

# Development of a method Sin-QuEChERS for the determination of multiple pesticide residues in oilseed samples

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## Abstract

The determination of pesticide residues in oilseeds is a formidable challenge because compound pesticides are widely used in farming oilseeds. In this work, a novel method named Sin-QuEChERS (single-step, cheap, effective, rugged, safe) was established for the analysis of multiple pesticide residues in oil-bearing crop samples (rapeseed, peanut, sesame and melon seeds), based on the improvement of QuEChERS (quick, easy, cheap, effective, rugged, and safe) approach. In the Sin-QuEChERS method, acetonitrile was used for sample extraction and primary-secondary amine (PSA) using C18 cartridge as purification media. By using Sin-QuEChERS, 38 pesticide residues in 4 oilseeds were detected by high performance liquid chromatography mass spectrometry (HPLC-MS/MS) within 5 min. and the correlation coefficient was more than 0.99. The average recoveries were 80.2 to 99.8%, and the relative standard deviation was less than 15%. Application of Sin-QuEChERS to monitor the pesticide residues of 100 batches of oilseeds showed that the established method was high throughput, accurate, sensitive, and reliable, and the limited detection ranged from 0.006 to 0.054 mg/kg.

**Keywords:** Sin-QuEChERS, oilseeds, multiple pesticide residues, monitor

## 1. Introduction

Oilseeds are seeds of oil-bearing crops including peanut, soybean, rapeseed, sunflower, cotton and sesame, which are commercially used as a source of vegetable oil. Pesticides are widely used in the cultivation of oil-bearing crops to control the size of pest populations and increase production (Wang *et al.*, 2017). The widespread and unreasonable use of pesticides has caused serious problems with pesticide residues in oilseeds and edible oils (Yang *et al.*, 2018), which poses a threat to food safety and human health. To solve this problem, many countries and organisations have constituted the maximum limit of pesticide residues in oilseeds and vegetable oils (Fang *et al.*, 2017). For example, the International Codex Alimentarius Commission has established standards for more than 50 pesticide residues in edible oils. The European Union have imposed strict residue limits on 136 pesticides in edible oils. The United States has announced residue standards for more than 130 pesticides in edible oils. The FAO has developed detailed provisions

on pesticide residue limits standards for different oilseeds and their products (Golge and Kabak, 2018). In Japan, pesticide residue limits standard have been established for sesame, safflower, sunflower and other oil-bearing crops. In China, the 'Food Safety National Standard of Food Pesticide Maximum Residue Limit' (GB 2763) also stipulates the maximum residue of more than 100 pesticides in oilseeds. The residues limits for most of the pesticides in edible oils and oilseeds range from 0.01 to 8 mg/kg.

At present, QuEChERS (quick, easy, cheap, effective, rugged, safe) in sample pretreatment technology is the most predominant method for preparing samples and extracting pesticide residues. Researchers have established different methods by using QuEChERS to simultaneously analyse multiple pesticide residues in different crops, including artichoke, fruits, teas, sorghum, rice hull, tomatoes, dry herbs and Chios Mastic Gum (Abbas *et al.*, 2017; Andrade *et al.*, 2015; Golge and Kabak, 2015; Han *et al.*, 2017; Li *et al.*, 2017; Machado *et al.*, 2017; Malhat *et al.*, 2017; Psoma *et al.*,

2015). Many researchers dynamically monitored pesticide residues of oilseeds, which can evaluate the food safety (Delcour *et al.*, 2015; Santarelli *et al.*, 2018). The detection of pesticide residues enables consumers to know the safety of oilseeds and oils and improve their understanding on food safety (Pirsaheb *et al.*, 2017; Sivaperumal *et al.*, 2015).

Pesticide residues detection methods mainly include gas chromatography, gas chromatography tandem mass spectrometry (Han *et al.*, 2017; Xu *et al.*, 2017) and liquid chromatography tandem mass spectrometry, which can simultaneously analyse various types of pesticide residues (Khan *et al.*, 2018; Ozkan, 2015). In recent years, liquid chromatography tandem time-of-flight mass spectrometry has been widely used for the screening of pesticide residues (Liu *et al.*, 2017; Sivaperumal *et al.*, 2015; Yang *et al.*, 2018). However, all of these methods are not extensively applied in all conditions. Most of them are primarily applicable to organophosphorus and carbamate pesticides. Therefore, it is necessary to develop a more widely applicable method for simultaneously detecting multiple pesticide residues in oilseeds.

In this paper, we have established a novel method named Sin-QuEChERS (single-step, cheap, effective, rugged, safe) dispersive solid phase extraction, which integrates extraction and purification into one step. Sin-QuEChERS (Song *et al.*, 2019) is a new rapid sample pretreatment technique based on QuEChERS method, which can avoid the loss of test components caused by solvent transfer, reduce the solvent usage, save sample preparation time and guarantee the recovery rate. In our study, 38 pesticide residues in four oilseeds including rapeseed, peanut, sesame and melon seeds were detected by ultra-high performance liquid chromatography tandem mass (UPLC-MS/MS) using Sin-QuEChERS method.

## 2. Materials and methods

### Reagent and preparation of standard solutions

High purity pesticide standards (Purity 96 to 99%) were purchased from Ehrenstorfer GmbH (Augsburg, Germany) and the chemical structures of 38 pesticides are shown in Figure S1. Methanol, formic acid, and high performance liquid chromatography (HPLC) grade acetonitrile were purchased from Fisher Scientific (Fair Lawn, NJ, USA). The solid phase extraction reagent kit of Sin-QuEChERS was purchased from Lumiere Technologies (Beijing, China). The analytical reagent grade anhydrous magnesium sulphate was purchased from Agela Technologies (Tianjin, China). Ultrapure water was obtained from Milli Q purification system (Millipore, Molsheim, France). The stock standard solution of 1000 mg/l pesticides was prepared in acetonitrile. The multi-standard mixture containing 10 mg/l of each pesticide was prepared in acetonitrile and stored at -18 °C

for less than 3 months. Mixed multi-standard working solutions were freshly prepared to avoid the degradation of pesticides by serial dilution. For two reference standards (EN 15662 and AOAC2007.01), and three Sin-QuEChERS purification columns, including (A) 900 mg MgSO<sub>4</sub> + 150 mg PSA + 150 mg C18, (B) 1,200 mg MgSO<sub>4</sub> + 400 mg PSA + 400 mg C18, and (C) 900 mg MgSO<sub>4</sub> + 150 mg PSA + 150 mg GCB were used to compare the purification effects.

### Samples

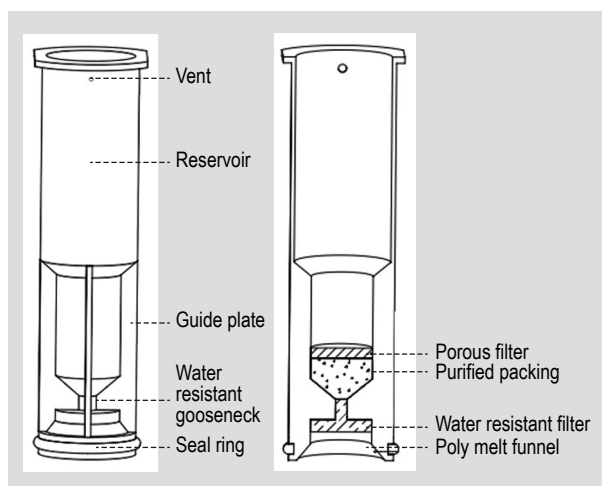
From January to December 2017, 100 oilseeds of each oilseed crop (rapeseed, peanut, sesame and melon seeds) were randomly collected from the market in Shanxi Province, China. A representative portion of 500 g of oilseed sample was sent to the laboratory and stored at 4 °C before analysis.

### Sin-QuEChERS columns

Sin-QuEChERS columns are constructed according to AOAC2007.1 and EN 15662 standards. The Sin-QuEChERS column allowed the organic extract to enter the reservoir, and the liquid level rises, followed by the air in the reservoir exits through the vent. The waterproof gooseneck contains a porous polyethylene waterproof filter to ensure that the aqueous solution is not exposed to the purification fillers and reservoir. A porous polyethylene filter is used to immobilise the purified filler and purified filler adsorbs impurities in the organic extract. The bottom of the Sin-QuEChERS column is funnel-shaped, allowing all of the upper organic extract to pass through the purified packing and be purified into the reservoir. The purified filler could be selected among C18, PSA, NH<sub>2</sub>, and SAX silica gel bonders or polymer matrix filler according to the sample impurities and the physical/chemical properties of the components. A prerequisite for the selection is to ensure that impurities in the extract can be adsorbed by the purified filler and the components can enter the reservoir. Sin-QuEChERS is designed for one time use only (Figure 1).

### Sample preparation

A total of 5.0 g of pre-homogenised oilseed samples (rapeseed, peanut, sesame and melon seeds) were transferred to a 50 ml centrifugal tube and then added with 15.0 ml of acetonitrile/water mixture (containing 66.6% of acetonitrile). The tube was capped tightly and vortexed for approximately 3 min. Anhydrous 900 mg of MgSO<sub>4</sub> was then added to the centrifuge tube. The tube was capped tightly and immediately vortexed for another 1 min. Samples were then centrifuged at 4,000 rpm for 10 min. For determining the recovery rate, three concentrations of 38 pesticides were added to the blank samples and recycled (n=6 at each concentration level). The Sin-QuEChERS column was then inserted into a centrifuge tube and the



**Figure 1. Schematic presentation of Sin-QuEChERS column.**

pressure was applied slowly at a rate of 1 mm/s. The upper organic layer was transferred from the centrifuge to the purified filler by absorbing impurities dissolved in the organic extract, and then transferred to a storage tank. The extracts was then filtered through a 0.22  $\mu\text{m}$  PVDF filter (Millex FG, Millipore, Milford, MA, USA) to an autosampler vial for analysis by LC-MS/MS. The purification step was shown in Figure 2.

### LC-MS/MS analysis

The LC-MS/MS system consists of a Waters UPLC system (Waters, Milford, MA, USA), a Quattro Premier XE quadrupole mass spectrometer (Waters), and MassLynx software V4.1 quadrupole tandem mass spectrometer equipped with a Turbo V Electrospray Ionisation (ESI) interface source. Nitrogen (99%) generated from a Peak Scientific nitrogen generator (Billerica, MA, USA) was used in the ESI source. Chromatographic separations were performed on a BEH C18 column (1.7  $\mu\text{m}$ , 2.1 $\times$ 150 mm, Waters, Wexford, Ireland). Aliquots of sample extract (10  $\mu\text{l}$ ) were injected into the column. A mobile phase consisting of eluent A (0.1% formic acid in water) and eluent B (acetonitrile) was used at a flow rate of 0.3 ml/min. The gradient elution was performed as follows: 5% B (0-30 sec.), 5-10% B (30-60 sec.), 10-20% B (1-2 min.), 50-90% B (2-3 min.), 90-5% B (3-4 min.), and 5% B (4-5 min.). The temperature of column oven was set at 35  $^{\circ}\text{C}$ .

Mass analysis was performed in positive mode using the ESI source. The following general MS parameters were employed: ion spray with voltage of 3.5 kV and the ion source with temperature of 125  $^{\circ}\text{C}$ . 600 l/h of nitrogen was used as the spray gas; 50 l/h of nitrogen was used as the desolvation gas; and helium was used as the collision gas. The LC-MS/MS system was operated in multiple reaction monitoring mode (MRM) with two transitions per drug. Five MRM segments were collected based on retention

time. The MRM settings are summarised in Table S1. For the maximum intensity of molecular ions and selected product ions, all analytical conditions were optimised by continuous infusing of standard solutions and using, the LC-MS/MS chromatograms of 38 pesticide standards was shown in Figure S2.

### Statistical analysis

The analytical method was validated on the basis of 'Basic rules for the preparation of physicochemical methods for the determination of food and cosmetics for export' (SN/T0001-2016, China's inspection and quarantine standards). The performance characteristics of the LC-MS/MS method included specificity and selectivity, linearity, limit of detection (LOD), limit of quantification (LOQ), method repeatability and method trueness in terms of recovery evaluated by using pesticide-free rapeseed, peanut, sesame and melon seeds extract. The LOD and LOQ were measured by following a signal-to-noise ratios (S/N) of  $\geq 3$  and 10, respectively.

## 3. Results and discussion

### Optimisation of extraction conditions

Different purification methods were employed to find the best way for extracting pesticide residues from the matrix. The mechanism of Sin-QuEChERS is similar to HPLC and solid phase extraction. The test components can be purified by using adsorbent fillers to adsorb impurities in the matrix interaction. The matrix components of fuel had similar polarities to pesticides. Therefore, most traditional solvents could not separate the analytical material from the matrix and the lipids were incompatible with the LC system. Since the lipid is almost insoluble in acetonitrile and incompatible with LC system, acetonitrile extraction could eliminate or minimise its effects. The Sin-QuEChERS method used less solvent with less pollution, lower cost and did not use chloride solvents. It could analyse the range of pesticides, including polar and non-polar pesticides. Therefore, it can be used to achieve a better recovery rate. For large number of polar and volatile pesticides, it was fast and had a high recovery rate of greater than 85% (Ambrus *et al.*, 2016). Therefore, acetonitrile was selected as the extraction solvent.

### Optimisation of purifying conditions

The four types of oilseeds greatly reduced the instrument pollution by Sin-QuEChERS method, and the purifying effect fulfil the test requirement. In the analysis of pesticide residue, GCB had an excellent purification effect. However, in the analysis of many types of pesticide residues, GCB was not commonly used since GCB had a strong retention effect on chemicals with the aromatic ring structure and certain

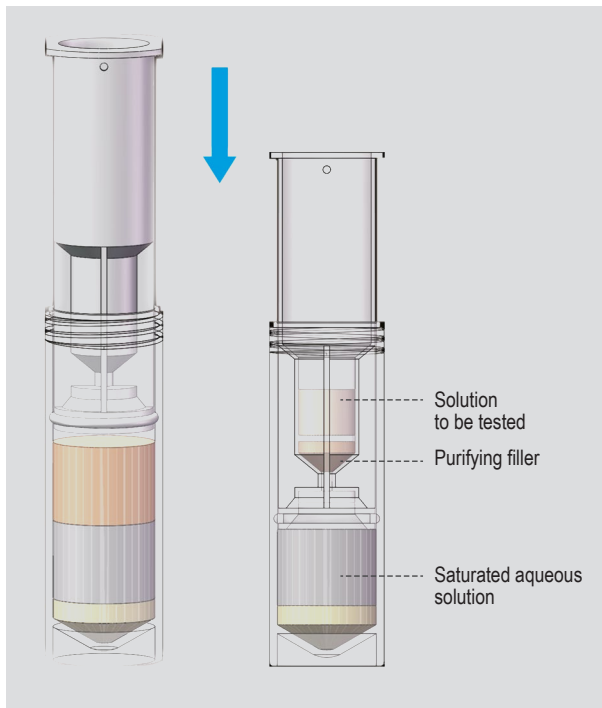


Figure 2. Purification schematic.

symmetry, such as chlorothalonil, dichlobenil, dichlorvos, dichlofluanid, folpet, methacrifos, imazalil, thiabendazole, and tolylfluanid. The purification effect of Sin-QuEChERS Column C was less than that of the Sin-QuEChERS Column A. It was found that the combination of 900 mg  $MgSO_4$  + 150 mg PSA + 150 mg C18 had the best effect on the four types of oilseeds. Therefore, Sin-QuEChERS Column A was selected for the solid-phase dispersing purification. The purification conditions were compared and the results were shown in Figure 3-6.

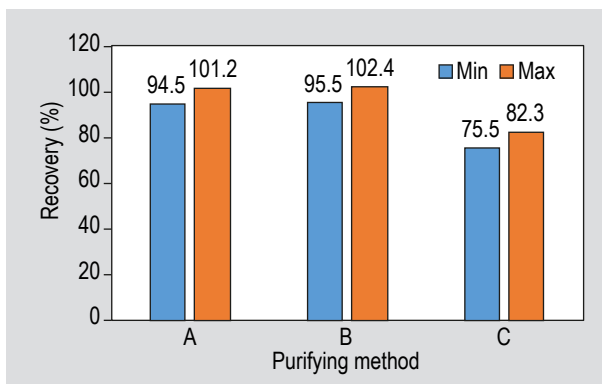


Figure 3. Comparison of different purification methods of rapeseed.

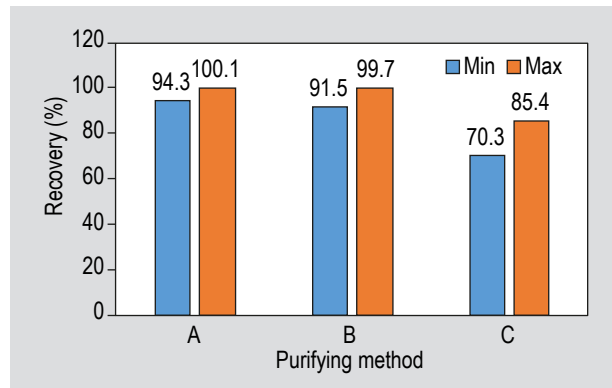


Figure 4. Comparison of different purification methods of peanut.

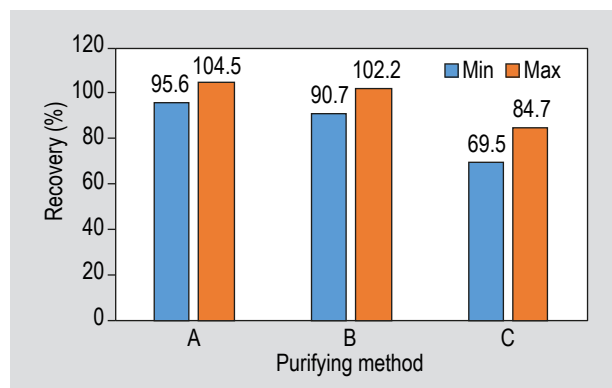


Figure 5. Comparison of different purification methods of sesame.

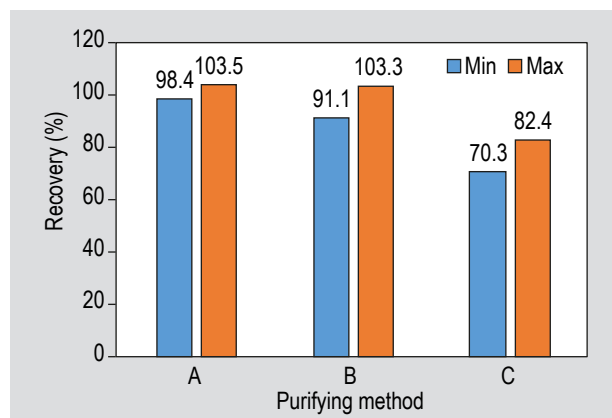


Figure 6. Comparison of different purification methods of seeds.

### Method validation and quality control

The selectivity of these methods were analysed by comparing the chromatograms of several blank pesticide residues and spiked pesticide residues. The recovery rate of various pesticides was 80.2-99.8%, and the relative standard deviation (RSD) was less than 16%. The recoveries and RSD values in spiked rapeseed, peanut, sesame and melon



seeds samples were shown in Table S2. The LC-MS/MS spiked pesticide chromatogram was shown in Figure S3. The concentrations of the multi-standard working solution were 10, 25, 50, 100 and 250 µg/kg. The corresponding concentration (x-axis) was plotted by the peak area (y-axis), and the results showed that the correlation coefficient of 38 pesticides was greater than 0.99 in the linear range. The concentration of the pesticide to be measured showed a good linear relationship with the corresponding peak area, as shown in Table S3.

#### Interlaboratory verification

To verify the effectiveness of the method, the recovery rate, precision and sensitivity were verified by Shanxi entry-exit inspection and Quarantine Bureau (CIQ), Hebei CIQ, Heilongjiang CIQ, Jilin CIQ and Chinese Academy of Inspection and Quarantine (CAIQ). Interlaboratory validation tests of 38 pesticides in peanuts were shown in Table S4. The recovery rate of various pesticides in peanuts was 71.1-92.2% and the RSD was 4.7-19.4%.

#### Application to oilseeds samples

A validated method was used to determine the selected pesticides in oilseed samples from China from four different periods. 100 samples were obtained from the market of Shanxi Province, China, including 25 batches of rapeseed, peanuts, sesame seeds and melon seeds, respectively. Ten pesticides were detected in these oilseeds (Table S5). Interestingly, the study found no pesticide residual contamination in oilseeds without shells. Among them, the detection rate of acetochlor and propisochlor was higher, and the maximum residue level (MRL) value of acetochlor and propisochlor in China rapeseed, peanut, sesame and melon seeds were referenced. The residual amount of acetochlor and propisochlor in oilseeds does not exceed the standard value. The residual amount of 2,4-D, acetamiprid, thiamethoxam and propisochlor in the oilseeds did not exceed the standard values. At present, the MRL standard of thiamethoxam in oilseeds has not been established to evaluate the safety of its residual levels. However, all samples were within the MRL of 38 pesticides in oil seeds of every country (Table S6). This indicates that the safety of oilseed products in the market is guaranteed.

#### Extended uncertainty

The components of uncertainty such as repeatability, weighing, pretreatment, recovery rate and working curve were analysed, according to the inclusion factor  $k=2$  (95% of confidence level), the relative extended uncertainty of 38 pesticides in oil seeds by liquid chromatography tandem mass spectrometry detection method was calculated:

$$U_{rel} = k U_{rel}(X) 0.1374 - 0.1542$$

## 4. Conclusions

In this work, a novel method Sin-QuEChERS for multiple pesticide residues detection was established based on the QuEChERS method. Sin-QuEChERS integrated the extraction and purification into one step, which can be easily avoided the loss of test components during solvent transfer and greatly improve extraction efficiency. The effects of Sin-QuEChERS were tested on 38 pesticide residues in four type of oilseeds, including rapeseed, peanuts, sesame seeds and melon seeds. The results of the Sin-QuEChERS method fulfilled regulatory requirements and were superior to traditional methods in terms of sensitivity, precision, and accuracy. With the support of selectivity of LC-MS/MS, the Sin-QuEChERS method can further identify and quantify compounds in these oilseeds at the residue levels of  $\leq 0.005$  mg/kg. In addition, the technical index of the Sin-QuEChERS method established in this study met the requirement of detecting the substances in oilseed samples. The Sin-QuEChERS method also quantitatively detected the maximum allowable level of pesticide prescriptions. Overall, the high-throughput, accurate, and sensitive method Sin-QuEChERS has great potential to monitor pesticide residues in oilseed samples. For example, it has been applied in more than 1000 oilseed samples every year in China Customs.

#### Acknowledgements

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#### Conflict of interest

The authors declare that they have no conflict of interest.

#### Supplementary material

Supplementary material can be found online at <https://doi.org/10.3920/QAS2019.1557>.

**Table 1.** MS/MS parameter for the analysis of target analytes in the MRM ESI mode.

**Table 2.** Recoveries and RSD values in spiked rapeseed, peanut, sesame and melon seeds samples.

**Table 3.** LODs, LOQs, linear regression equation, and correlation coefficients of studied pesticides.

**Table 4.** Interlaboratory validation test of 38 pesticides in Peanut.

**Table 5.** Results of 10 out of 38 detected pesticide residues in oilseeds (Shanxi, n=100).

**Table 6.** The MRL of 38 pesticides in oil seeds of every country (mg/kg).

**Figure S1.** Chemical structures of 38 studied pesticides.

**Figure S2.** LC-MS/MS chromatograms of 38 pesticide standards.

**Figure S3.** LC-MS/MS chromatograms of pesticides for the spiked (0.005 mg/kg).

## References

Abbas, M.S., Soliman, A.S., El-Gammal, H.A., Amer, M.E. and Attallah, E.R., 2017. Development and validation of a multiresidue method for the determination of 323 pesticide residues in dry herbs using QuEChERS method and LC-ESI-MS/MS. *International Journal of Environmental Analytical Chemistry* 97(11): 1003-1023.

Ambrus, Á., Buczkó, J., Hamow, K.Á., Juhász, V., Solymosné Majzik, E., Szemánné Dobrik, H. and Sztítás, R., 2016. Contribution of sample processing to variability and accuracy of the results of pesticide residue analysis in plant commodities. *Journal of Agricultural and Food Chemistry* 64(31): 6071-6081.

Andrade, G.C.R.M., Monteiro, S.H., Francisco, J.G., Figueiredo, L.A., Botelho, R.G. and Tornisielo, V.L., 2015. Liquid chromatography-electrospray ionization tandem mass spectrometry and dynamic multiple reaction monitoring method for determining multiple pesticide residues in tomato. *Food Chemistry* 175: 57-65.

Delcour, I., Rademaker, M., Jacxsens, L., De Win, J., De Baets, B. and Spanoghe, P., 2015. A risk-based pesticide residue monitoring tool to prioritize the sampling of fresh. *Food Control* 10: 1016.

Fang, Y., Tian, W., Pei, F., Li, P., Shao, X., Fan, Y. and Hu, Q., 2017. Simultaneous determination of pesticide residues and antioxidants in blended oil using a liquid-liquid extraction combined with dispersive solid phase extraction method. *Food Chemistry* 229: 347-353.

Golge, O. and Kabak, B., 2015. Evaluation of QuEChERS sample preparation and liquid chromatography-triple-quadrupole mass spectrometry method for the determination of 109 pesticide residues in tomatoes. *Food Chemistry* 176: 319-332.

Golge, O. and Kabak, B., 2018. Pesticide residues in table grapes and exposure assessment. *Journal of Agricultural and Food Chemistry* 66(7): 1701-1713.

Han, Y., Song, L., Liu, S., Zou, N., Li, Y., Qin, Y., Li, X. and Pan, C., 2017. Simultaneous determination of 124 pesticide residues in Chinese liquor and liquor-making. *Food Chemistry* 241: 258-267.

Khan, Z., Kamble, N., Bhongale, A., Girme, M., Chauhan, B.V. and Banerjee, K., 2018. Analysis of pesticide residues in tuber crops using pressurised liquid extraction. *Food Chemistry* 241: 250-257.

Li, J., Sun, M., Chang, Q., Hu, X., Kang, J. and Fan, C., 2017. Determination of Pesticide residues in teas via QuEChERS combined with dispersive liquid-liquid microextraction followed by gas chromatography-tandem mass spectrometry. *Chromatographia* 80(9): 1447-1458.

Liu, H., Yao, G., Liu, X., Liu, C., Zhan, J., Liu, D., Wang, P. and Zhou, Z., 2017. Approach for pesticide residue analysis for metabolite prothioconazole-dethio in animal origin food. *Journal of Agricultural and Food Chemistry* 65(11): 2481-2487.

Machado, I., Gérez, N., Pistón, M., Heinzen, H. and Cesio, M.V., 2017. Determination of pesticide residues in globe artichoke leaves and fruits by GC-MS and LC-MS/MS using the same QuEChERS procedure. *Food Chemistry* 227: 227-236.

Malhat, F., Boulangé, J., Abdelraheem, E., Abd Allah, O., Abd El-Hamid, R. and Abd El-Salam, S., 2017. Validation of QuEChERS based method for determination of fenitrothion residues in tomatoes by gas chromatography-flame photometric detector: decline pattern and risk assessment. *Food Chemistry* 229: 814-819.

Ozkan, A., 2015. Determination of pesticide residues in some oilseeds and nuts using LC-MS/MS analysis. *Fresenius Environmental Bulletin* 24(2A): 615-620.

Pirsaheb, M., Fattahi, N., Rahimi, R., Sharafi, K. and Ghaffari, H.R., 2017. Evaluation of abamectin, diazinon and chlorpyrifos pesticide residues in apple. *Food Chemistry* 15: 148-155.

Psoma, A.K., Pasiadis, I.N., Bletsou, A.A. and Thomaidis, N.S., 2015. Development and validation of a multi-residue method for the determination of pesticides in chios mastic gum by QuEChERS and liquid chromatography-tandem mass spectrometry. *Food Analytical Methods* 8(3): 624-634.

Santarelli, G.A., Migliorati, G., Pomilio, F., Marfoggia, C., Centorame, P., D'Agostino, A., D'Aurelio, R., Scarpone, R., Battistelli, N., Di Simone, F., Aprea, G. and Iannetti, L., 2018. Assessment of pesticide residues and microbial contamination in raw leafy green vegetables marketed in Italy. *Food Control* 85: 350-358.

Sivaperumal, P., Anand, P. and Riddhi, L., 2015. Rapid determination of pesticide residues in fruits and vegetables, using ultra-high-performance liquid chromatography/time-of-flight mass spectrometry. *Food Chemistry* 168: 356-365.

Song, L., Han, Y., Yang, J., Qin, Y., Zeng, W., Xu, S. and Pan, C., 2019. Rapid single-step cleanup method for analyzing 47 pesticide residues in pepper, chili peppers and its sauce product by high performance liquid and gas chromatography-tandem mass spectrometry. *Food Chemistry* 279: 237-245.

Wang, J., Tao, J., Yang, C., Chu, M. and Lam, H., 2017. A general framework incorporating knowledge, risk perception and practices to eliminate pesticide residues in food: a structural equation modelling analysis based on survey data of 986 Chinese farmers. *Food Control* 80: 143-150.

Xu, M.L., Gao, Y., Han, X.X. and Zhao, B., 2017. Detection of pesticide residues in food using surface-enhanced Raman spectroscopy: a review. *Journal of Agricultural and Food Chemistry* 65(32): 6719-6726.

Yang, X., Luo, J., Duan, Y., Li, S. and Liu, C., 2018. Simultaneous analysis of multiple pesticide residues in minor fruits by ultrahigh-performance liquid chromatography/hybrid quadrupole time-of-flight mass spectrometry. *Food Chemistry* 241: 188-198.