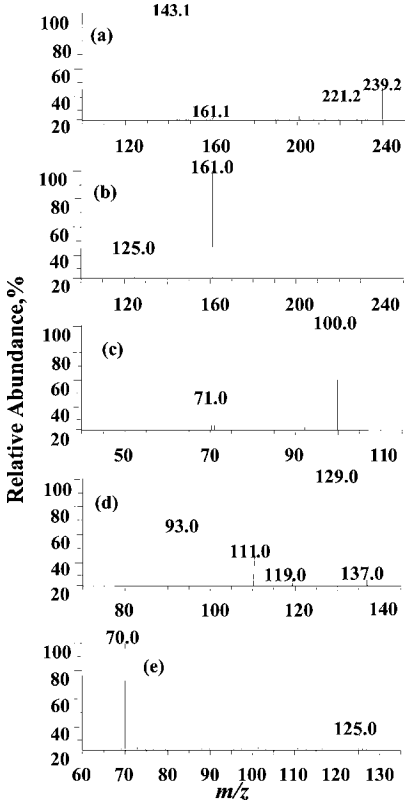

Figure 2. ESI−MS/MS product scan spectrum of five target PGRs: (a) GA_3, (b) 2,4-D, (c) thidiazuron, (d) forchlorfenuron, and (e) paclobutrazol.

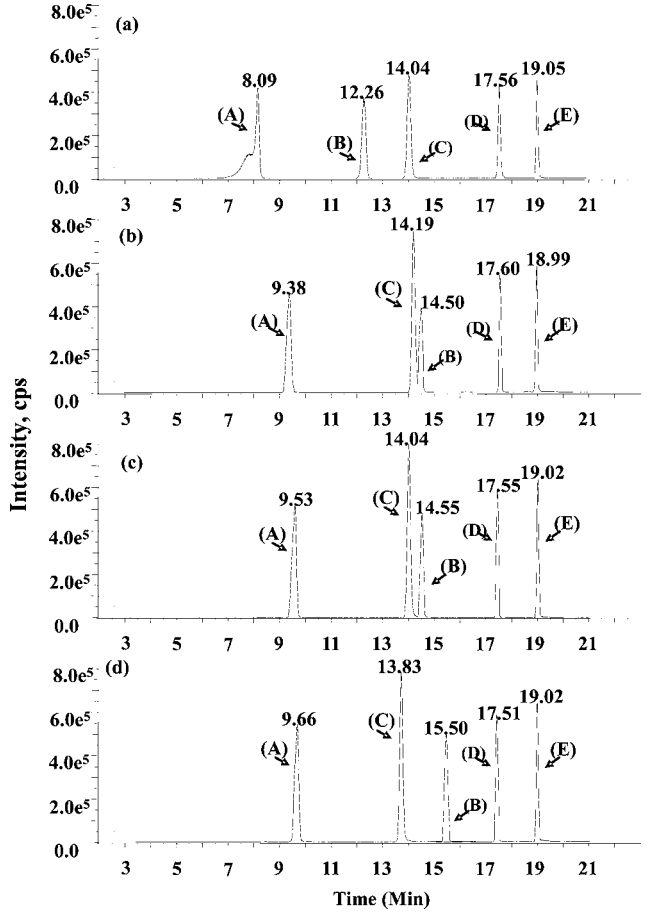

Figure 3. HPLC−MS/MS chromatograms of five target PGRs [(A) GA_3, (B) 2,4-D, (C) thidiazuron, (D) forchlorfenuron, and (E) paclobutrazol] under different compositions of mobile phases: (a) free of acetic acid, (b) 0.2% acetic acid, (c) 0.5% acetic acid, and (d) 0.5% acetic acid and 5 mM/L ammonium acetate.

Therefore, 0.5% acetic acid and 5 mM/L ammonium acetate added in the mobile phase were used in the current study.

3.2. Optimization of the Sample Preparation. Among the five target PGRs, GA_3 and 2,4-D were relatively strong acids with $pK_a < 4$.[12,27] Therefore, the pH condition of the extraction is critical for developing a multi-residue extraction method. Figure 4 shows the extract efficiencies of target PGRs at different pH conditions. As expected, the recoveries of GA_3 and 2,4-D were greatly improved when the pH value of extraction was decreased from 6.38 to 4.23, which can be attributed to the dissociation equilibrium moving toward the neutral forms with the acidity increasing. Similar results were also found for the phenoxy acid analytes, which obtained a dramatic drop of recoveries when the pH value was above 5.5.[28,29] For thidiazuron, forchlorfenuron, and paclobutrazol, the recoveries were in the range of 82−100% and were not changed greatly. Thus, acetonitrile added to 0.1% acetic acid (pH 4.32) was chosen as the extraction solution.

To obtain accurate data and lower method limits, the dispersive SPE method was used to further purify the acetonitrile phase. In the current study, the dispersive SPE sorbents PSA, GCB, and C18 were evaluated by purifying the crude sample extracts spiked with 100 μg/kg of target PGRs. As shown in Figure 5, PSA showed good recoveries for thidiazuron (100.6%), forchlorfenuron (90.1%), and paclobutrazol (82.2%) but not good enough recoveries for GA_3 (52.3%) and 2,4-D (62.5%). This result may be associated with an anion-exchange

dx.doi.org/10.1021/jf204183d | J. Agric.Food Chem. 2012, 60, 60−65

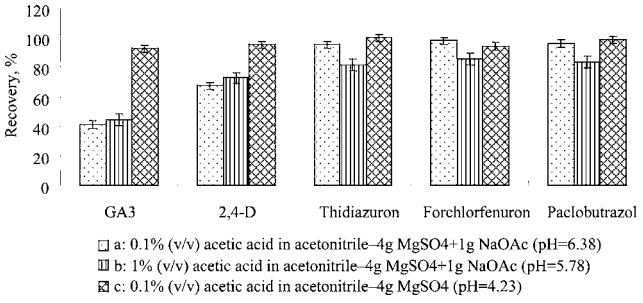

Figure 4. Effect of pH of the extraction on the recoveries of the five target PGRs spiked at 100 μg/kg: (a) 0.1% (v/v) acetic acid in acetonitrile−4 g of $MgSO_4$ + 1 g NaOAc (pH 6.38), (b) 1% (v/v) acetic acid in acetonitrile−4 g of $MgSO_4$ + 1 g of NaOAc (pH 5.78), (c) 0.1% (v/v) acetic acid in acetonitrile−4 g of $MgSO_4$ (pH 4.23) (n = 3) .

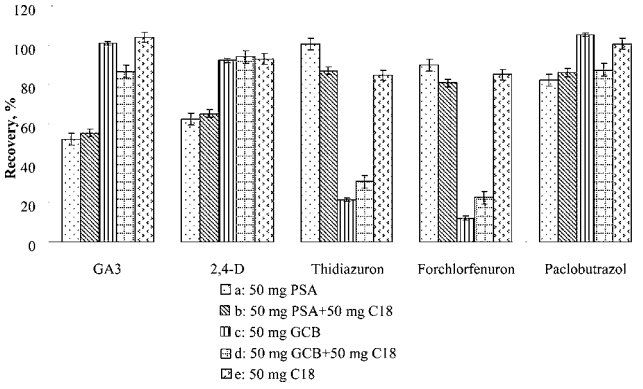

Figure 5. Effect of dispersive sorbents on the recoveries of the five PGRs spiked at 100 μg/kg: (a) 50 mg of PSA, (b) 50 mg of PSA + 50 mg of C18, (c) 50 mg of GCB, (d) 50 mg of GCB + 50 mg of C18, and (e) 50 mg of C18 (n = 3).

capacity between PSA and GA_3 and 2,4-D, which had a carboxyl group.[30,31] GCB showed good recoveries for GA_3 (101.3%), 2,4-D (92.4%), and paclobutrazol (105.3%) but not good recoveries for thidiazuron (21.6%) and forchlorfenuron (12.2%). The losses in recoveries up to 70% for thidiazuron and forchlorfenuron were possibly attributed to the strong retention between the GCB sorbents and phenylurea PGRs.[32] C18 is a nonpolar sorbent that more effectively retains trace amounts of lipids, cholesterol, sterols, vitamins, and other complex components from the extract.[33,34] Comparatively, C18 provides good recoveries (85−104%) for all target PGRs and, thus, was selected as the clean sorbent for the purification procedure in this study.

3.3. Method Validation. In this study, calibration curves were prepared using matrix-matched standard samples. Wide linear ranges were 10−1000 μg/L for GA_3 and 5−500 μg/L for the other four PGRs. All correlation coefficients (r^2) were bigger than 0.998. As shown in Table 2, satisfactory method recoveries were obtained for the PGRs spiked at three concentration levels in orange samples [83−109%, relative standard deviation (RSD) < 10%], apple samples (76−112%, RSD < 8%), and grape samples (78−106%, RSD < 7%). The limits of detection (LODs) and quantification (LOQs) of the target PGRs were estimated by analyzing spiked samples at low concentrations. LODs and LOQs were calculated on the basis of a peak−peak signal-to-noise (S/N) value that was S/N = 3 and 10, respectively. LOQs (0.5−16.5 μg/kg) were lower than the maximum limit of residues established for PGRs. The LOQs were several times lower than those obtained using the LC−MS/MS method developed by Banerjee et al.[21−25,35,36]

3.4. Applications of the Method. The modified QuEChERS method was successfully applied to the determination of PGR residues in 79 fruit samples from a market in Beijing, China, in 2010, and the concentrations of detected analytes were listed in Table 3 and Table S1 of the Supporting Information. As shown in Table 3 and Table S1 of the Supporting Information, 58 fruit samples detected the analytes, which indicated that PGRs were widely used in the pre-harvest treatment to control a wide variety of fruits. In this study, paclobutrazol was detected in all peach samples (n = 30) with concentrations between 1.0 and 1381 μg/kg. Similarly, 2,4-D was detected in all orange samples (n = 9), and the relatively high concentration ranged from 5.1 to 1503 μg/kg. It can be concluded that the presence and levels of 2,4-D in orange and paclobutrazol in peach should be a matter of concern in China in the future.

Table 2. Average Recoveries (%), Repeatability (% RSD), and LOD and LOQ (μg/kg) Obtained with the Modified QuEChERS Method in Orange, Apple, and Grape Samples (n = 3)

		recovery percentage (% RSD)				
analyte	spiking levels (mg/kg)	orange	apple	grape	LOD	LOQ
	0.1	96.2 (7.0)	86.2 (3.0)	89.5 (4.8)		
GA_3	0.2	102.3 (2.7)	112.0 (1.8)	85.4 (4.6)	5.0	16.5
	0.4	89.9 (4.6)	87.2 (3.0)	98.4 (1.5)		
	0.005	91.3 (8.1)	84.9 (2.7)	78.2 (3.8)		
2,4-D	0.01	108.5 (1.9)	111.2 (2.8)	80.1 (4.4)	1.0	3.3
	0.02	89.0 (4.1)	86.8 (3.4)	95.1 (2.5)		
	0.005	91.0 (2.6)	76.0 (1.4)	84.0 (1.8)		
thidiazuron	0.01	108.1 (1.8)	103.2 (1.7)	80.9 (2.0)	0.3	0.5
	0.02	90.2 (2.8)	79.9 (6.3)	89.8 (2.2)		
	0.005	83.3 (6.2)	86.0 (2.5)	82.0 (4.8)		
forchlorfenuron	0.01	109.1 (0.8)	108.5 (2.5)	80.1 (4.6)	0.4	1.2
	0.02	85.0 (6.7)	87.3 (3.0)	94.3 (1.1)		
	0.005	102.9 (10.4)	85.3 (8.0)	105.1 (3.7)		
paclobutrazol	0.01	103.8 (2.1)	93.2 (4.9)	95.8 (7.3)	0.5	1.6
	0.02	91.8 (2.2)	80.3 (1.9)	106.2 (5.7)		

dx.doi.org/10.1021/jf204183d | J. Agric.Food Chem. 2012, 60, 60−65

Table 3. Concentration Levels of Five Target PGRs in Fruit Samples from a Market in Beijing, China, in 2010 (μg/kg)

			concentration detected (μg/kg)				
sample	number of samples	samples with PGR residues	GA_3	2,4-D	thidiazuron	forchlorfenuron	paclobutrazol
apple	5	2 (40%)	*a*	*a*	1.5−2.3	*a*	1.3
pear	5	1 (20%)	*a*	*a*	*a*	*a*	2.7
grape	5	2 (40%)	*a*	3.6−4.8	*a*	1.2−13.3	*a*
orange	9	9 (100%)	*a*	5.1−1503.0	*a*	*a*	*a*
mango	5	3 (60%)	*a*	4.8−6.3	1.6	*a*	2.6
kiwifruit	5	2 (40%)	*a*	3.7	*a*	2.1−3.7	*a*
watermelon	5	3 (60%)	*a*	*a*	1.4	3.5−4.4	*a*
peach	30	30 (100%)	16.5−20.0	*a*	*a*	*a*	1.0−1381
cherry	10	4 (40%)	*a*	*a*	*a*	*a*	1.7−68.7

[a]Under the LOQ.

In conclusion, in the present study, a rapid and sensitive method for the simultaneous determination of five PGRs in fruit samples by modified QuEChERS extraction and LC−MS/MS was developed. The optimal sample preparation procedure involved the following steps: (1) 10 mL of acetonitrile with 0.1% (v/v) acetic acid were used for extraction; (2) 4 g of anhydrous magnesium sulfate was added for partitioning; and (3) finally, 50 mg of C18 was employed as dispersive sorbents to purify the samples. This method was validated with fortified samples, and good recoveries with excellent RSD were obtained. The high concentrations of 2,4-D and paclobutrazol detected in orange and peach indicated that more attention should be paid to the safe use of PGRs in China.

■ ASSOCIATED CONTENT

Supporting Information

Concentrations of five target PGRs in fruit samples from a market in Beijing, China, in 2010 (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Telephone: 010-82106570 (F.J.); 010-82106568 (J.W.). E-mail: jinfenbj@163.com (F.J.); w_jing2001@126.com (J.W.).

Funding

Financial support from the National Key Technology R&D Program of China (2009BADB7B04) and the National Natural Science Foundation of China (21107138) is gratefully acknowledged.

■ REFERENCES

(1) Zhang, Y. B.; Zhang, Y.; Wu, X. Y. *New Progress in the World Pesticides*, 2nd ed.; Chemical Industry Press: Beijing, China, 2010; p 25.

(2) http://www.apvma.gov.au/residues/ (accessed Aug 2011).

(3) http://www.epa.gov/pesticides/food/viewtols.htm (accessed Aug 2011).

(4) https://secure.pesticides.gov.uk/MRLs/ (accessed Sept 2011).

(5) http://www.tbtsps.com/foodsafe/xlbz/Pages/japan.aspx (accessed Sept 2011).

(6) Swiader, J. M.; Ware, G. W. *Producing Vegetable Crops*, 5th ed.; Interstate Publisher, Inc.: Danville, IL, 2002.

(7) Rademacher, W.; Brahm, L. *Plant Growth Regulators*, 1st ed.; Wiley-VCH Verlag GmbH and Co. KgaA: Weinheim, Germany, 2002.

(8) Xie, W.; Han, C.; Zheng, Z. Q.; Chen, X. M.; Qian, Y.; Ding, H. Y.; Shi, L.; Lv, C. H. *Food Chem.* **2011**, *127*, 890−892.

(9) Sancho, J. V.; Pozo, O. J.; Zamora, T.; Grimalt, S.; Hernández, F. *J. Agric. Food Chem.* **2003**, *51*, 4202−4206.

(10) Cunha, S. C.; Fernandes, J. O.; Alves, A.; Oliveira, M. B. P. P. *J. Chromatogr., A* **2009**, *1216*, 119−126.

(11) Park, J. Y.; Choi, J. H.; Abd El-Aty, A. M.; Kim, B. M.; Oh, J. H.; Do, J. A.; Kwon, K. S.; Shim, K. H.; Choi, O. J.; Shin, S. C.; Shim, J. H. *Food Chem.* **2011**, *128*, 241−253.

(12) Koesukwiwata, U.; Sanguankaewa, K.; Leepipatpiboona, N. *Anal. Chim. Acta* **2008**, *626*, 10−20.

(13) Wang, J.; Leung, D.; Chow, W. *J. Agric. Food Chem.* **2010**, *58*, 5904−5925.

(14) Mezcua, M.; Malato, O.; García-Reyes, J. F.; Molina-Díaz, A.; Fernández-Alba, A. R. *Anal. Chem.* **2009**, *81*, 913−929.

(15) Ramalhosa, M. J.; Paíga, P.; Morais, S.; Delerue-Matos, C.; Oliveira, M. B. P. P. *J. Sep. Sci.* **2009**, *32*, 3529−3538.

(16) Mastovska, K.; Lightfield, A. R. *J. Chromatogr., A* **2008**, *1202*, 118.

(17) Keegan, J.; Whelan, M.; Danaher, M.; Crooks, S.; Sayers, R.; Anastasio, A.; Elliott, C.; Brandon, D.; Furey, A.; O'Kennedy, R. *Anal. Chim. Acta* **2009**, *654*, 111−119.

(18) Stubbings, G.; Bigwood, T. *Anal. Chim. Acta* **2009**, *637*, 68−78.

(19) Akiyama, Y.; Matsuoka, T.; Mitsuhashi, T. *J. Pestic. Sci.* **2009**, *34*, 265−272.

(20) Potter, T. L.; Marti, L.; Belflower, S.; Truman, C. C. *J. Agric. Food Chem.* **2000**, *48*, 4103−4108.

(21) Banerjee, K.; Oulkar, D. P.; Dasgupta, S.; Patil, S. B.; Patil, S. H.; Savant, R.; Adsule, P. G. *J. Chromatogr., A* **2007**, *1173*, 98−109.

(22) Valverde, A.; Aguilera, A.; Ferrer, C.; Camacho, F.; Cammarano, A. *J. Agric. Food Chem.* **2010**, *58*, 2818−2823.

(23) Romero-González, R.; Garrido Frenich, A.; Martínez Vidal, J. L. *Talanta* **2008**, *76*, 211−225.

(24) Sannino, A.; Bolzoni, L.; Bandini, M. *J. Chromatogr., A* **2004**, *1036*, 161−169.

(25) Hou, S. J.; Zhu, J.; Ding, M. Y.; Lv, G. H. *Talanta* **2008**, *76*, 798−802.

(26) Ma, Z.; Ge, L. Y.; Lee, A. S. Y.; Yong, J. W. H.; Tan, S. N.; Ong, E. S. *Anal. Chim. Acta* **2008**, *610*, 274−281.

(27) Rogis, C.; Gibson, L. R.; Knapp, A. D.; Horton, R. *Crop Sci.* **2004**, *44*, 549−552.

(28) Anastassiades, M.; Scherbaum, E.; Tasdelen, B.; Štajnbaher, D.; Ohkawa, H.; Miyagawa, H.; Lee, P. W. *Crop Protection*; Public Health, Environmental Safety, Wiley-VCH: Weinheim, Germany, 2007; pp 439−458.

(29) Lehotay, S. J.; Son, K. A.; Kwon, H.; Koesukwiwat, U.; Fu, W. S.; Mastovska, K.; Hoh, E.; Leepipatpiboon, N. *J. Chromatogr., A* **2010**, *1217*, 2548−2560.

(30) Mastovska, K.; Dorweiler, K. J.; Lehotay, S. J.; Wegscheid, J. S.; Szpylka, K. A. *J. Agric. Food Chem.* **2010**, *58*, 5959−5972.

(31) Banerjee, K.; Oulkar, D. P.; Patil, S. B.; Jadhav, M. R.; Dasgupta, S.; Patil, S. H.; Bal, S.; Adsule, P. G. *J. Agric. Food Chem.* **2009**, *57*, 4068−4078.

(32) Gilbert-López, B.; García-Reyes, J. F.; Lozano, A.; Fernández-Alba, A. R.; Molina-Díaz, A. *J. Chromatogr., A* **2010**, *1217*, 6022−6035.

(33) Koesukwiwat, U.; Lehotay, S. J.; Mastovska, K.; Dorweiler, K. J.; Leepipatpiboon, N. *J. Agric. Food Chem.* **2010**, *58*, 5950−5958.
(34) Koesukwiwat, U.; Lehotay, S. J.; Miao, S.; Leepipatpiboon, N. *J. Chromatogr., A* **2010**, *1217*, 6692−6703.
(35) Huang, Z. Q.; Zhang, Y.; Wang, L. B.; Ding, L.; Wang, M. L.; Yan, H. F.; Li, Y. J.; Zhu, S. H. *J. Sep. Sci.* **2009**, *32*, 1294−1301.
(36) Park, S.; Lee, S. J.; Kim, H. G.; Jeong, W. Y.; Shim, J. H.; Abd El-Aty, A. M.; Jeong, S. W.; Lee, W. S.; Kim, S. T.; Shin, S. C. *J. Sep. Sci.* **2010**, *33*, 493−501.