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Research Article

NEW RAPID ANALYSIS OF TWO CLASSES OF PESTICIDES IN FOOD WASTEWATER BY QUECHERS-LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY

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ABSTRACT

The rapid analytical method was developed in response to increasing concern over the environmental impact of azoles (sterol biosynthesis inhibitors) and neonicotinoids (nicotinic acetylcholine receptor site). These chemicals are commonly used to protect fruit and vegetables crops against fungi and pests. Seven insecticides and twenty one fungicides commonly occurring in food industrial wastewater have been determined. For this purpose, active substances from two new pesticide classes were extracted and isolated by QuEChERS by addition of acetonitrile, buffering salts and chitin as a clean-up sorbent. The novelty of this procedure was one step sample preparation including extraction and removing of co-extracts in short time. Instrumental analysis was conducted by liquid chromatography coupled with mass spectrometry using multiple reaction monitoring. The limits of detection ranged from 0.002 to 0.005 $\mu g \cdot L^{-1}$ with satisfactory accuracy and precision The recoveries for the pesticides ranged from 81–103%, with high repeatability (n = 3, RSD ≤ 9%) and low LOQs (0.01 $\mu g \cdot L^{-1}$). Matrix effects calculated were less than 12% for all analyses. The method was applied to routine analysis of food industrial wastewater. Concerning the results, total pesticide levels in most cases were below 1 $\mu g \cdot L^{-1}$. The most significant pesticides in terms of concentration and frequency of detection were acetamiprid (0.07 $\mu g \cdot L^{-1}$); tebuconazole (1.2 $\mu g \cdot L^{-1}$) and thiacloprid (0.04 $\mu g \cdot L^{-1}$).

Keywords: wastewater, azole, neonicotinoids, QuEChERS, LC-MS/MS

INTRODUCTION

Typically, fruit and vegetable industry produce large amounts of wastes. These wastes include solids (i.e., peels, cores, seeds, stems, dirt, etc.) and liquids (i.e., juices, wash water, chilling water, cleaners, sanitizers, etc.). Disposing these wastes generally requires permits from regional environmental agencies to ensure minimal environmental impact. The volume and the quality of the water from recycling facilities highly depend on the product and season. The preservation of fruit and vegetables is achieved by canning, drying, or freezing, and by the preparation of juices, jams and jellies. The main steps include the preparation of the raw material (cleaning, trimming, and peeling) and cooking, canning, and freezing. Approximately 50% of water in fruit and vegetable processing is used for washing and rinsing [Environ Poland, 2004].

Wastewater characteristics greatly depend upon the type of fruit or vegetable processed and the processing techniques used (e.g., washing, blanching, peeling, etc.). Before being dis-

charged, wastewater needs additional treatment to reduce such components as TSS, FOG, COD, TKN, total phosphorous [Nawirska A., 2007].

The wastes, among different impurities, very often contain pesticide residues washed from the raw materials. Chemical pesticides are extensively used in fruit and vegetable cultivation in order to obtain better quality and yields of crops [Skoczko I., 2009]. The presence of such a large number of pesticide pollution in the wastewater requires effective and economical analytical methods for pesticide control.

Azoles are synthetic antifungal compounds derived from triazole or imidazole. Azole-derivatives are used for control of fungal pathogens in plants. Thousands of tons of azoles are sold annually for the purpose of plant protection [FAO, 2012]. The main advantages are their broad spectrum of antifungal activity and their relatively long persistence. Mixtures of azoles are considered of interest for disease control because they prevent unidirectional selection and may both stabilize phenotypes with reduced sensitivity and optimize resistance management strategies [EPPO Workshop, 2010]. Besides the concern for worker exposure, their large use in agriculture and their presence as residues in certain food items carry the potential for human exposure to individual or multiple compounds [Hof H., 2001; EFSA, 2009a].

Neonicotinoids are a new class of insecticides chemically related to nicotine. The neonicotinoids act on certain kinds of receptors in the nerve synapse and they are much more toxic to insects, than they are to mammals, birds and other higher organisms. Neonicotinoids are important as they provide an alternative mode of action to organophosphate and pyrethroid insecticides. This allows them to play a key role in helping to prevent the build up of resistance in the pests concerned. Neonicotinoids insecticides are popular in pest control because of their water solubility, which allows them to be applied to soil and be taken up by plants. There are several different kinds of neonicotinoids insecticides [BASF, 2013]. The first neonicotinoids to reach the market was imidacloprid, a common ingredient in Bayer Advanced Garden insecticides. This product can be sprayed on the plant, but is often more effective (especially on sucking insects) when applied to the soil [TLC, 2012]. Initially neonicotinoids were praised for their low-toxicity to many beneficial insects, including bees; however, recently this claim has come into question. New research points to potential toxicity to bees and other beneficial insects through low level contamination of nectar and pollen with neonicotinoid insecticides used in agriculture.

Many techniques can be used for the determination of pesticide compounds in wastewater. A review of the literature showed that methods such as liquid-liquid extraction [Kuranchie-Mensah et al., 2012] or solid-phase extraction [Singer et al., 2010; El-Kabbany et al., 2000; Al-Degs et al., 2009] coupled to LC-MS/MS, GC-MS and HPLC-UV or GC-ECD are commonly used. Solid-phase extraction technique has many modifications, for example: soil-phase microexstraction (SPME) [Silva et al., 2015; Bonansea et al., 2013], HF-SPME (hollow fiber solid-phase microextraction) [Ebrahimi et al., 2011] and stir bar sorptive extraction followed by liquid desorption (SBSE-LD) [Margoum et al., 2013]. Other sample prepartion methods based on solvent demulsification dispersive liquid-liquid microextraction (SD-DLLME) [Souza Caldas et al., 2016], extraction using tannic acid azo polyurethane sorbent (PUF-azo-Tan) [Moawed et al., 2015] or electrochemical method using a boron-doped diamond electrode [Svorc, 2013].

According to our best knowledge, no scientific reports describing QuEChERS method as sample preparation of wastewater in pesticide analysis. The goal of this study was to apply QuEChERS method for trace levels for determination of two new classes of pesticides including azoles and nenicotinides.

The novelty of this method was one step sample preparation including extraction and removing of co-extracts in short time and application validated methods to wastewater real samples.

MATERIALS AND METHODS

Materials and reagents

The 28 pesticide standards were purchased from Dr. Ehrenstorfer Laboratory (Augsburg, Germany) with purities ranged from 96.0% to 99.8%.

Formic acid and ammonium formate were purchased from Merck (Darmstadt, Germany). LC-MS grade methanol was purchased from POCh (Gliwice, Poland) and LC-grade water (18 MΩ cm) from a MilliQ water purification system (Millipore Ltd., Bedford, MA, USA). Mag-

nesium sulphate, sodium chloride, sodium citrate dibasic sesquihydrate, sodium citrate tribasic dehydrate were purchased from Agilent Technologies (Santa Clara, USA) and Chitin from Sigma-Aldrich (Steinheim, Germany).

Preparation of standards

Stock solutions of pesticides (around 1000 μg mL^{-1}) were prepared separately by dissolving an accurately weighed amount of each reference standard in acetone. The combined working standard solutions were generated by serial dilution of the stock solutions with the same solvent. The working standard solutions were used for the preparation of matrix-matched standards within the concentration range of 0.005–2.0 μg mL^{-1} and for the spiking of samples in the validation studies. All the stock and working standard solutions and IS was stored in freezer at about -20 °C until analysis.

Sample preparation

Ten milliliters of wastewater sample (pH 4) was transferred into a 50 mL disposable polypropylene centrifuge tube and 10 mL of acetonitrile was added. The tubes were immediately shaken for 1 min. Then 4 g anhydrous magnesium sulphate, 1 g sodium chloride, 1 g trisodium citrate dihydrate and 0.5 g disodium hydrogen citrate sesquehydrate and 1 g of chitin were added. The tubes were immediately shaken for 5 min and then centrifuge for 5 min at 4500 rpm. One ml of the extract was filtered through a 0.2 μm hydrophilic PTFE filter, transferred into the autosampler vial and analyzed via LC/MS/MS (Figure 1).

LC-MS/MS conditions

An Eksigent Ultra LC-100 (Eksigent Technologies, Dublin, CA, USA) liquid chromatography system was operated at a flow rate of 0.35 mL min^{-1} without split using a SunFire C18 2.5 μm, 2.1 × 75 mm (Waters) analytical column, maintained at 40 °C during the experiments. The volume injected into the LC/MS/MS system was 10 μL. The binary mobile phase consisted of water with 0.5% formic acid and 2mM ammonium formate (phase A) and methanol with 0.5% formic acid and 2 mM ammonium formate (phase B). The gradient elution starting at 99% A and 9% B was held for 1.0 min, rising linearly to 10% A and 90% B in 5.5 min and was held for 3.5 min. After ramping, the mobile phase composition was returned to the initial condition in 1 min, and this was held for 4 min for re-equilibration.

System MS/MS 6500 QTRAP (AB Sciex Instruments, Foster City, CA) was used for mass spectrometric analysis, equipped with an electrospray ionization source (ESI). The capillary voltage was maintained at 5000V for positive ion mode and the temperature of the turbo heaters was set at 450 °C. As the nebulizer gas (GS1), auxiliary gas (GS2) and curtain gas (CUR) the nitrogen was used at a pressure of 55, 45 and 35 psi respectively. As the nebulizer and collision gas nitrogen was used, too. All pesticides were detected in the multiple reaction monitoring mode (MRM). One product ion for quantification and one for qualification. The MRM transitions for the pesticides are given in Table 1.

Validation study

The developed method was subjected to validation study using wastewater (previously checked to be free of the target pesticides) in order to determine linearity, recovery, precision, limit of quantification (LOQ), matrix effects (ME) and uncertainty.

The linearity of the method was determined by analysis of a series of standard samples with five different concentrations in pure solvent and in matrix of sewage on three consecutive days.

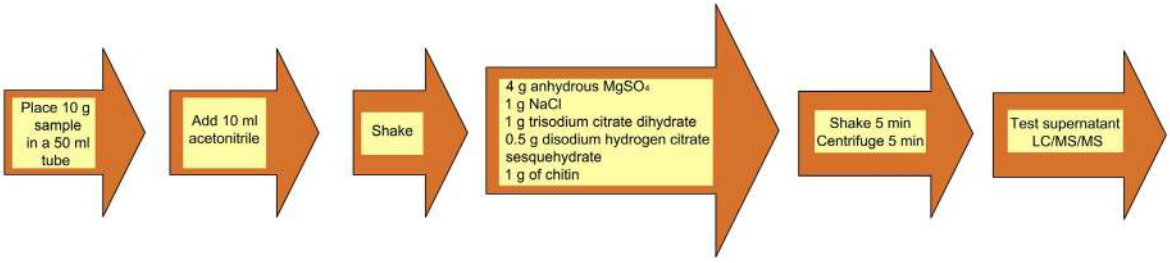

Figure 1. One step procedure of extraction and clean up for determination of two classes pesticides.

Table 1. Optimised parametres of analysis LC-MS/MS of two classes pesticides.

No of sample	Active substance	Retention time [min]	Quantification				Confirmation				EP [V]
			MRM transition m/z	DP [V]	CE [V]	CXP [V]	MRM transition m/z	DP [V]	CE [V]	CXP [V]	
1.	Acetamiprid	4.35	223>125.9	80	27	6	223>99	80	51	5	10
2.	Azaconazole	5.15	300>159	86	37	10	300>231	86	23	12	10
3.	Bromuconazole	5.95	378>159	91	35	10	378>70	91	61	8	10
4.	Clothianidin	4.2	250>169	6	19	10	250>132	6	21	6	10
5.	Cyproconazole	5.9	292>70	61	23	8	292>125	61	45	6	10
6.	Diclobutrazol	6.4	328>69.9	85	58	8	328.01>159	85	48	8	10
7.	Difenoconazole	6.85	406>251	96	35	14	406>188	96	59	10	10
8.	Diniconazole	6.9	326.1>70.1	25	63	8	326.1>158.9	25	39	10	10
9.	Epoxiconazole	6.1	330>121	61	27	6	330>101.1	61	65	6	10
10.	Etaconazole	6.1	328.1>159	61	37	10	328.1>123	61	75	6	10
11.	Fenbuconazole	6.2	337>125.1	96	35	8	337>70	96	23	8	10
12.	Flonicamid	3.7	230>173.9	81	25	10	230>147.9	81	37	8	10
13.	Fluquinconazole	6.05	376>306.9	26	35	18	376>349	26	27	18	10
14.	Flusilazole	6.25	316.1>247	26	25	14	316.1>165.1	26	35	10	10
15.	Hexaconazole	6.7	314.1>70	21	49	8	314.1>159	21	37	10	10
16.	Imibenconazole	7.5	411.1>125.1	86	43	8	411.1>171	86	29	10	10
17.	Imidacloprid	4.15	256>209.1	80	21	12	256>175.1	80	27	10	10
18.	Ipconazole	6.95	334.1>70	71	61	8	334.1>124.9	71	57	6	10
19.	Metconazole	6.7	320.1>70	56	63	8	320.1>124.9	56	55	6	10
20.	Nitenpyram	2.8	271.1>126	61	37	8	271.1>237	61	25	11	10
21.	Penconazole	6.45	284>70	56	21	8	284>158.9	56	35	8	10
22.	Propiconazole	6.5	342>159	100	37	10	342>69	100	23	8	10
23.	Tebuconazole	6.5	308.1>70	41	57	8	308.1>125.1	41	59	8	10
24.	Tetraconazole	6.1	372>159	26	37	10	372>70	26	73	10	10
25.	Thiacloprid	4.5	253>126	96	29	6	253>72.9	96	81	8	10
26.	Thiamethoxam	3.75	292>211	61	17	12	292>181	61	31	10	10
27.	Triticonazole	6.1	318>70	71	49	8	318>125	71	47	8	10
28.	Uniconazole	6.25	292.1>70	106	59	10	292.1>125	106	37	8	10

For the recovery experiments, pesticides-free wastewater samples were spiked by the addition of appropriate volumes of representative standards of pesticides at three different levels. The mixture was left standing for 1 h to allow equilibration and was then processed according to the procedure described above. For each fortification level, five replicate samples were analyzed. Precision was expressed in terms of relative standard deviation (RSD) and calculated for each spiking level.

To evaluate the percent of matrix effects (%ME) for each analyte, the slopes of the calibration curve obtained were used, at the same concentration levels which were determined by comparing solvent and matrix-matched calibration curves in terms of slope ratios according to formula: $\%ME=(slope_{matrix}/slope_{solvent}-1)\cdot 100$.

The measurement uncertainty was estimated based on the data obtained in the validation study. The relative expanded uncertainty was calculated by using the coverage factor k=2 at the confidence level of 95%.

RESULT AND DISCUSSION

Validation study

A series of experiments with regard to linearity, recovery, precision, limit of detection (LOD), limit of quantification (LOQ) and uncertainty (U) were performed to validate one-step extraction-cleanup method under optimized conditions by using wastewater samples (previously checked to be free of the target pesticides).

Linearity of calibration curves was studied by LC–MS/MS analysis of six calibration solutions at the pesticides concentrations of 0.005, 0.01, 0.05, 0.1, 0.5 and 2.0 μg mL^{-1} (n=3) in wastewater extracts (Figure 2). The linear regression data and satisfactory correlation coefficients for the 7 neonicotinoids and 21 azoles were obtained ranging from 0.99967 to 0.99999 are listed in Table 2.

The recoveries were determined in five repetitions at the three spiking levels: 0.01, 0.1 and 2 μg mL^{-1}. The level of quantification (LOQ) was defined as the lowest spiking level validated with satisfactory values of recovery (70–120%) and RSD (≤20%) [Sanco, 2013].

All of the compounds are presented satisfactory recoveries in the range between 75% and 128%. Only nitenpyram at the three concentration level (0.01–2 μg mL^{-1}) showed recoveries values insignificantly outside the acceptance range – 121%. All the pesticides gave a RSD lower than 24%. Generally, at three fortification levels the RSD didn't exceed 15%, except for nitenpyram (24%).

The LOD values of individual pesticides were calculated based on the noise level in the chromatograms at S/N of 3:1 and results are shown in Table 2. The limit of quantification (LOQ) was set at the lowest spiking concentration and for all the analytes 0.01 μg mL^{-1} was accepted as the practical LOQ.

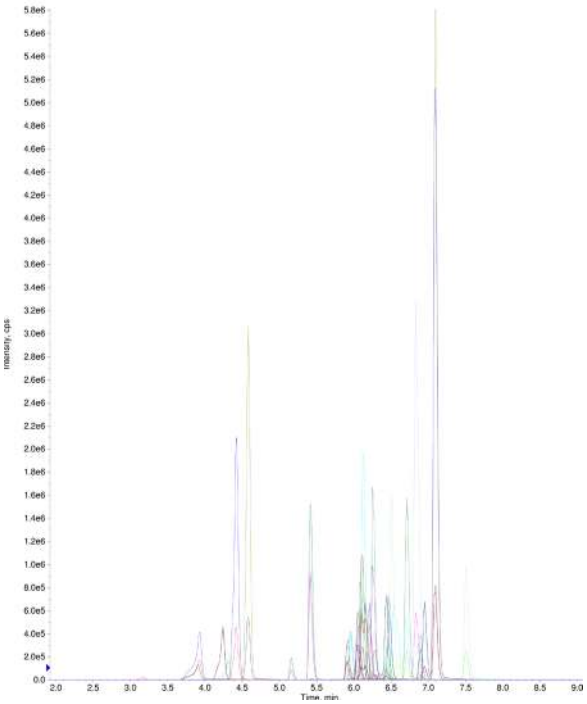

Figure 2. LC-MS/MS chromatogram of wastewater sample fortificated at 0.1 μg L^{-1} level.

The data derived from the validation study were used to estimate the measurement uncertainty (U) associated with the analytical results. The expanded measurement uncertainties were estimated employing a ''top-down'' empirical model [Medina-Pastor et al., 2011] as being between 9–28% (coverage factor k=2, confidence level 95%).

The precision was identified as the main contribution to the uncertainty. The uncertainty associated with the recovery, calculated from rectangular distribution, was also included in the uncertainty budget to avoid underestimation of the total uncertainty. The results are presented in Table 2, which clearly demonstrates suitability of the proposed method.

Matrix effect

Negative values of matrix effects signify suppression of the signal, and positive values signify enhancement [Kwon et al., 2012]. Twenty four of the target pesticides with ME in the acceptable range (-20–20%) were obtained using chitin as a clean up sorbent (Table 2). Two compounds etaconazole and ipconazole (ME -26%) had matrix effect below -20%, and diclobutrazol, imibenconazole and propiconazole (ME 22% and 24%) above 20%.

Extraction and clean up step

The QuEChERS method for pesticide residues analysis was first introduced by USDA scientists in 2003 year [Anastassiades et al., 2003]. The method was modified to address problematic pesticides, resulting in the official methods AOAC 2007.01 [Lehotay et al., 2005] and EN method 15662, a European variation of the QuEChERS method [CEN/TC, 2007; Paya et al., 2007] In summary, these methods consist from a three step: extraction, dispersive SPE and analysis. For the first extraction stage acetonitrile is added to the sample and various salts: anhydrous magnesium sulphate, NaCl and buffering citrate. The second step in above procedures based on dispersive solid phase extraction (d-SPE), used to minimize matrix effects with various combination depends on character of murices: of primary secondary amine (PSA) to remove organic acids, C18 for fat and lipid removal, GCB (graphitized carbon black) for pigment removal, and anhydrous magnesium sulphate to reduce remaining water in extract.

Table 2. Validation parameters for 28 pesticides in wasterwater matrix.

Pesticide	Recovery (RSD) [%]			ME [%]	R^2	LOD [µg L^{-1}]	LOQ [µg L^{-1}]	U [%]
	0.01 µg L^{-1}	0.1 µg L^{-1}	2.0 µg L^{-1}					
Acetamiprid	83 (6)	92 (7)	94 (8)	-13	0.99999	0.004	0.01	16
Azaconazole	75 (7)	83 (6)	86 (7)	-9	0.99982	0.005	0.01	17
Bromuconazole	78 (8)	83 (7)	82 (8)	9	0.99986	0.003	0.01	15
Clothianidin	89 (9)	91 (11)	94 (10)	-15	0.99992	0.002	0.01	20
Cyproconazole	80 (7)	84 (8)	81 (8)	-3	0.99997	0.003	0.01	9
Diclobutrazol	99 (9)	93 (6)	82 (7)	22	0.99967	0.003	0.01	18
Difenoconazole	82 (5)	80 (7)	82 (6)	-15	0.99989	0.005	0.01	10
Diniconazole	96 (4)	98 (5)	94 (5)	14	0.99992	0.003	0.01	9
Epoxiconazole	89 (6)	94 (6)	97 (5)	-15	0.99991	0.002	0.01	13
Etaconazole	84 (4)	98 (5)	94 (6)	-26	0.99999	0.005	0.01	15
Fenbuconazole	87 (5)	98 (6)	96 (7)	10	0.99996	0.003	0.01	17
Flonicamid	86 (6)	91 (5)	92 (6)	-14	0.99988	0.005	0.01	14
Fluquinconazole	92 (5)	96 (9)	101 (9)	20	0.99993	0.002	0.01	19
Flusilazole	109 (11)	104 (14)	110 (12)	-20	0.99998	0.003	0.01	21
Hexaconazole	96 (6)	93 (7)	97 (6)	-14	0.99978	0.003	0.01	14
Imibenconazole	94 (7)	88 (5)	99 (6)	24	0.99999	0.004	0.01	18
Imidacloprid	80 (10)	94 (12)	100 (11)	-11	0.99985	0.002	0.01	25
Ipconazole	83 (12)	91 (14)	94 (15)	-26	0.99998	0.004	0.01	24
Metconazole	98 (4)	102 (5)	104 (6)	13	0.99996	0.003	0.01	14
Nitenpyram	128 (20)	119 (21)	122 (24)	-10	0.99998	0.005	0.01	28
Penconazole	87 (6)	98 (6)	106 (7)	-8	0.99994	0.003	0.01	20
Propiconazole	92 (8)	97 (7)	104 (6)	22	0.99997	0.003	0.01	17
Tebuconazol	78 (5)	88 (8)	99 (8)	-4	0.99996	0.003	0.01	19
Tetraconazole	86 (7)	85 (7)	94 (6)	-10	0.99988	0.003	0.01	17
Thiacloprid	88 (6)	90 (6)	97 (5)	19	0.99996	0.003	0.01	16
Thiamethoxam	79 (8)	89 (7)	101 (8)	-1	0.99999	0.003	0.01	17
Triticonazole	95 (7)	88 (7)	90 (5)	-13	0.99994	0.003	0.01	15
Uniconazole	80 (8)	96 (5)	92 (4)	-18	0.99998	0.004	0.01	16

In our one step proposal, acetonitrile is added to the sample followed by salting out of the water from the sample using anhydrous magnesium sulphate, NaCl and buffering citrate to introduce extraction partitioning and chitin as dispersive solid phase extraction (d-SPE) to remove organic acids, sugar, wax and lipids. Figure 3 shows total ion chromatograms of matrix-matched standard without cleanup (blue line) and after cleanup with chitin (red line).

Pesticide extraction in wastewater has been considered difficult due to complicated fruit/vegetable matrix and the critical point of proposed method was removed matrix impurities. The chitin added during extraction step yielded a cleaner extract, therefore it was chosen for the wastewater procedure. This natural sorbent, chitin, is excellent and minimizes matrix effect. QuEChERS is a very good sample extraction and clean up method that is suitable for broad varieties of pesticides. Our modification extraction and clean up steps were used for 28 pesticides analysis in fruit/vegetable wastewater matrix.

Literature suggests using selective methods of detection of pesticides such groups as, for example: chlorinated hydrocarbons, organophosphates, triazines, chloroacetanilide, pyrethroids, carbamates, phthalimides from using GC - MS/MS [Papadakis et al., 2015]. These selective detection methods are limited and specific for certain pesticides groups. In this work we demonstrated that liquid chromatography - mass spectrometry as a very good technique for determining the concentration of azoles and neonicotinoids in wastewater from fruit and vegetable processing.

Real samples application

The wide range of compounds analyzed (Table 1), demonstrated the applicability of this method for identifying pesticide contaminants in wastewater samples.

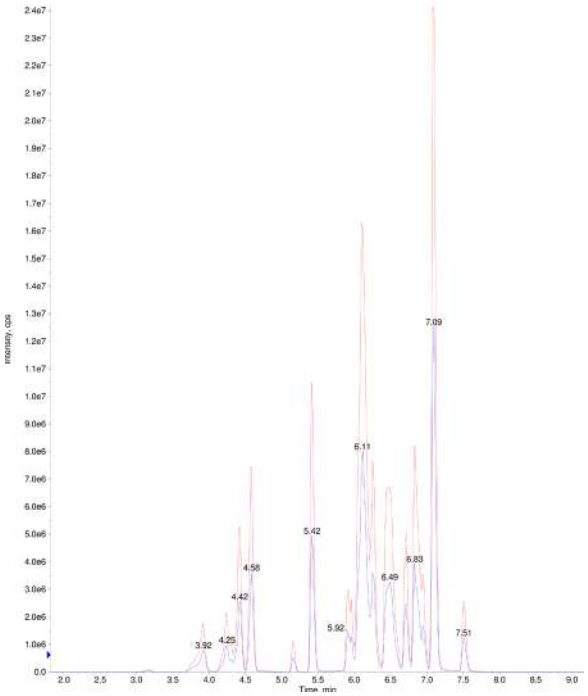

Figure 3. Total ion chromatograms of matrix-matched standard: without cleanup (blue line) and after cleanup (red line).

Developed and validated method was used for detection and identification of wasterwater. During the 2014–2015 years (between June - October) method was applied for the analysis of about 30 wasterwater samples from the fruit/vegetables food industry factory. Figure 4 shows chromatograms of real wastewater samples, one pesticide

Figure 4. Chromatograms of real wastewater samples containing: a) acetamiprid (0.07 μg L^{-1}); b) tebuconazole (1.2 μg L^{-1}) and c) thiacloprid (0.04 μg L^{-1}).

in each sample were detected: acetamiprid (0.07 μg L^{-1}); tebuconazole (1.2 μg L^{-1}) and thiacloprid (0.04 μg L^{-1}). Therefore, this method can be used as a routine monitoring tool for azoles and neonicotinoids pesticides in food wastewater matrices.

CONCLUSIONS

1. Our one step QuEChERS method including extraction and clean up provided a simple, fast and effective method in wastewater samples.
2. The recovery and reproducibility of two pesticide classes were acceptable for multiresidue determination in complexes matrices as wastewater.
3. The most common pesticides were acetamiprid, tebuconazole and thiacloprid.

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