Application of the QuEChERS Sample Preparation Method for the Determination of Carbamate Pesticides in Flos Carthami Samples by UPLC-MS/MS

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Abstract

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) sample preparation method was used for the determination of 11 carbamate pesticide (methomyl, propoxur, pirimicarb, carbofuran, bendiocarb, carbaryl, isoprocarb, methiocarb, fenobucarb, furathiocarb and indoxacarb) residues in Flos carthami (Carthamus tinctorlus L.). The method involved extraction with acetonitrile, liquid-liquid partitioning with the addition of MgSO4 and NaCl, DSPE (dispersive solid-phase extraction) sample cleanup with PSA, Al2O3-N and GCB sorbents, and the analyses using UPLC-MS/MS equipment. The method was validated using a Flos carthami sample spiked with each analyte at 0.01, 0.02, 0.04 and 0.08 mg kg-1. The average recoveries of the 11 carbamate pesticides studied varied from 81.1% to 104.2%, with RSDs < 10%. The limits of detection (LODs) and the limits of quantification (LOQs) ranged from 0.3 μg kg-1 to 6.0 μg kg-1 and from 1.0 μg kg-1 to 19.0 μg kg-1, respectively. This multi-residue analytical method could allow the rapid, efficient, sensitive and reliable determination of target carbamate pesticides in Flos carthami and other similar medicinal herbs.

Keywords

Flos carthami, Carbamate pesticide residues, QuEChERS, UPLC-MS/MS

1. Introduction

Flos carthami (*Carthamus tinctorlus* L.) has been popularly used as an herbal medicine in China[1]. Carbamate pesticides, efficient broad-spectrum insecticides similar to organochlorine and organophosphorus [2], are applied to protect Flos carthami plants from damage and infestation by pest insects. Pesticide residues in Flos carthami plants are routinely monitored for the safe consumption of the plants. The most widely used method for the analysis of carbamate pesticides is HPLC with post-column hydrolysis and derivatization by fluorescence detection [3-5]. However, this method is time-consuming and requires additional confirmatory techniques. In recent years, an HPLC-based method combined with sensitive mass spectrometric detection (LC-MS) and versatile tandem mass spectrometry (LC-MS/MS) using a multiple reaction monitoring (MRM) mode has become both a reliable and an acceptable analytical tool for the simultaneous sensitive quantification and unequivocal confirmation of a wide range of target pesticides in complex matrices. Sample pre-treatment is a crucial procedure in the analytic process, especially when a large number of samples are involved and where rapid extraction becomes even more essential.

QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method based on DSPE (dispersive solid-phase extraction) has been implemented as a new sample preparation method [6-7]. This method has many advantages, including a high recovery of pesticides with a wide range of polarities and volatilities, a high sample throughput, the use of smaller volumes of organic solvents and no chlorinated solvents are involved. Additionally, very little labor is required, and the safety of laboratory workers is improved [8]. However, there is, to date, few published method describing the

adaptation of the QuEChERS extraction technique in herbs, especially in Flos carthami for the analysis of carbamate pesticide residues. Therefore, the study presented here aimed to evaluate and optimize the QuEChERS sample preparation method for the analysis of carbamate pesticide residues in complex matrices, and to develop an accurate and high-throughput method for determination of carbamate pesticides in Flos carthami plants and similar samples.

2. Experimental

2.1 Reagents and Chemicals.

HPLC-grade acetonitrile was obtained from J.T. Baker (Phillipsburg, NJ, USA). Analytical grade formic acid was purchased from Sigma Chemical Co., Ltd.; HPLC-grade ammonium acetate was obtained from Fisher (New York, USA). A Milli-Q-Plus Ultra-pure water system from Millipore (Milford, MA, USA) produced the HPLC-grade water used in this study. Other chemicals were of analytical grade and purchased from Agela Technologies (Beijing, China).

2.2 Preparation of Standards.

Eleven pesticide standards listed in Table 1 with a purity of greater than 95.1% were purchased from Sigma Chemical Co., Ltd. Individual stock standard solutions (~ 1000 μg mL^{-1}) of the pesticides were prepared by dissolving 10 mg of each compound in 10 mL of acetonitrile; the solution were stored at -20℃. Mixed-compound stock standard solutions at a concentration of 10 μg mL^{-1} were prepared in acetonitrile and stored in brown bottles at -20℃.

2.3 Flos Carthami Samples.

Flos carthami samples were purchased from Tong Ren Tang Chinese Traditional Medicine Imports and Exports Co. Ltd. (Beijing, China). The samples were crushed, sieved through a mesh of 200 and stored at a temperature below 20℃. These samples were used as controls in the spiked experiments because pesticides were not used during their growth and processing.

2.4 Sample Preparation.

As per the QuEChERS method, which was originally designed for samples with more than 75% moisture, 5 g of the homogenized sample and 15 mL of distilled water were mixed in a 50-mL Teflon centrifuge tube. The tube was vigorously shaken for 1 minute on a vortex mixer, followed by 1 hour of equilibration at room temperature. Then, 10 mL of acetonitrile was added, and the tube was again shaken vigorously for 1 minute. Anhydrous $MgSO_4$ (4 g) and 1 g of NaCl were added, and the mixture was shaken to prevent the anhydrous $MgSO_4$ from congealing. The mixture was homogenized in an ultrasonic bath for 30 min and the extract was centrifuged for 10 min at 6000 rpm.

A 1-mL aliquot of the supernatant (acetonitrile phase) was transferred to a 2-mL micro-centrifuge tube containing 50 mg PSA, 50 mg Al_2O_3-N, 20 mg GCB and 150 mg anhydrous $MgSO_4$ and vigorously shaken for 1 minute. The extract was then centrifuged for 5 minutes at 10,000 rpm to produce an extract in 100% acetonitrile. Prior to analysis, the extract was filtered through a 0.20-μm PTFE filter and transferred to a vial. Five microliters of the filtrate was used for the UPLC-MS/MS analysis.

Matrix extracts were used for validation of the method by the appropriate spiking of the pesticide mixture in the subsequent analysis.

2.5 UPLC-MS/MS Analysis.

The separation of the analytes from the extracts was performed on a UPLC system consisting of a vacuum degasser, an auto-sampler, a column heater and a binary pump (AcquityTM Ultra Performance LC, Waters, Milford, MA, USA). The UPLC was equipped with a reversed-phase rapid-resolution C18 analytical column of 50 mm × 2.1 mm i.d. with a 1.7-μm particle size (Waters, Milford, MA, USA). For each analysis, 5 μL of extract was injected. Mobile phase A consisted of 0.1% (v/v) formic acid and ammonium acetate in water (5 mmol L^{-1}); mobile phase B was acetonitrile. Both mobile phases were pumped at a flow rate of 0.25 mL min^{-1}. The gradient elution program

began at 70% A, with a linear decrease to 45% A over 3 min, then a further decrease to 10% A over 6 min. The mobile phase was then kept at 10% A for 0.2 min, followed by a return to 70% A over 7 min, where it was held for 2 min to re-equilibrate the column prior to the next injection. The auto-sampler tray was maintained at 10℃.

The UPLC system was connected to a triple quadrupole mass spectrometer (Waters Quattro Premier XE, Manchester, UK) that was equipped with an electrospray ionization (ESI) interface (Z-spray). The MS/MS system was operated in the positive ion mode using the following operation parameters: capillary voltage, 3500 V; desolvation gas, nitrogen (99.999% purity), 50 L h^{-1}; cone gas, nitrogen (99.999% purity), 798 L h^{-1}; source temperature, 110 ℃; desolvation temperature, 350℃; and collision cell pressure, 3.2 $\times 10^{-3}$ mbar. Optimization of the cone voltage and the collision energy (CE) for each individual pesticide was carried out by infusion of the pesticide directly into the LC effluent using a syringe pump (Harvard, Kent, UK) at a flow rate of 10 μL min^{-1} in the respective mobile phase composition. MassLynx software v4.1 was used for the instrument control, data acquisition and processing. The analytes were measured in the multiple reaction monitoring (MRM) mode using scheduled time windows. The total ion current (TIC) chromatogram of the 11 carbamate pesticides is shown in Fig. 1. The compound-specific mass spectrometry parameters (i.e., fragmentor voltage and collision energy) are summarized in Table 1.

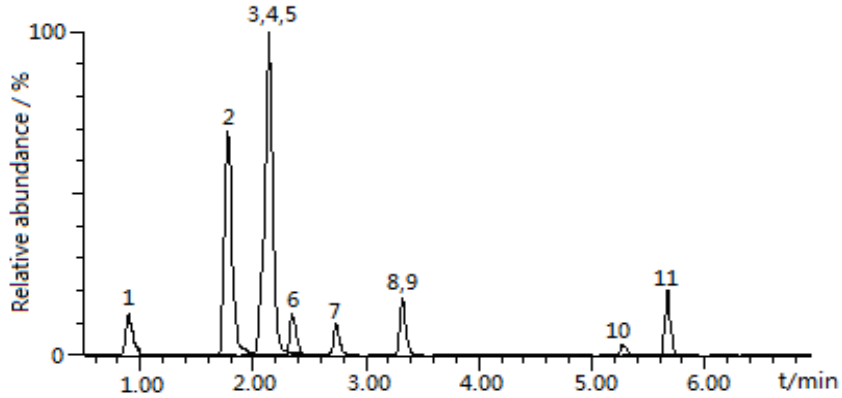


Fig. 1 UPLC-MS/MS total ion current chromatograms of the mixed standard solution of 11 carbamate pesticides (with a concentration of 0.08 mg L-1 for each compound)

Note: For peak identification, see Table 1.

Table 1 UPLC-MS/MS parameters for 11 carbamate pesticides.

Peak No. in Fig. 1	Analyte	Retention time (min)	Parent ion (m/z)	Daughter ion (m/z)	Dwell time (ms)	Cone voltage (V)	Collision energy (ev)
1	Methomyl	0.86	162.9	87.6*, 105.7	50	15	10 / 10
2	Pirimicarb	1.80	239.1	181.9*, 71.7	50	20	15 / 15
3	Propoxur	2.05	210.0	110.7*, 167.8	50	18	15 / 8
4	Carbofuran	2.11	222.1	122.8*, 164.9	50	25	20 / 12
5	Bendiocarb	2.09	224.0	108.7*, 166.8	50	18	18 / 10
6	Carbaryl	2.29	202.0	126.9*, 144.8	50	20	25 / 13
7	Isoprocarb	2.69	194.0	94.6*, 151.7	50	20	15 / 10
8	Methiocarb	3.28	226.0	120.8*, 168.8	50	20	20 / 10
9	Fenobucarb	3.29	208.1	94.8*, 151.8	50	20	15 / 10
10	Indoxacarb	5.29	528.0	150.0*, 218.2	50	31	20/20
11	Furathiocarb	5.63	383.2	166.9*, 195.0	50	10	25/20

* quantitativeion

2.6 Calibration and Recovery Studies.

Matrix-matched standards were used in this study to reduce matrix effects; the Flos carthami sample was used as the blank for preparation of the standards. To obtain the respective calibration curves, a series of standard solutions containing different concentrations of the target analytes were determined. Three replications were conducted for each concentration. For the recovery study, the spiked level were 0.01, 0.02, 0.04 or 0.08 mg kg^{-1} for each compound; a one-hour equilibration at room temperature was required. The peak areas of the spiked samples were measured and plotted against the spiked concentration to generate the calibration curves. The extraction, cleanup and analysis procedures were the same as those described above.

3. Results and Discussion

3.1 Optimization of the Extraction Conditions

Selection of the Extraction Method

Two methods, shaking extraction and ultrasonic extraction, were evaluated for their extraction efficiency. The results showed that the recoveries of the 11 carbamate pesticides spiked in the Flos carthami samples were significantly different when extracted by these two methods (Fig. 2).

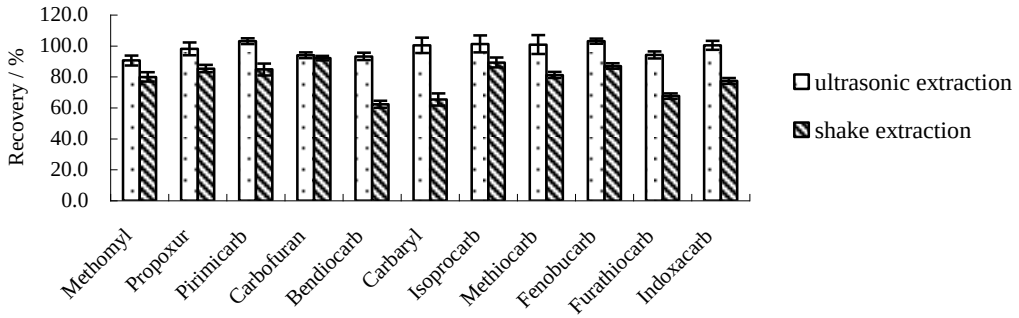


Fig. 2 Effect of two different extraction methods on the recoveries of 11 carbamate pesticides spiked in Flos carthami samples at 0.08 mg kg-1

As shown in Fig. 2, under the same QuEChERS conditions, the recoveries of the 11 carbamate pesticides were higher when using the ultrasonic extraction method than when using the shaking extraction method. By ultrasonic extraction, the average recoveries of the 11 carbamate pesticides ranged from 90.6% to 103.0%, whereas the average recoveries obtained with shaking extraction ranged from 62.3% to 92.0%. The ultrasonic extraction method was, therefore, chosen for use in this study.

Selection of the Extraction Solvent

The most commonly used extraction solvents in the QuEChERS system have been acetonitrile and an acetonitrile solution containing 0.1% acetic acid solution [9]. This is most likely because the distinct properties of acetonitrile allow the effective extraction of polar and nonpolar analytes from various sample matrices with less interference. In addition, there is a well-defined salting-out phase separation of the hydrophilic acetonitrile in undiluted aqueous solution, and it has the capability of a efficient removal of the residual water from the water-miscible solvent with drying salt. Using acetonitrile containing 0.1% acetic acid solution as the extraction solvent has been shown to improve the storage stability of certain base-sensitive pesticides. Therefore, the extraction efficiencies of acetonitrile and acetonitrile containing 0.1% acetic acid were then compared through the determination of the recoveries of the 11 carbamate pesticides.

Fig. 3 shows that the recoveries of the 11 carbamate pesticides ranged from 92.4% to 104.2% after extraction with acetonitrile and from 113.6% to 128.2% after extraction with acetonitrile plus 0.1% acetic acid solution. The latter far exceeded the range of 70% - 120%; therefore, acetonitrile was selected as an extraction solvent for the subsequent analyses.

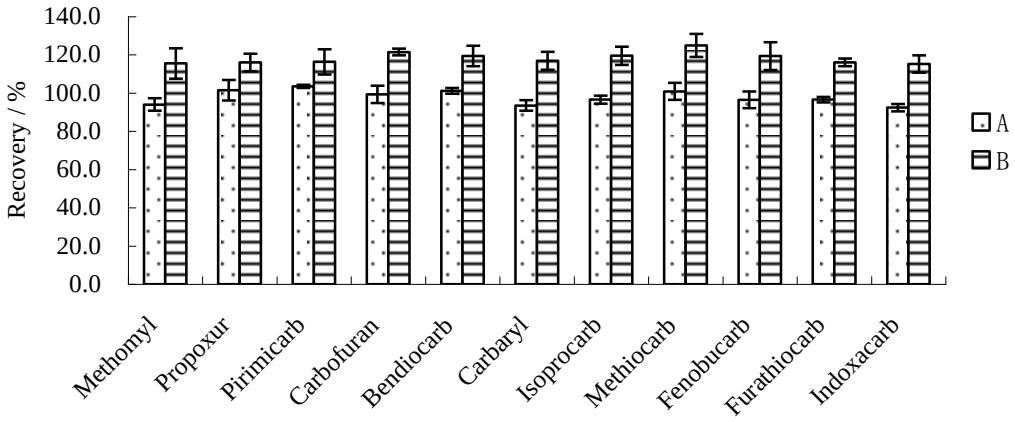


Fig. 3 Effect of two extraction solvents on the recoveries of 11 carbamate pesticides spiked in Flos carthami samples at 0.08 mg kg-1

Note: A: acetonitrile; B: acetonitrile containing 0.1% acetic acid.

3.2 Optimization of the QuEChERS Cleanup Conditions

A combination of extraction and liquid-liquid partitioning was tested after the initial single-phase extraction with acetonitrile. Acetonitrile extracts of the samples were heavily pigmented, which clearly contained large amounts of matrix co-extractants. Thus, the acetonitrile extracts were unsuitable for further analysis due to the high levels of endogenous interfering compounds. To eliminate this interference in the detection of pesticides at trace levels, an additionally efficient cleanup is necessary for the QuEChERS procedure. A 1-mL aliquot of the sample extract was added to a vial containing a small amount of SPE sorbent (50 mg PSA, 50 mg Al_2O_3-N, and 20 mg GCB), and the mixture was shaken or mixed with a vortex mixer briefly to distribute the SPE material evenly. The sorbent was then removed by centrifugation or filtering, and an aliquot of the final extract was analyzed. This approach is most convenient because the SPE sorbent acts as a “chemical filter” to remove interfering matrix components, without retaining the analytes. By using a much smaller quantity of sorbent, DSPE saves time, labor, cost and solvent in comparison with the traditional SPE approach.

Selection of the Sorbent Combination

For maximizing the efficiency of the cleanup using DSPE approach without inadvertently affecting the recoveries, it was necessary to select the best combination of PSA, Al_2O_3-N, GCB, florisol and ODS C18. The PSA sorbent, as a weak anion exchanger, has been commonly used in QuEChERS to remove various co-extractive interferences due to its remarkable active trapping of polar organic acids, fatty acids, some sugars and anthocyanin pigments. It has been reported that GCB is able to remove planar molecules, such as natural pigments (e.g., chlorophyll and carotenoids) from sample matrices. ODS C18 is known as a reversed-phase sorbent to retain lipophilic plant lipids and sterols from fat-containing samples, whereas Al_2O_3-N and florisol are known as normal-phase sorbents, yet their role is similar to ODS C18. Moreover, the supplemental use of anhydrous $MgSO_4$ with these multiple dispersive sorbents helps to remove much of the excess water and to provide a better cleanup of the sample [10]. Therefore, the effects of the sorbent type and composition on the cleanup efficiency and extraction recovery were evaluated.

As shown in Fig. 4, the sequential brightness in the color of the extract was as follows: PSA/Al_2O_3-N/GCB > PSA/Florisil/GCB > PSA/ODS/GCB. Therefore, the efficiency of cleanup was as follows: PSA/Al_2O_3-N/GCB > PSA/Florisil/GCB > PSA/ODS/GCB. The combination of PSA/ Al_2O_3-N/GCB was the most appropriate sorbent combination and was selected for the subsequent analyses. The high cleanup efficiency of this combination could be attributed to the strong lipid adsorbility of Al_2O_3-N.

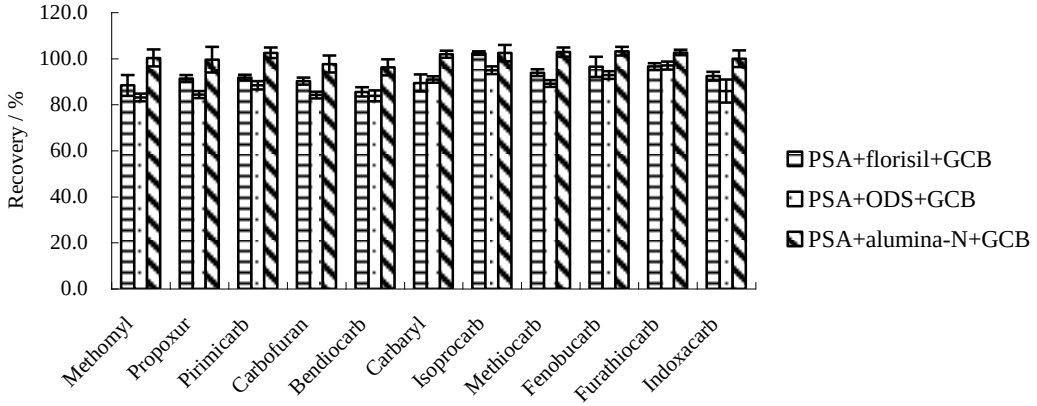
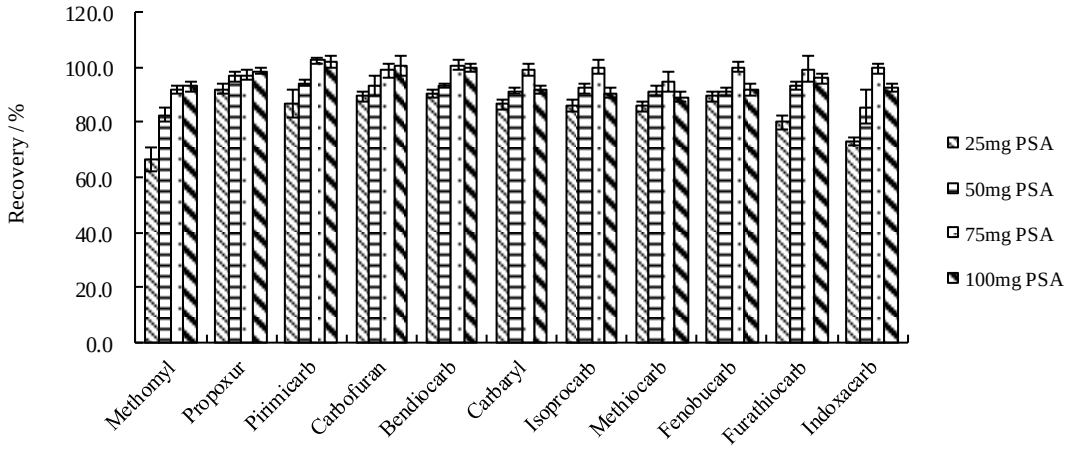


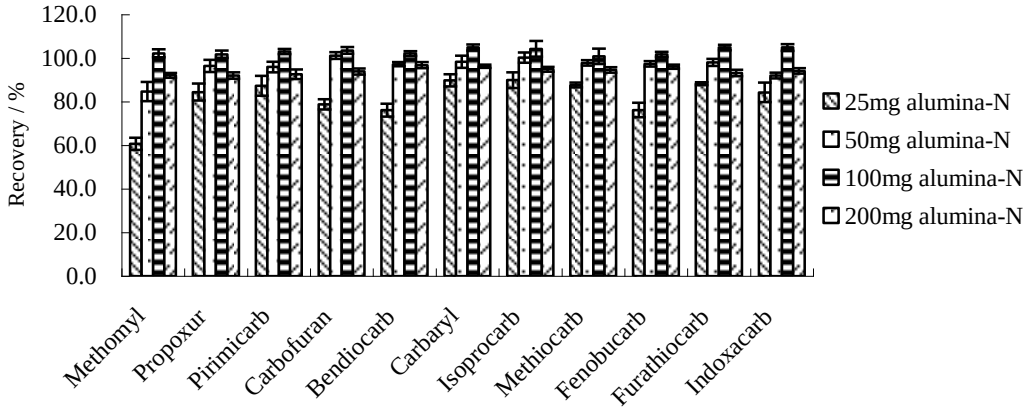
Fig. 4 Effect of different sorbent combinations on the recovery of 11 carbamate pesticides spiked in Flos carthami samples at 0.08 mg kg-1

Capacity of the Different Sorbents in DSPE

To determine the most economical dosage, the effects of different amounts of sorbent on the cleanup efficiency and pesticide recovery were compared.



(a)



(b)

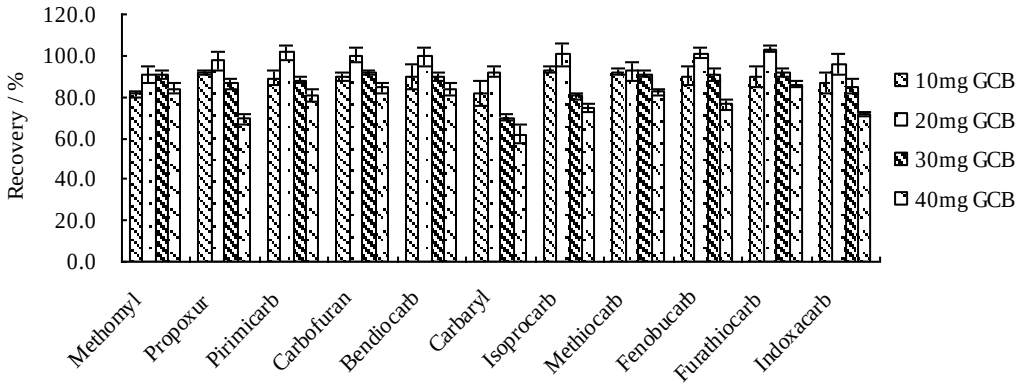
Fig. 5a shows the effect of different amounts of PSA in the DSPE for the cleanup of the Flos carthami extracts. The PSA was included at 25, 50, 75 or 100 mg in the sorbent combination. When 25 mg of PSA was used in combination with 50 mg Al_2O_3-N and 20 mg GCB to cleanup 1 mL of the sample extracts, the recovery of methomyl was less than 70%, and the other 10 carbamate pesticides

exhibited satisfactory recoveries (ranging from 70% to 120%). In contrast, the 11 carbamate pesticides showed recoveries of 70-120% after treatment with 50, 75 or 100 mg PSA in combination with 50 mg Al_2O_3-N and 20 mg GCB. Although the recoveries with 75 or 100 mg PSA ranged from 80-120%, in order to save the sorbent, 50 mg of PSA was chosen for use in the remainder of the study.

The Al_2O_3-N was used at 25, 50, 100 or 200 mg in the sorbent combination. As indicated in Fig. 5b, when 25 mg Al_2O_3-N was combined with 50 mg PSA and 20 mg GCB to cleanup 1-mL of the sample extracts, 10 carbamate pesticides had satisfactory recoveries (ranging from 70% to 120%), except that of methomyl, which was less than 70%. After treatment with 50, 100 or 200 mg Al_2O_3-N in combination with 50 mg PSA and 20 mg GCB, all of the 11 carbamate pesticides showed recoveries of 70-120%. Although the recoveries with 100 mg and 200 mg Al_2O_3-N also fell within this range, in order to save the sorbent, 50 mg Al_2O_3-N was selected for use in the remainder of the study.

Fig. 5c summarizes the pesticide recovery with different dosages of GCB (at 10, 20, 30 or 40 mg) in combination with 50 mg PSA and 50 mg Al_2O_3-N. With increasing amount of GCB, the color of the co-extractive became more transparent. Although the recoveries with 10 mg of GCB ranged from 70% to 120%, the darker color of the co-extractive suggested that residual (pigmented) compounds remained, which could potentially obstruct or clog the equipment. At 20 mg GCB, the recoveries of the analytes reached the highest and most satisfactory values, whereas at the amounts of 30 mg and 40 mg GCB, the recoveries dramatically decreased. An explanation of this phenomenon could be that the higher amount of GCB retained more of the carbamate pesticides.

Based on the above experiments, our DSPE protocol adopted the ternary combination of PSA/Al_2O_3-N/GCB (50 mg/50 mg/20 mg per mL of extract) to remove efficiently a variety of matrix materials and achieve satisfactory recoveries of all of the target analytes in Flos carthami samples.



(c)

Fig. 5 Effect of different amounts of sorbent (a: PSA, b: Alumina-N and c: GCB) on the recovery of 11 carbamate pesticides spiked in Flos carthami samples at 0.08 mg kg-1

3.3 Analytical Method Performance

The linearity was evaluated using matrix-matched standards in the range of 5 ng mL^{-1} to 200 ng mL^{-1}. A good linearity was found for all of the analytes, with correlation coefficients higher than 0.99 (Table 2). The sensitivity of the method was determined in terms of the limits of detection (LODs) and limits of quantification (LOQs). The LODs and LOQs were calculated as the minimum amount of target analyte that produced a chromatogram peak with a signal-to-noise ratio of 3 and 10, respectively. The LODs and LOQs obtained for the different carbamate pesticides are shown in Table 2. The LODs ranged from 0.3 to 6.0 μg kg^{-1} and the LOQs were in the range of 1.0-19.0 μg kg^{-1}.

The accuracy and reproducibility of the assessed quantitative method (QuEChERS sample preparation and UPLC-MS/MS determination) were evaluated by means of a recovery study on the blank Flos carthami samples spiked at four concentration levels, with six replicates at each level. The mean recoveries and the corresponding relative standard deviations (obtained on each spiking level) are indicated in Table 2. Sufficent recoveries, ranging from 81.1% to 104.2% with RSD values < 10%, were obtained for all of the carbamate pesticides studied. The good recoveries and reproducibility of

the proposed method make it suitable for the quantification of a wide polarity range of carbamate pesticides at trace level in Flos carthami.

Table 2 Calibration curves, correlation coefficients (r2), spiked recoveries, limits of detection (LODs) and limits of quantification (LOQs) for 11 carbamate pesticides in Flos carthami samples.

Analyte	Calibration curve (linear range: 5-200 ng mL^{-1})	r^2	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	Average recovery ± RSD (n=6)			
					0.01 mg kg^{-1}	0.02 mg kg^{-1}	0.04 mg kg^{-1}	0.08 mg kg^{-1}
Methomyl	Y=85.32X-10.5025	0.999	0.0019	0.0064	81.1±6	92.3±6	99.3±5	98.1±5
Propoxur	Y=391.50X+245.278	0.999	0.0030	0.0100	87.6±10	96.9±4	103.5±1	101.2±3
Pirimicarb	Y=1313.74X-1808.43	0.999	0.0020	0.0700	89.1±8	96.3±6	100.8±8	101.1±4
Carbofuran	Y=564.89X+39.959	0.999	0.0030	0.0100	92.0±5	95.9±6	101.4±4	103.4±5
Bendiocarb	Y=57.09X+41.4539	0.999	0.0060	0.0190	91.8±1	99.2±4	103.2±3	103.9±6
Carbaryl	Y=49.31X-3.61149	0.999	0.0021	0.0700	88.3±5	97.7±7	102.4±2	104.2±6
Isoprocarb	Y=70.25X+57.3845	0.999	0.0021	0.0700	86.1±3	101.1±1	101.9±2	99.8±7
Methiocarb	Y=74.23X+11.2219	0.999	0.0024	0.0790	90.0±4	97.7±6	98.8±5	98.2±7
Fenobucarb	Y=111.31X+28.4587	0.999	0.0012	0.0039	90.3±8	99.7±3	102.0±4	99.3±7
Furathiocarb	Y=261.37X-164.535	0.999	0.0003	0.0010	82.9±3	99.4±3	101.8±3	100.5±6
Indoxacarb	Y=55.80X+45.1225	0.998	0.0015	0.0050	87.5±7	100.1±2	100.6±4	102.3±6

Y : peak area ; X : mass concentration , μg L^{-1}.

3.4 Application to Real Samples

To evaluate the effectiveness of the proposed methodology in practice, four real Flos carthami samples purchased from different parts of China, including Beijing, Xinjiang Uygur Autonomous Region and Gansu Province, were analyzed. The quantification was performed by an external calibration. A frequent appearance of carbofuran and triallat was found in the Flos carthami samples in the range of 0.007-0.037 mg kg^{-1}.

4. Conclusion

In the study presented here, we optimized a multi-residue analytical method using QuEChERS sample preparation and UPLC-MS/MS analysis, in which two different extraction methods, five different sorbent materials and two solvents were compared for removing interfering materials out of the extracts. The proposed method is simple, rapid, effective and environmentally friendly and accomplished the simultaneous analyses of 11 pesticides with satisfactory recoveries, low limits of detection, the potential for high throughput and a short analytical turnround time (6 minutes). Our study suggested that the QuEChERS method could be extended and applied in analysis of carbamate pesticides and their metabolites in a variety of medicinal herbs, in addition to Flos carthami.

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