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# DETERMINATION OF PESTICIDE MULTI-RESIDUES IN GREEN TEA USING A MODIFIED QUECHERS EXTRACTION AND LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY TECHNIQUE

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A modified QuEChERS method was developed and validated for determination of pesticide multi-residues in green tea by liquid chromatography tandem mass spectrometry. Lead acetate was first time used together with primary secondary amine and graphite carbon black to eliminate tannin, caffeine, and other pigments in tea and thus reduced the matrix effects. The method was compared to the original QuEChERS method as well as A.O.A.C. QuEChERS method. For accurate quantification, the matrix matched calibration technique was used. The method showed good performance in the concentration range from 0.01 to 1 mg $kg^{-1}$. All pesticides could be quantified at and lower than 0.01 mg $kg^{-1}$. Recoveries were from 70 to 120% and repeatabilities were <15% RSD depending on the compounds.

**Keywords:** pesticide multi-residues, green tea, QuEChERS, liquid chromatography-mass spectrometry

Tea is one of the most favoured beverages worldwide especially in Asian countries. The most tea producing and consuming countries are China, India, Sri Lanka, Kenya, Turkey, Indonesia, and Vietnam (Rediff.com, 2012). Pesticides were used in tea farming to control insects, mites, leaf-eating beetles, and caterpillars. Therefore, determination of pesticide residues in tea is an important contribution to a safer tea.

QuEChERS (Quick, easy, cheap, effective, rugged, and safe) is a sample preparation methodology for pesticide multi-residue analysis, which was first published by Anastassiades and co-workers (2003). The method uses a single-step acetonitrile or buffered acetonitrile extraction and salting out liquid-liquid partitioning from the water in the sample with anhydrous magnesium sulphate. Then, the dispersive solid phase extraction (d-SPE) clean-up is done to remove excess water and matrix components with a combination of sorbents including $MgSO_4$ and primary secondary amine (PSA). The final extracts are analysed by mass spectrometry (MS) technique after a liquid or gas chromatographic separation (A.O.A.C., 2010). This method has many advantages. Firstly, it is a multi-residue method, which can be applied to determine hundreds of pesticides in one single procedure. Secondly, the final extract in acetonitrile can be used both for gas chromatography and liquid chromatography. Last but not least, QuEChERS is definitely a cheap, easy, effective, rugged, and safe method like its name (Lehotay et al., 2005). For over a decade, QuEChERS has been developing quickly and was accepted by many international organizations (e.g. A.O.A.C. No.

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2007.01, BS EN 15662:2008, etc.) for determination of pesticide residues in fruit and vegetables (BS EN, 2008; A.O.A.C., 2010). The A.O.A.C. method uses acetate buffer as solvent extraction, while EN method uses citrate buffer. The pH value around 4.5 to 5.5 of buffers is favourable with the acidic or basic compounds and matrices. Pesticide multi-class, multi-residue determination relies on the QuEChERS extraction combined to LC-MS/MS and/or GC-MS(/MS) instrumentation could be used to identify a few hundreds of pesticides in one single test (Lehotay et al., 2005; Nguyen et al., 2010; Dai et al., 2011). Its applications have also spread to other matrices like tea, herb, rice, and other grains (Steiniger et al., 2010; Chen et al., 2011; Fan et al. 2013; Guan et al., 2013; Rajski et al., 2013).

Determination of pesticides in tea is somewhat difficult, due to the presence of large amounts of polyphenols, caffeine, and especially tannin (Graham, 1992), which can result in a high matrix effect. A larger number of analytical methods have been published for the determination of pesticide residues in tea. Some methods include the solvent extraction combined to many clean-up techniques, such as solid phase extraction (SPE) or gel permeation chromatography (GPC) (Huang et al., 2007; Cho et al., 2008). These methods, however, are time- and labour-consuming and require large volumes of various kinds of solvents. Recently, QuEChERS method has been applied to extract pesticides from tea (Steiniger et al., 2010; Chen et al., 2011; Lozano et al., 2012; Guan et al., 2013; Rajski et al., 2013; Shoeibi et al., 2013). To deal with the matrix effect problem, many techniques have been tried including a sample dilution, matrix calibration, various types and amounts of sorbent addition, or SPE cleanup (Stahnke et al., 2012; Fan et al., 2013; Guan et al., 2013; Rajski et al., 2013; Wang et al., 2013). However, the high amount of tannin in tea requires a method with a further clean-up step. Until now, the reaction of tannin with lead(II) acetate forming lead(II) tannate is used for the isolation of tannin from green tea.

The aim of this work is the evaluation of lead(II) acetate as a clean-up material for pesticides analysis in tea matrices. This study also included the validation results of a LC-MS/MS technique combined with a modified QuEChERS procedure using lead(II) acetate in the partitioning step for determination of pesticide multi-residues in green tea.

## 1. Materials and methods

### *1.1. Chemicals and reagents*

All pesticide reference standards, of purity ≥ 95%, were from Dr. Ehrenstorfer (Augsburg, Germany). These pesticides (showed in Table 1) were chosen based on their use in tea crops and were applicable with LC-MS/MS. The application could be generally spread to other pesticides. The internal standard, triphenyl phosphate (TPP), was from Sigma-Aldrich (St. Louis, MO, USA). The stock solutions of 1000 μg $ml^{-1}$ were prepared in acetonitrile and stored in dark at –4 °C. The intermediate standard-mix solutions of 0.1, 1, 5, and 10 μg $ml^{-1}$ were diluted from stock solutions in acetonitrile. TPP working solution was of 2 μg $ml^{-1}$.

Acetonitrile and methanol of HPLC grade were from Merck (Darmstadt, Germany). Acetic acid, anhydrous magnesium sulphate, sodium acetate trihydrate, lead acetate, and sodium chloride were also supplied by Merck. Primary-secondary amine (PSA) and graphite carbon black (GCB) sorbents were obtained from Agilent Technology (USA). Ultra-pure water was obtained by using a SG purification system (Germany).

*Table 1.* List of pesticides with HPLC retention times and MS/MS conditions

| Pesticides | Retention time (min) | Precursor ion (M+H) | Quantification ion (CE, eV) | Confirmation ion (CE, eV) |
|---|---|---|---|---|
| Acetochlor | 10.80 | 270.0 | 224 (13) | 148 (25) |
| Aldicarb | 8.03 | 213.0 | 116 (15) | 89 (15) |
| Atrazine | 9.61 | 216.0 | 96 (31) | 104 (37) |
| Azoxystrobin | 9.83 | 404.0 | 372 (19) | 344 (31) |
| Abamectin | 13.90 | 890.5 | 305 (31) | 567.5 (17) |
| Acetamiprid | 6.90 | 223.0 | 126 (25) | 56 (19) |
| Carbaryl | 9.10 | 202.0 | 145 (13) | 127 (37) |
| Carbofuran | 8.74 | 222.0 | 165 (15) | 123 (29) |
| Carbendazim | 5.35 | 192.0 | 160 (23) | 132 (39) |
| Carboxin | 9.08 | 236.0 | 143 (19) | 87 (29) |
| Dichlorvos | 8.71 | 221.0 | 109 (23) | 127 (18) |
| Dimethoat | 7.03 | 230.0 | 199 (13) | 125 (27) |
| Edifenphos | 11.00 | 311.0 | 283 (17) | 109 (35) |
| Emamectin | 11.00 | 886.5 | 158 (39) | 302 (35) |
| Fenobucarb | 10.10 | 208.0 | 152 (11) | 95 (19) |
| Imidacloprid | 6.32 | 256.0 | 209 (21) | 175 (27) |
| Indoxacarb | 11.30 | 528.0 | 249 (21) | 293 (17) |
| Isoprocarb | 9.55 | 194.0 | 95 (19) | 137 (11) |
| Methiocarb | 10.30 | 226.0 | 169 (11) | 121 (23) |
| Methomyl | 4.89 | 163.0 | 88 (13) | 106 (13) |
| Profenophos | 11.90 | 373.0 | 303 (23) | 345 (17) |
| Propoxure | 8.67 | 210.0 | 111 (19) | 93 (31) |
| Terbuconazole | 11.10 | 308.0 | 125 (39) | 151 (31) |
| Thiamethoxam | 5.29 | 292.0 | 211 (15) | 181 (29) |
| Trichlorfon | 6.97 | 257.0 | 109 (23) | 221 (15) |
| TPP (IS) | 11.10 | 327.0 | 77 (61) | – |

Samples were dried Vietnamese green teas (produced from *Camellia sinensis* leaves and flower buds) collected from the market. Blank samples were chosen from the samples in which pesticides had not been detected.

### *1.2. Instrumentation*

An AB Sciex 5500 triple quadrupole mass spectrometer (AB Sciex, USA) coupled with LC-20AD high pressure pumps, column compartment, and autosampler (Shimadzu, Japan) was used to detect and quantify the pesticide residues. LC separation was obtained by using a X-Bridge BEH C18 (150 mm × 2.1 mm, 2.5 µm particle size) and a pre-column BEH C18 (5 mm × 2.1 mm, 1.7 µm) (Waters, USA) with a mobile phase composed of 0.1% (v/v) acetic acid in water (eluent A) and methanol (eluent B). The gradient program was initially set at 25% B in 1 min then increased linearly to 90% B over 8 min. After that, the eluent composition was maintained at 90% B for 4 min, and re-equilibrated over 3 min. The flow rate used was kept constant at 0.7 ml $min^{-1}$. Total run time was 15 min. The injection volume was 20 µl.

The mass spectrometer was operated in positive ESI mode with capillary voltage and temperature set at 5000 V and 450 °C, respectively. A Peak Scientific AB-3G gas generator (UK) was used to generate $N_2$ used as curtain gas and air was used as source gas. Curtain gas, collision gas, source gas 1, and source gas 2 were set at 25 psi, 7 psi, 30 psi, and 20 psi, respectively. MS experiments were carried out in multiple reaction monitoring modes with two transitions for each pesticide (Table 1). The higher intensities of the precursor-to-product ion transition were used for quantification; the others were used for confirmation. In addition, the ion ratios were also the criteria for pesticide confirmation.

### *1.3. Sample preparation*

A modified QuEChERS method was applied to extract pesticides in green tea samples. After homogenization, a 3 g portion of sample was weighed in a 50 ml centrifuge tube. Internal standard (TPP) was added to make a sample concentration of 100 μg $kg^{-1}$. Then, 15 ml of water was added for sample hydration. The tube was carefully shaken by hand for 30 s and let stand for 30 min. After that, 15 ml of acetonitrile were added and the tube samples were shaken vigorously by hand for 1 min. A portion of 6.0 g of anhydrous $MgSO_4$, 1.5 g of NaCl and 1.5 g of $Pb(CH_3COO)_2$ was gradually added and the tubes of samples were tightly capped, shaken as mentioned above, and centrifuged at 6000 r.p.m. (3904×*g*) for 5 min. For clean-up, 1 ml of supernatant was transferred to a 2 ml centrifuge tube containing 150 mg of anhydrous $MgSO_4$, 50 mg of PSA, and 7.5 mg of GCB. The tube was vortexed for 30 s and centrifuged at 12 000 r.p.m. (13 684×*g*) for 1 min. A portion of 0.5 ml of the supernatant was dried under a nitrogen stream at 40 °C. The residue was then reconstituted with 0.5 ml of mobile phase (0.1% acetic acid and acetonitrile, 75:25) and the extract was filtered through a 0.2 μm membrane (Minisart RC 15, Sartorius, Germany) to a LC-MS/MS sample vial. In this procedure, the sample weight was 3 g and the extract volume was 15 ml, so the sample was 5 times diluted.

### *1.4. Matrix-matched calibration technique*

The blank tea sample was extracted with acetonitrile as mentioned above. In the clean-up step, 6 ml of the acetonitrile extract was transferred to a 15 ml centrifuge tube containing 900 mg of anhydrous $MgSO_4$, 300 mg of PSA, and 45 mg of GCB. The final extracts were used to prepare matrix-matched calibration solutions by diluting the intermediate standard-mix solutions to give the final concentrations of 0, 1, 2, 20, 100, and 200 ng $ml^{-1}$ (corresponding to 0, 5, 10, 100, 500, and 1000 μg $kg^{-1}$ in samples). These solutions were used to evaluate the recoveries and to quantify analytes in real samples. Furthermore, a series of standard solutions in solvent (acetonitrile) at the same concentration levels were also prepared for the assessment of matrix effects.

### *1.5. Method validation*

The method was validated for linearity, matrix effects, limits of detection, repeatability, and recovery. To test the linearity, the matrix-matched calibration solutions were analysed. The matrix effects were assessed by comparing the slopes of matrix-matched calibration curves to solvent calibration curves and given in percentage. The repeatability and recovery was evaluated at three concentration levels (sample concentrations were 10, 100, and 1000 μg $kg^{-1}$) of spiked samples with 6 replicates per level.

## 2. Results and discussions

### *2.1. Optimization of LC-MS/MS*

The precursor ions, product ions, and collision energy were chosen and optimized by the injection of a pesticide solution of 100 ng $ml^{-1}$ directly into mass spectrometry. The precursor ions were of the highest m/z and most intense ion beam, which were M+H m/z in most cases. Then, the product ions and collision energies were automatically optimized using the system software (Analyst). Other LC and MS parameters were also investigated to obtain peaks of Gaussian shape and the signal to noise ratios (S/N) of the 10 µg $kg^{-1}$ matrix standard with values above 10. A chromatogram of a mixture of matrix pesticide standards is shown in Figure 1.

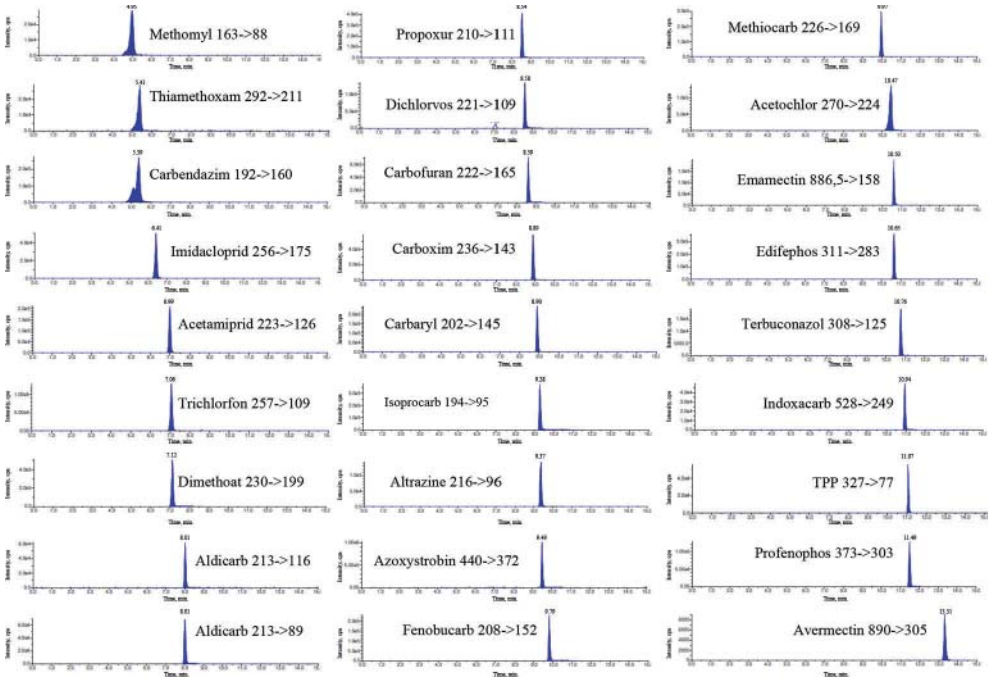


*Fig. 1.* Exact ions chromatogram of a matrix standard of 25 pesticides and internal standard TPP at the concentration of 100 µg $kg^{-1}$ (Annotations are the names and the transitions of the quantification ions, aldicarb showed two transitions)

Most of the peaks are symmetric except for methomyl, thiamethoxam and carbendazim peaks. These compounds are more polar than others and thus, have strong interaction with residual silanol groups on the packing surface of the LC column. Modifying the mobile phase with a buffer, amine, or ion-pairing reagent is used to improve the peak shape. However, the MS/MS detection could give enough selectivity and sensitivity to gain acceptable accuracy for these three compounds.

### *2.2. Investigation of sample preparation*

The QuEChERS extraction method showed good performances for many types of vegetables and fruit. The method requires a sample moisture content of about 80% or above for maximal pesticide extraction (Anastassiades et al., 2003). Therefore, water was added to dried tea before extraction to hydrate the sample. To get the moisture content of around 80%, the water to sample ratio was set at 5:1 (w/w). The sample then was left for 30 min to ensure a complete hydration without further investigation of the amount of water and the soaking duration (Steiniger et al., 2010; Chen et al., 2011; Rajski et al., 2013).

Two versions of public QuEChERS method including the original version (Anastassiades et al., 2003) and the A.O.A.C. version (Lehotay et al., 2005) were tested and compared to a modified QuEChERS method. The modified one relies on the addition of lead acetate (1.5 g) in the extraction step to adsorb polyphenols, caffeine, and pigments in tea and the addition of GCB in the clean-up step to remove chlorophylls. The extraction efficiencies, the co-extracted materials, and the extract pH values of the three methods were compared. pH values of the extracts obtained from original, A.O.A.C., and modified methods were 5.23, 5.76, and 5.63, respectively. The amount of co-extractives from the initial extraction solvent of the modified method was a half of those of the other methods (Table 2). Therefore, the matrix effects of this method were reduced. Figure 2 shows that the recoveries of eight compounds obtained with the proposed method were higher than the other ones. Most of these compounds are carbamate and organo-phosphorus insecticides. There were no significant differences in recoveries among the three methods for other analytes. After these experiments, we found that the use of lead acetate helped achieve a better cleaning and a higher recovery, overall. Besides, the green tea matrices, having a pH about 6, did not require the addition of a pH buffer.

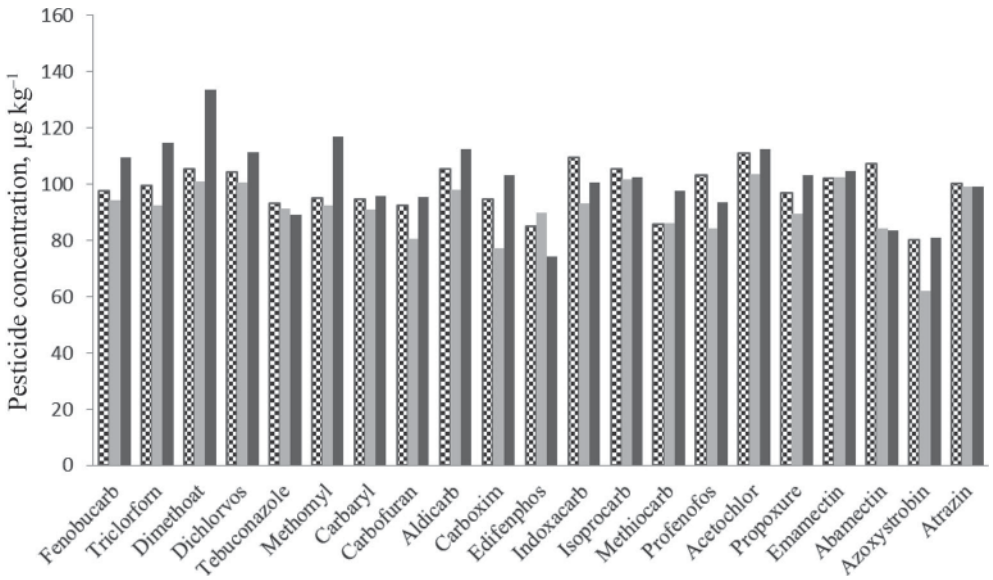


*Fig. 2.* Comparison of three QuEChERS methods (▩ : the original method; ■ : the AOAC method; ■ : the modified method) for the extraction of pesticide residues in green tea

*Table 2.* Co-extracted materials and pH values in MeCN or 0.1% acetic acid in MeCN extracts prior to d-SPE step

| QuEChERS method | Extraction solvent | Partitioning salts | pH | Co-extracted material (mg $ml^{-1}$) |
|---|---|---|---|---|
| Original | MeCN | 6 g $MgSO_4$ & 1.5 g NaCl | 5.23 | 20.5 |
| AOAC | MeCN (0.1% acetic acid) | 6 g $MgSO_4$ & 1.5 g $CH_3COONa$ | 5.72 | 21.3 |
| Modified | MeCN | 6 g $MgSO_4$, 1.5 g NaCl & 1.5 g $(CH_3COO)_2Pb$ | 5.63 | 10.5 |

The optimal amount of lead acetate was also investigated. Different amounts of lead acetate including 0.5, 1.0, 1.5, and 2.0 g were used in the extraction step and the recoveries of pesticides derived were compared. The more salt was used the better recovery was obtained. However, the recovery of the samples with above 1.5 g lead acetate decreased, because the pesticide absorption increased and the solubility of lead salt reached a limit. The highest recoveries for most pesticides were obtained when using 1.5 g of lead acetate.

In the dispersive SPE step, GCB was used to eliminate chlorophylls and some of the polyphenols and other pigments. The amount of GCB used was of 7.5 mg $ml^{-1}$ of extract according to previous researches. GCB can absorb some planar pesticides when used at higher concentrations. In this investigation, the use of GCB gave equal or better recoveries for most pesticides (Fig. 3). The higher recoveries were obtained by the reduction of the matrix effect, which was a result of the application of GCB.

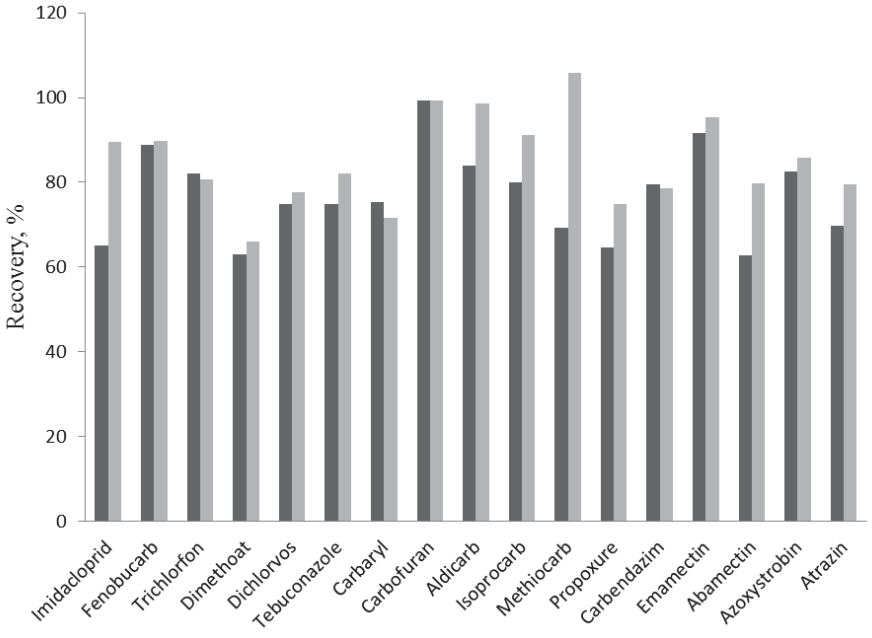


*Fig. 3.* The recoveries of pesticides obtained from two procedures with using and not using GCB (7.5 mg) in d-SPE step (■ : d-SPE without using GCB and ■ : d-SPE with using GCB)

### *2.3. Matrix effect assessment*

Matrix effect is the effect on an analytical method caused by all other components of the sample beside the specific compound to be quantified. Ion suppression and enhancement are the two causes of the matrix effect. That is why matrix effect is an important criterion in every mass spectrometry method. A matrix effect higher than 20% must be eliminated or compensated. Matrix effects vary according to the cleanliness of the extracts and the compounds.

The matrix effect is the drawback of QuEChERS method especially for complex matrices. Green teas give a very high matrix effect because of the existence of many pigments. This modified QuEChERS method eliminated most of the pigments and with that it could minimize the matrix effect. Figure 4 shows the matrix effect on the analysed pesticides. Most pesticides gave signals of lower intensities in the matrix than in solvents. However, the matrix effects on all analysed pesticides were within ±20%. To eliminate efficiently the effects of matrix, the matrix-matched calibration technique was used.

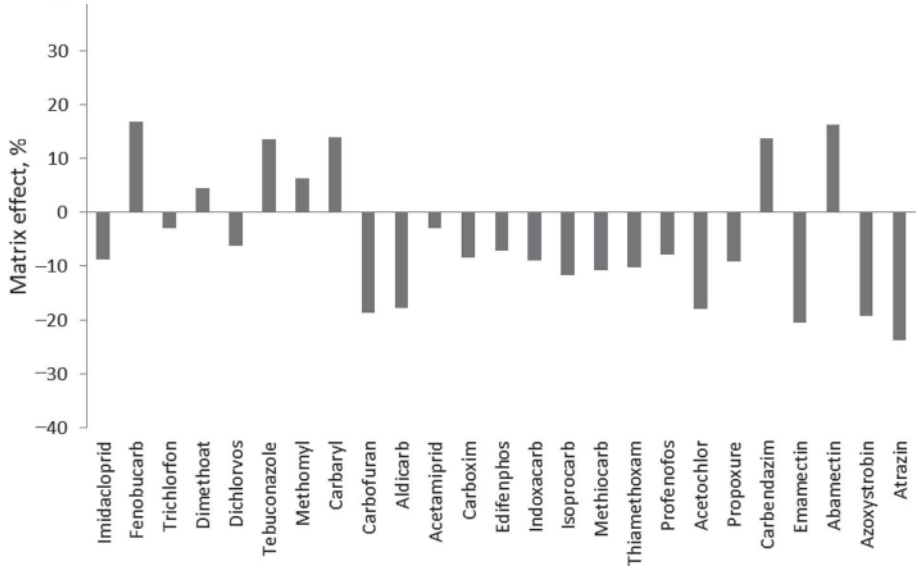


*Fig. 4.* Green tea matrix effect of pesticides by using modified QuEChERS method

### *2.4. Method validation*

For selectivity, every compound had two signals from two product ions (Table 1). Ion ratios of the compounds in the samples were also compared to that in the standards. The relative ion intensities have to meet the criteria given by EU (European Commission, 2002).

The repeatabilities and recoveries obtained with this method are presented in Table 3. For most pesticides at three levels of concentration, the relative standard deviations (RSD%) were lower than 20% (except for profenofos at 100 μg $kg^{-1}$) and the recoveries (R%) were between 70–120%. These indicated that this method had accuracy appropriate for the quantification of pesticide multi-residues in green tea.

*Table 3.* The repeatability and recovery at 3 concentration levels (n=6)

| Pesticides | 10 μg kg$^{-1}$ | | 100 μg kg$^{-1}$ | | 1000 μg kg$^{-1}$ | |
|---|---|---|---|---|---|---|
| | RSD% | R% | RSD% | R% | RSD% | R% |
| Acetochlor | 11 | 76.9 | 6.3 | 90.5 | 9.3 | 83.0 |
| Aldicarb | 8.4 | 111 | 9.0 | 118 | 8.1 | 109 |
| Atrazine | 12 | 91.2 | 9.6 | 91.2 | 4.4 | 96.7 |
| Azoxystrobin | 18 | 71.1 | 17 | 78.5 | 15 | 75.3 |
| Abamectin | 16 | 85.4 | 19 | 93.9 | 12 | 92.0 |
| Acetamiprid | 17 | 89.5 | 15 | 94.4 | 11 | 91.4 |
| Carbaryl | 6.2 | 87.8 | 8.8 | 89.3 | 7.6 | 81.9 |
| Carbofuran | 9.4 | 88.9 | 9.1 | 89.4 | 5.9 | 89.1 |
| Carbendazim | 7.6 | 110 | 5.4 | 113 | 5.0 | 111 |
| Carboxin | 7.5 | 82.5 | 7.7 | 87.6 | 8.9 | 86.6 |
| Dichlorvos | 16 | 75.2 | 13 | 73.2 | 9.1 | 82.2 |
| Dimethoat | 5.9 | 82.0 | 9.2 | 75.4 | 4.4 | 77.3 |
| Edifenphos | 9.6 | 74.6 | 7.8 | 82.3 | 7.1 | 83.2 |
| Emamectin | 15 | 98.8 | 8.0 | 96.7 | 18 | 93.9 |
| Fenobucarb | 8.4 | 84.3 | 7.2 | 83.6 | 7.3 | 90.5 |
| Imidacloprid | 11 | 97.8 | 10 | 95.9 | 6.1 | 96.8 |
| Indoxacarb | 16 | 93.3 | 12 | 81.9 | 11 | 88.4 |
| Isoprocarb | 8.2 | 79.4 | 7.4 | 75.8 | 7.0 | 73.4 |
| Methiocarb | 19 | 76.0 | 19 | 78.6 | 13 | 80.3 |
| Methomyl | 19 | 89.9 | 6.3 | 94.5 | 3.1 | 92.0 |
| Profenophos | 17 | 82.6 | 23 | 73.5 | 19 | 71.3 |
| Propoxure | 5.8 | 81.9 | 5.6 | 85.2 | 5.4 | 83.6 |
| Terbuconazole | 10 | 108 | 11 | 108 | 9.9 | 113 |
| Thiamethoxam | 7.5 | 82.5 | 8.7 | 95.5 | 5.2 | 86.2 |
| Trichlorfon | 10 | 91.9 | 6.9 | 83.2 | 4.3 | 81.2 |

The limit of detection (LOD) and limit of quantification (LOQ) were estimated from the signal to noise (S/N) ratios of the pesticide peaks. All pesticides could be quantified at the concentration of 10 μg kg$^{-1}$ without any concentration steps. This value is acceptable compared to the default maximum residue level (MRL=10 μg kg$^{-1}$).

The linearity was checked in the range of 1–200 ng ml$^{-1}$. The response of the matrix matched standard was considered linear when the coefficient of determination ($r^2$) was equal to or higher than 0.99. For all analysed pesticides, the linearity range was from 2 ng ml$^{-1}$ to 200 ng ml$^{-1}$. A few pesticides even showed lower sensitivity. Because the sample weight was 3 g and the acetonitrile extract volume was 15 ml, the linearity calculated for samples was from 10 μg kg$^{-1}$ to 100 μg kg$^{-1}$.

### *2.5. Analysis of real samples*

Once validated, the proposed method was applied to determine 25 pesticides in 20 different dried green tea samples collected in the Hanoi market.

The results are shown in Table 4. Ten of twenty samples were found to be positive to pesticides from different chemical groups, especially imidacloprid and acetamiprid (neonicotinoid insecticides). Most of the pesticide concentrations were of above 10 μg $kg^{-1}$ (default MRL).

*Table 4.* Pesticide residues found in dried green tea samples and their concentration

| Sample ID | Pesticides | Sample conc., μg $kg^{-1}$ | Class |
|---|---|---|---|
| S1 | Imidacloprid | 10 | Neonicotinoid insecticide |
| | Acetamiprid | 154 | Neonicotinoid insecticide |
| S2 | Acetamiprid | 5.7 | Neonicotinoid insecticide |
| S9 | Imidacloprid | 5.6 | Neonicotinoid insecticide |
| | Acetamiprid | 21 | Neonicotinoid insecticide |
| | Carbendazim | 6.4 | Benzimidazole fungicide |
| S10 | Imidacloprid | 42 | Neonicotinoid insecticide |
| | Acetamiprid | 19 | Neonicotinoid insecticide |
| | Thiamethoxam | 150 | Neonicotinoid insecticide |
| S11 | Imidacloprid | 28 | Neonicotinoid insecticide |
| | Acetamiprid | 45 | Neonicotinoid insecticide |
| | Fenobucarb | 6.7 | Carbamate insecticide |
| S12 | Imidacloprid | 32 | Neonicotinoid insecticide |
| | Acetamiprid | 48 | Neonicotinoid insecticide |
| | Fenobucarb | 17 | Carbamate insecticide |
| S13 | Emamectin | 64 | Macrycyclic lactone insecticide |
| S16 | Acetamiprid | 16 | Neonicotinoid insecticide |
| S18 | Acetamiprid | 22 | Neonicotinoid insecticide |
| | Carbofuran | 86 | Carbamate insecticide |
| S20 | Acetamiprid | 19 | Neonicotinoid insecticide |

## 3. Conclusions

A modified QuEChERS method was proposed for the determination of pesticide multi-residues in dried green tea. The green tea matrix effects were reduced by the addition of lead acetate in the partition step and the use of GCB in the clean-up step. The validation data show that this method has good accuracy and sensitivity and could be applied for the determination of pesticide multi-residue in green tea samples.

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