Analytical Methods

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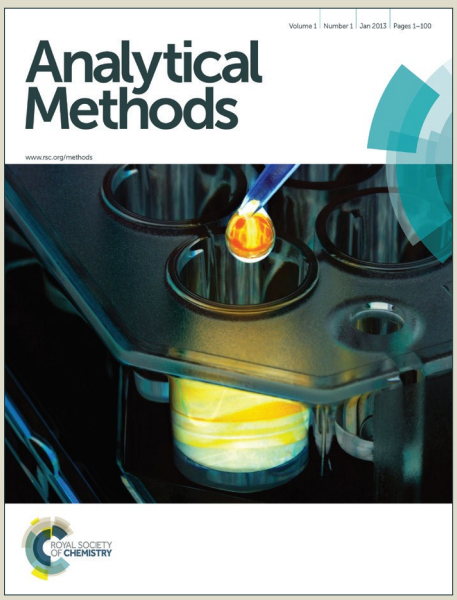

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ARTICLE

Simultaneous determination of seven insecticides in soft drinks and fruit juices using ultraperformance liquid chromatography tandem mass spectrometry with Product Ion Confirmation Scan mode

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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An analytical method for the simultaneous determination of seven insecticides, including six neonicotinoids and one pyridine-azomethine, in drinks by LC-MS/MS using Product Ion Confirmation Scan (PICS) mode was developed and validated. The compounds were extracted by modified QuEChERS and purified by d-SPE. The separation of all compounds was achieved in less than 3 minute using a BEH C18 reverse-phase column and a mobile phase composed of 0.01% formic acid in water and methanol in gradient elution mode at 0.4 mL/min. Except for the two transitions and retain time demanded by EU/2002, identification was further carried out by the match of mass spectrum between reference and sample produced by PICS if necessary. The LODs and LOQs for all compounds were lower than 0.014 μg/L and 0.05 μg/L, respectively. The calibration curves were ranging from the LOQ to 0.02 mg/L with r^2 higher than 0.9917 and reasonable recoveries were between 81.19 % and 105.79% with RSD <15.0%. This work illustrates the advantages of using the PICS mode to build MRM acquisition methods in the application field of pesticide multi-residues analysis. It is very effective when the only one MRM transition was obtained or the confirmation ion transition was too weak. It was proved that this is a rapid and reliable analytical method.

Introduction

Soft drink and fruit juice are the most widely consumed beverages in the world [1]. Soft drinks are water-based flavored drinks and typically contain carbon dioxide and sweeteners. The sweeteners are usually sugar, high-fructose corn syrup, fruit juice, sugar substitutes or some combination of these. Others, such as nutritive and extract from herbs, also have been added for the purpose of nutrition and health. Fruit juices are the unfermented products obtained from fruit which is sound and ripe, fresh or preserved. Fruit juices rich in folate, magnesium, witamins A, C, and K, and essential for disease prevention. Today, various soft drinks and fruit juices, such as Coca-Cola, green tea, juices, herbal tea, and so on, are consumed in daily time for the purpose of health. However, because of wide usage of pesticides in agriculture, diet also becomes an important source of exposure to pesticides.

Neonicotinoids are the most commonly used insecticides in the world following the organochlorine, organophosphorus, carbamate and pyrethroid [2]. As one of the fastest growing new generation of insecticides, neonicotinoids have contributed to a significant reduction of toxicity for the environment because of high efficiency and selectivity [3]. Neonicotinoid insecticides act as agonists at the insect nicotinic acetylcholine receptor (nAChR), which cause a blockage of signal transmission and result in insect paralysis to death. This class of pesticides is commonly used to against aphides, whiteflies and some lepidoptera species in various stages of cultivation and during postharvest storage [4]. The distinct advantages of neonicotinoids are the absence of cross-resistance to longer-established insecticide classes and against which many pests have developed resistances over the years [5-6]. Pymetrozine is the only representative of the pyridine azomethines and being developed worldwide for control of aphids and whiteflies similar to neonicotinoids. Nevertheless, both neonicotinoids and pyridine azomethines were showed toxicity and biochemical changes [7].

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Some neonicotinoids, such as thiamethoxam and imidacloprid, have been reported negative effects on human health by recent toxicological studies [8-9]. Furthermore, pymetrozine and neonicotinoids, as polar compounds, can be easily released from fruits, tea leaves and other dry plants into the drinkable infusions during the juicing process. This increase the health risks from pesticide residues in drink stuff. To ensure consumer health and safety, many countries and international organizations have defined maximum residue levels (MRLs) for several neonicotinids in vegetable, tea, honey and beeswax [10-11]. While MRLs of juices have not been set up by the China Food and Drug Administration and a guide for the authorities to make their decision regarding MRLs for juice is required in the forthcoming future.

Several pre-treatment methods for determining neonicotinoids in soft drinks and fruit juices have been reported, such as matrix solid-phase dispersion (MSPD) [34], hollow fiber microporous membrane liquid- liquid extraction [35], Ionic Liquid-Based Vortex-Assisted Liquid–Liquid Microextraction (ILBV-LLME) [36] and Vortex-assisted surfactant-enhanced-emulsification liquid-liquid mocroextraction with solidification of floating organic droplet (VSLLME-SFO) [37]. However, these methods are tedious and time-consuming, or detecting less neonicotinoid compounds. A treatment named QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) has been introduced in 2003, and showed to be a powerful technique in analysis of pesticide residues in foodstuffs. QuEChERS methodology presents some advantages, such as its simplicity, minimum steps, and effectiveness for cleaning-up complex samples [38]. So a modified QuEChERS has been used in this study.

Although certain analytical approaches, such as enzyme-linked immune-sorbent assays (ELISA) [12], electrochemical [13] and GC-MS [14] methods, have been employed to analyze this group of compounds, liquid chromatography (LC) method using C 18 based analytical columns are usually taken into consideration because of the low volatility and high polarity [15-18]. Diode array (DAD) detection [15-16] and mass detection (MS) [17-18] are two frequently detections used to combined with LC in single and multiple neonicotinoids analysis. LC-DAD is useful in the determination because of none matrix effect, but limited sensitivity is an obstacle. LC-MS in SIM mode improved the sensitivity relative to LC-DAD [19], but still fail than LC-MS/MS in MRM mode. According to the European Commission Decision 2000/657/EC two transitions (corresponding to one precursor ion and two product ions) have to been needed in order to achieve four identification points when LC-MS/MS were used. However, if only one transition can be obtained, accurate identification has not been realized. Recently, highly efficient ultraperformance liquid chromatography combined with tandem mass spectrometry (UPLC-MS/MS) method has been successfully introduced to determine multi-neonicotinoids in MRM mode [20]. UPLC uses columns with 1.7μm diameter particles which can operate at higher back pressures. This technique generates higher chromatographic performance and improves the resolution, speed and sensitivity [21]. UPLC coupled with MS/MS in MRM mode can be used as one of the most promising techniques for the analysis of pesticide residues in food and other matrices. In this paper, UPLC-MS/MS with Product Ion Confirmation Scan (PICS) has been firstly used for simultaneous determination of the six neonicotinoids and one pyridine-azomethine.

The goal of this study was to develop a method for identification and quantification of seven insecticide residues in drinks using modified QuEChERS and UPLC-MS/MS. PICS has been used to build MRM acquisition methods to realize the accurate identification for compounds with not perfect MS conditions have been obtained. To the best of our knowledge, this is the first time that PICS mode has been used in the application field of neocicotnoid residues analysis. The method was development and validated using several artificially spiked samples of different drinks and proved to be rapid, sensitive and rugged. The proposed method is an alternative approach to analysis of neonicotinoids and being more reliable and promising in multi-residues analysis.

Results and discussion

Optimization of MS/MS

The analysis of pesticides using liquid chromatography triple quadrupole mass spectrometer is commonly performed by MRM mode. The European Commission Decision 2002/657/EC introduced the concept of identification points (IPs) for the confirmation and identification strategy [23-24]. According to this reference and LC-MS/MS configuration, analysis using two ion transitions allows safety confirming the identity of the compound which resulting in four IPs (one IP for precursor ion and 1.5 IP per each product ions). Thus, for confirmation purposes, at least two transitions must be recorded. Meanwhile, an increase in the limits of detection must be occurs when the second transition is less abundant [25]. Usually, transitions from the most abundant precursor to the most abundant product ions are selected. Small fragments with m/z ratios of < 80 were generally omitted if alternative product ions are available [25-26]. Kmellár [27] also concluded that higher background noise would be observed for low masses. In this study, for acetamiprid, only two transitions have been obtained and the second product ion is m/z 56 which is much smaller than 80. Furthermore, for the transitions of imidaclothiz, the abundant of the secondary trace (262.03>180) is much less than the primary trace (262.03>181) and dramatically increased the LOD (see Fig.1).

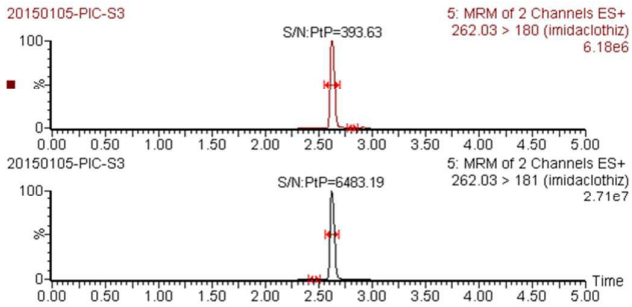

Fig. 1. MRM chromatograms of imidaclothiz at 10 µg/L (s/n for 262.03>181 is 6483, s/n for 262.03>180 is 394)

In this case, PICS mode was introduced. PICS, as a new technology, were composed of MS scan, daughter scan, scanwave MS scan and scanwave daughter scan. Daughter scan and scanwave daughter scan are used for identification purpose among them. Daughter scan would be used when the target response intensity is over background noise level threshold during MRM acquisition. If not, scanwave daughter scan would be selected. Match of mass spectrum between reference and sample produced by PICS mode was performed to identify the compound except for retention time and quantification ion. The PICS mass spectrum monitored for acetamiprid and imidaclothiz are given in Fig. 2. PICS will be more useful for confirming thepesticides with the secondary trace cannot be obtained, such as acephat, oxamyl, carbendazim and spinosyn D [27-28]. Further experiments will be performed to extend to these compounds for the purpose of a fully test for the method.

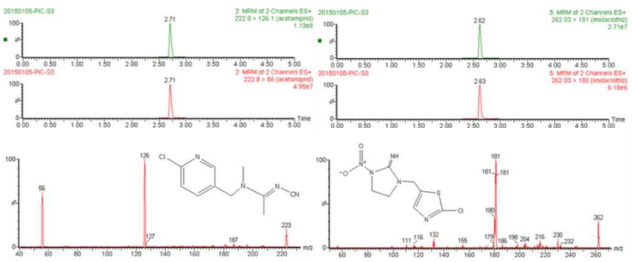

Fig.2. PICS mass spectrum for acetamiprid and imidaclothiz (spiking in 1.0 µg/L)

Optimization of chromatography

In order to achieve good separation of seven compounds with high sensitivity and unambiguous identification, several experiments were conducted. Reversed phase chromatography was used based on the published works [15-18]. The most commonly used mobile phases were component mixtures of water with acids (acetic acid and formic acid) or salts (ammonium acetate) and organic solvents like methanol or acetonitrile. In this work, an UPLC system has been employed with high throughput and fast separation. The optional separation conditions were established by injecting 5 µL of the seven insecticides mixture working standard solutions with the concentration level of 1 µg/L, on the BEH C18 column (50mm×2.1mm, 1.7µm particle size). Mobile phase composed of acetionitrile and 0.1% formic acid was evaluated as the starting condition for optimizing the LC parameters because of the frequent use in published works [19]. The results showed that all seven compounds were well separated in less than 5 min. However, wide peak shapes with peak width more than 15 ms were obtained for all insecticides and pymetrozine suffers to a serious solvent effect due to its higher polarity.

Hence, it was decided to change the organic modifier and use the methanol instead of acetonitrile. After several tests, a full separation of the seven compounds has been obtained under the condition of methanol-water with 0.01% formic acid, by using the gradient elution program mode proposed in Section 2.2. The compounds were eluted in the following order: pymetrozine, thiamethoxam, nitenpyram, imidacloprid, acetamiprid, thiacloprid and imidaclothiz. As shown in Table.1, the analysis time of the seven insecticides were less than 3.0 min. Especially, the use of Acquity UPLC BEH C18 column in this study allowed a considerable reduction of LC analysis time for seven compounds compared with reference [19] (25 min) and reference [17] (12min).

Optimization of extraction and purification procedure

Acetonitrile is the most commonly used solvent for sample preparation in QuEChERS method due to its distinct properties [17]. Some buffering agents, such as 0.25%(v/v) formic acid [29] and 1% (v/v) acetic acid [30], have been added into acetonitrile to extract and partition the neonicotinoids in modified QuEChERS. In order to ensure the best extraction efficiency for the matrices in this work, all of the three solvents, including pure acetonitrile, 0.25% formic acid in acetonitrile and 1% acetic acid in acetonitrile, have been evaluated. The results show that there were no significant differences in recoveries. However, acetonitrile with 1% acetic acid has been selected as the final extraction solvent because of better RSD valves relative to other solvents.

Furthermore, in order to reduce the interference from the acidity of the samples, NaOAC has been compared to the conventional NaCl in designing of the sample extraction procedure. All seven compounds were not significantly affected by the nature of buffered salts, as showed in Fig.3(A). However, the recovery values of NaOAC were more close to the actual values than NaCl. Thus, NaOAC was used in all further experiments.

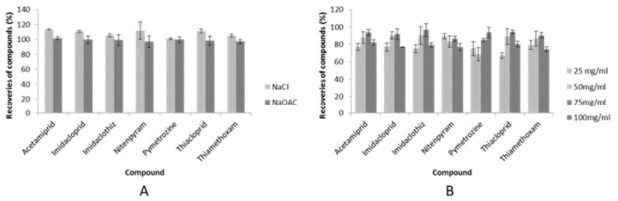

Fig.3. Recoveries of insecticides using different extraction methods and clean-up methods for compound (10 ng/mL) fortified in blank tea samples (n=5). A Different salts. B Different amount of PSA sorbents.

Besides, to obtain satisfying cleanup effect for pretreatment, two common types of sorbent, PSA and GCB, were evaluated in this work. GCB at a level of 10 mg/mL was firstly selected because of its stronger adsorptions to pigments and carotenoids [24]. PSA has been reported to remove the organic acids, fatty acids and sugars which are main additive in juice samples [24]. In the traditional QuEChERS method, PSA was used as adsorbent at a level of 25 mg/mL [31]. However, because there are more sugars and organic acids in drinks, this amount of PSA may not enough to remove the impurities. Therefore, the amount of PSA has been evaluated. As indicated in Fig.3(B), a satisfactory purification effect and recoveries of the targets were obtained when 75 mg/mL PSA combined with 10 mg/mL GCB have been used.

Method validation

The method was validated for seven different insecticides. Three matrices, for example, green tea, orange juice and herbal tea, have been selected as the test samples. The validation was performed according to a scheme in which spiked samples have been used. Samples free of target insecticides were selected as the blank samples for spiking.

The calibration curves for all of the compounds in pure solvent and in blank matrix were constructed by plotting the analyte peak areas obtained against the corresponding concentration values at seven calibration levels ranging from the LOQ to 0.02 mg/L. The linearity of calibration curve was expressed by the correlation coefficient (r^2). Satisfactory linearity was obtained for all the compounds with r^2 higher than 0.9917 in the linear range. The results are summarized in Table 2. A rough limit of detection (LOD) values and Limits of quantification (LOQ) values were evaluated by injection of matrix-matched standard solutions at the lowest concentration levels that yielded a signal to background noise (S/N) ratio of three and ten, respectively. The LODs and LOQs obtained for each insecticide are shown in Table 2.

Table 2. Calibration curves, LOD, LOQ and matrix effect.

a solvent; b green tea; c herbal tea; d orange juice; e values of matrix effect

It can be observed that LODs and LOQs for all compounds were lower than 0.014 μg/L and 0.05 μg/L, respectively. As previously seen, few studies have been published in which neonicotinoid insecticides were determined in soft drink and juice. If the comparison is extended to the limits calculated for neonicotinoid insecticides in other products, such as crops [32], honey [17], beewax [19], grains [29], and soil [30], the excellent sensitivity achieved with the proposed method has been demonstrated (LODs 0.2-0.85μg/kg [32], LODs 0.6-10 μg/kg [17], LODs 0.4-2.3μg/kg [19], LODs 2-5μg/kg [29], LODs 2-9μg/kg [30]). Furthermore, MRL for acetamiprid (1 mg/kg in orange, 0.1 mg/kg in tea), pymetrozine (0.3 mg/kg in orange, 0.01 mg/kg in tea) and thiamethoxam (0.2 mg/kg in orange, 0.1 mg/kg in tea) in orange and tea set up by EU/2008 have also been compared. While, it must be stated that it is not a true comparison because the matrix usually plays an important role when using MS detection. As indicated in Table 2, a strong matrix effect has been found for all compounds except for nitenpyram and pymetrozine.

The matrix effect of the proposed method was calculated by the ratio of the slopes for the calibration curves obtained in matrices (sample free of pesticides) and in pure standard solutions (chromatographic mobile phase). Thus, an accurate quantification of the insecticides required the use of matrix-matched calibration curves. The accuracy and precision of the proposed method were evaluated by spiking blank sample at 0.005, 0.01 and 0.02 mg/L concentration levels. Percentage recoveries ranged from 81.19 % to 105.79% with RSD <15.0% for all compounds have been obtained. The results in Table 3 provide evidences that the optimized method achieves acceptable recoveries in line with criteria set by the DGSANCO/2007/3131 of the European Quality Control Guidelines: 70–120% [33].

Table 3 Recoveries (%) and RSD (%, n=3) of the target compounds in different matrices at three spiked levels.

aRSD, intra-day RSD (n=3); bRSD, inter-day RSD (n=3).

Application to real samples

The developed method was applied to the analysis of 9 commercial samples purchased from local supermarket (Changchun, Jilin, China). No target insecticide has been detected in any of the samples analyzed. The applicability of the proposed method on the samples was also demonstrated by spiking the samples at different concentrations. The results were shown in Table 3. The average recoveries and RSDs of analyzed samples were fulfilled the SANCO criteria.

Experimental

Materials and chemicals

The reference standards for pymetrozine [CAS# 123312-89-0] and nitenpyram [CAS# 150824-47-8] were purchased from Dr. EhrenstorferGmbH (Germany). Acetamiprid [CAS# 135410-20-7], imidaclothiz [CAS# 105843-36-5], imidacloprid [CAS# 138261-41-3], thiacloprid [CAS# 111988-49-9] and thiamethoxam [153719-23-4] were purchased from Beijing North Research Institute of Chemical Substances (Beijing, China). All of the reference standards were >98% purity. The following HPLC grade solvents, including acetonitrile and methanol were purchased from Fisher Scientific (Beijing, China) and used without further purification. The HPLC grade acetic acid and LC-MS/MS grade formic acid were purchased from Aladdin (Shanghai, China) and ultrapure water was generated by a Milli-Q laboratory water purification system (Siemens, Germany). ACS grade anhydrous magnesium sulfate ($MgSO_4$), anhydrous sodium acetate (NaOAC) and sodium chloride (NaCl) were purchased from Beijing Chemical Factory (Beijing, China). Anhydrous magnesium sulfate ($MgSO_4$) was activated by heating at 650℃ for 4 h and sodium chloride at 105℃ for 4 h before use and kept in desiccator. Bulk sorbents (50 μm particle size) for dispersive-SPE, including primary secondary amine (PSA) and graphitized carbon black (GCB) were purchased from Sigma–Aldrich (USA).

Instrumentation and UPLC-MS/MS conditions

Method development and validation were executed on a Waters TQS triple quadrupole mass spectrometry (Waters, Manchester, USA) coupled with an Acquity UPLC system (Waters, Milford, MA, USA) controlled with the Masslynx v4.1 software. The system consists of an Iclass binary solvent pump with the max pressure-tolerant 15000 psi. Chromatographic separations were achieved using an Acquity UPLC BEH C18 column (50 mm×2.1 mm, 1.7 μm particle size) from Waters at a flow rate of 0.4 mL/min. The mobile phases were consisted of H_2O with 0.01% formic acid (A) and MeOH (B). The gradient was 5% B at 0 min, 40% B at 2 min, 95% B at 2.1 min, 95% B at 3.0 min, 5% B at 3.2 min. The post time was 1.8 min and the stop time 5 min. Injecting volume was 5.0 μL throughout this work.

Mass spectrometry analysis was carried out using a multiple reaction monitoring (MRM) analyzer set-up with PICS mode. The instrument was operated using an electrospray ionization (ESI) source in positive mode. ESI parameters were: capillary voltage 3.0 kV, extractor voltage 2 V, source temperature 150 ℃, desolvation temperature 350 ℃, cone gas (nitrogen) flow 60 L/h and desolvation gas (also nitrogen) flow 700 L/h. Collision-induced dissociation was performed using argon as the collision gas at the flow rate of 0.15 mL/min in the collision cell. The specific MS/MS parameters for each analyte are shown in Table 1. The PICS has been used for acetamiprid and nitenpyram with daughter scan function. The activation threshold was 20 and minimum threshold 500000. The collision energy was 14 eV and 10 eV, respectively, according to the infusion experiments by the target insecticides.

Table 1 UPLC-MS/MS parameters and molecular weight for the insecticides investigated

a collision energy for primary trace, b collision energy for secondary trace, c calculated by MRM transitions, d calculated by precursor ion to product ion

Compounds identification

The identification procedure for LC-TQ-MS/MS was based on the retention time and two transitions according to EU/2002. In the present paper, the MS analysis was carried out by traditional MRM combined with PICS mode. Retention time, two transitions and the MRM ratio of the transitions were selected as the identification factors. For acetamiprid and nitenpyram, product ion spectrum obtained by PICS has been used as a supplementary measure except for the secondary trace. The match of the ion ratios calculated by the precursor ion and product ion was used for the purpose of confirmation. The ion-ratio statistics for the transitions monitored was based on the DG SANCO European Quality Control guide lines.

Sample treatment

Three classes of drinks under investigation including green tea, orange juice and herbal tea were obtained from different supermarkets in Changchun city (Jilin, China). Seven insecticides were extracted from the samples using a procedure similar to the modified QuEChERS [22]. Briefly, 5 mL of the samples was put into a 50 mL Teflon centrifuge tube. Then, 5 mL of acetonitrile (acetic acid 1%) was added into the tube and the mixture was shaken vigorously for 1 min using a vortex mixer. After that, a mixture of 4 g of anhydrous $MgSO_4$ and 1 g of NaOAC was added into the tube. The tube was shaken vigorously by vortex mixer for 1 min and centrifuged for 5 min at 3500 rpm and 4 ℃. After standing to room temperature, an aliquot of 2 mL upper latter was transferred into a 5 mL microcentrifuge vial containing 300 mg $MgSO_4$, 150 mg PSA and 20 mg GCB. The vial was vigorously shaken for 1 min and centrifuged for 5 min at 3500 rpm and 10 ℃. One milliliter of the supernatant was evaporated to dryness at 30 ℃ under a gentle stream of nitrogen. The residue was redissolved in 1 mL of methanol/water 10:90 (v/v) and subjected to UPLC-MS/MS analysis.

Conclusions

This work demonstrates the advantages of PICS mode in the application field of pesticide multi-residues analysis. It is very effective in compound identification when the only one MRM transition was obtained or the confirmation ion transition was too weak. More importantly, for the first time, this work introduced PICS mode into residues analysis, and proved to be a valuable tool for further avoiding false positive. Meanwhile, the linearity, matrix effect, LOD, recovery and reproducibility were studied in three matrices, namely green tea, orange juice and herbal tea.. The results show that it was feasible to quantify and identify seven insecticides in drinks. This method provided high sensitivity, selectivity and efficiency and thus had a promising potential to play an enhanced role in multi-residue analysis. So further experiments will be performed to extend the pesticides in both kind and level to achieve a fully test for the method. It will be expected to expand the application of this new technology.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No.31170326, 31370374), team project of Jilin Provincial Science, Technology Department (No.20130413043 GH) and Natural Science Foundation of Changchun Normal University.

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Table 1 UPLC-MS/MS parameters and molecular weight for the insecticides investigated

Compound	Molecular formula	Molecular weight	Retain time (min)	Precursor ion (m/z)	Primary ion (m/z)	Secondary ion (m/z)	Cone voltage (kV)	CE[a] (eV)[a]	CE[b] (eV)[b]	Ion ratio
Acetamiprid	$C_{10}H_{11}ClN_4$	222.68	1.75	222.8	126.1	56	14	18	15	0.20[c]
Imidacloprid	$C_9H_{10}ClN_5O_2$	255.66	1.62	256.1	175.1	209.1	20	19	16	1.03[d]
Imidaclothiz	$C_7H_8ClN_5O_2S$	261.50	2.11	262.03	181	180	17	17	13	0.30[c]
Nitenpyram	$C_{11}H_{15}ClN_4O_2$	270.72	1.42	271.2	225.17	99.05	20	10	15	1.65[d]
Pymetrozine	$C_{10}H_{11}ClN_5O$	217.23	0.79	217.9	105	79	20	18	30	3.1[d]
Thiacloprid	$C_{10}H_9ClN_4S$	252.72	1.99	253	126	90.1	30	20	37	6.03[d]
Thiamethoxam	$C_9H_{10}ClN_5O_2$	291.71	1.36	292	211	132	14	13	23	1.04[d]

[a] collision energy for primary trace, [b] collision energy for secondary trace, [c] calculated by MRM transitions, [d] calculated by precursor ion to product ion

Table 2 Calibration curves, LOD, LOQ and matrix effect.

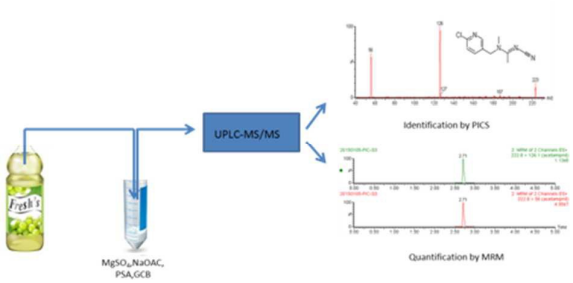
Compound	r^2				LOD (μ g/L)				LOQ (μ g/L)				ME[e]		
	S[a]	M1[b]	M2[c]	M3[d]	S[a]	M1[b]	M2[c]	M3[d]	S[a]	M1[b]	M2[c]	M3[d]	M1[b]	M2[c]	M3[d]
Acetamiprid	0.9971	0.9943	0.9961	0.9997	0.002	0.003	0.003	0.002	0.005	0.006	0.009	0.008	0.5091	0.6215	0.4822
Imidacloprid	0.9978	0.9974	0.9955	0.9992	0.002	0.004	0.002	0.002	0.007	0.010	0.008	0.008	0.4207	0.5529	0.4973
Imidaclothiz	0.9982	0.9967	0.9934	0.9994	0.002	0.002	0.003	0.012	0.006	0.008	0.010	0.040	0.3693	0.4473	0.2233
Nitenpyram	0.9917	0.9989	0.9971	0.9997	0.004	0.003	0.007	0.014	0.010	0.012	0.024	0.048	0.9703	1.0724	1.0279
Pymetrozine	0.9982	0.9955	0.9974	0.9975	0.002	0.002	0.002	0.004	0.006	0.006	0.006	0.014	0.8193	0.7265	0.9693
Thiacloprid	0.9977	0.9944	0.9947	0.9997	0.001	0.002	0.002	0.009	0.004	0.006	0.006	0.030	0.5144	0.4887	0.2891
Thiamethoxam	0.9984	0.9975	0.9958	0.9989	0.003	0.005	0.003	0.012	0.010	0.010	0.009	0.040	0.4624	0.7529	0.4059

[a] solvent; [b] green tea; [c] herbal tea; [d] orange juice; [e] values of matrix effect

Table 3 Recoveries (%) and RSD (%, n=3) of the target compounds in different matrices at three spiked levels.

Compound	Spiking level (mg/L)	Green tea			Herbal tea			Orange juice		
		Recovery (%)	RSD[a] (%)	RSD[b] (%)	Recovery (%)	RSD[a] (%)	RSD[b] (%)	Recovery (%)	RSD[a] (%)	RSD[b] (%)
Acetamiprid	0.005	93.89	1.07	2.94	94.85	1.59	5.17	93.39	1.95	5.56
	0.010	95.32	4.01	4.01	94.82	5.63	3.57	86.33	3.82	12.09
	0.020	92.59	1.00	6.74	93.47	2.96	4.23	85.16	6.11	11.04
Imidacloprid	0.005	105.79	4.65	11.02	90.26	1.28	3.51	87.88	2.50	6.19
	0.010	91.83	5.86	8.32	95.36	6.07	0.60	101.49	3.03	4.25
	0.020	88.83	1.90	9.95	89.92	1.76	6.52	81.65	3.01	12.45
Imidaclothiz	0.005	89.85	5.51	8.49	92.86	1.91	4.35	89.17	2.53	9.25
	0.010	89.92	3.08	9.47	89.18	2.83	5.00	103.14	3.27	3.20
	0.020	92.17	3.44	2.51	89.87	1.76	8.84	85.21	1.52	10.98
Nitenpyram	0.005	83.39	1.57	2.71	81.39	2.59	3.04	82.17	1.97	7.46
	0.010	84.36	2.29	1.58	87.09	4.72	6.72	89.13	1.72	4.71
	0.020	87.29	1.26	7.72	88.85	2.83	1.18	81.19	1.58	3.33
Pymetrozine	0.005	89.68	1.85	4.81	85.24	1.14	0.07	98.70	1.45	2.98
	0.010	89.83	8.28	12.09	81.46	1.52	1.52	85.02	2.41	10.37
	0.020	92.71	2.47	5.98	101.05	1.27	3.63	99.56	4.14	4.62
Thiacloprid	0.005	98.22	2.14	0.30	92.99	1.92	6.12	87.35	9.10	6.62
	0.010	89.30	7.51	5.02	94.00	2.64	2.18	97.79	2.59	0.86
	0.020	90.89	1.79	9.05	90.39	1.08	7.57	82.29	1.79	9.62
Thiamethoxam	0.005	94.26	4.86	7.21	88.65	4.71	5.94	81.48	1.78	11.00
	0.010	90.16	2.11	2.77	87.91	3.85	7.09	96.50	1.65	2.65
	0.020	88.30	8.34	5.75	98.86	2.04	1.01	83.34	0.52	5.64

[a]RSD, intra-day RSD (n=3); [b]RSD, inter-day RSD (n=3).



Graphic abstract

Highlighting:

A multi-residue determination of neonicotinoids and pyridine-azomethine in drinks using UPLC-MS/MS with PICS has been developed.