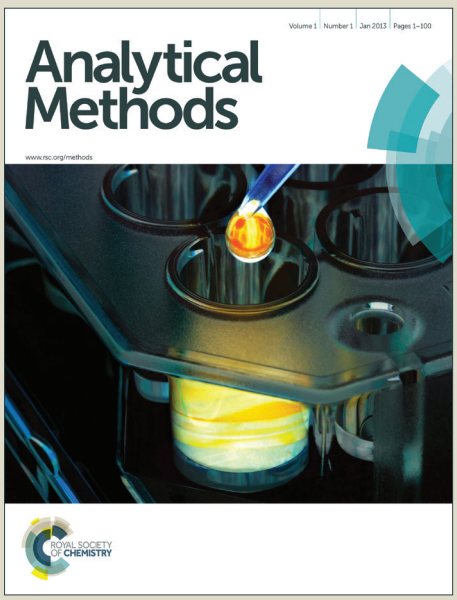
Analytical Methods

Accepted Manuscript



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Rapid and sensitive detection of abamectin in edible oils by solid phase extraction combined with ultra-high-pressure liquid chromatography-tandem mass spectrometry

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Abstract: This study proposed a fast, simple and sensitive ultra-high-pressure liquid chromatography-tandem mass spectrometry (UPLC-MS/MS)-based method for the detection of abamectin in edible oils. An effective one-step process of extraction and cleanup of abamectin from edible oils was achieved with the use of a humic acid-bonded silica (HAS) based solid phase extraction (SPE), providing good cleanup performance and satisfactory recovery of abamectin. The effects of experimental variables, such as the amount of sorbents, loading, washing and eluting solvents, and the flow rates of sampling and eluting have been studied in detail. Under the optimized conditions, the method validation was performed in terms of linearity, recovery and precision. Good linearity was obtained for abamectin with R^2 0.9996. The limit of detection (LOD) was found to be 0.16 μg/kg. The method recoveries of abamectin spiked at three concentration levels in a blank sample were from 91.7% to 101.8%, with inter- and intra-day relative standard deviations (RSDs) less than 7.0%.

1 Introduction

Abamectin, which is produced by the actinomycete streptomyces avermitilis, belongs to macrocyclic lactone compounds.[1, 2] It consists of a mixture of abamectin B_{1a} (at least 80%) (As shown in **Figure 1**) and abamectin B_{1b} (not more than 20%). Due to its high toxicity to agriculture pests by acting on nervous system, abamectin is widely used in agricultural crops against target mites and insect pests.[3] However, abamectin may be also toxic to mammals including human beings.[4] In China, maximum residue limit (MRL) of abamectin in vegetables and oil crops are from 10 to 100 μg/kg (GB/T 2763-2012). Therefore, it is significant to develop simple, efficient and sensitive method for the monitoring of the concentration level of abamectin in food.

At present, there have been many reports for the analysis of abamectin in vegetables and fruits,[1, 3-5] milk,[6, 7] animal tissues[8-11] and blood.[12] Abamectin with high n-octanol-water partition coefficient ($K_{O/W}$) maybe also easily concentrate in vegetable oils extracted from oil crops.[13] However, analysis of abamectin in edible oils is challenging owing to its low concentration relative to the high concentrations of endogenous compounds, such as triglyceride and tocopherol. A rigorous clean-up of sample extract is necessary to avoid high amount of fat residues in the final solution, which would decrease rapidly resolution efficiency and detection sensitivity. So far, there is only one reported method for analysis of abamectin in edible oils, in which liquid-liquid extraction (LLE) combined with low temperature purification (LTP) was performed to remove co-extracted interferences.[14] However, this method

involved with a multi-step process of extraction and purification and required a lot of time to freeze sample matrix. Meanwhile, no MRL of abamectin has been set in edible oils. Therefore, it is significant to develop simple, reliable, efficient and sensitive method for the monitoring of the concentration level of abamectin in edible oils.

Several high performance liquid chromatography (HPLC) methods have been proposed for the determination of abamectin in various food. HPLC-UV detection methods are not sensitive enough to ensure compliance with legislation.[1, 15] Although the use of fluorescence detection (FD) could provide lower detection limits,[3, 9-10, 16] the derivatization step made the whole analysis process time-consuming and labor-intensive, and the derivative was not stable.[17, 18] Compared to HPLC-UV or FD methods, HPLC combined with triple-quadrupole tandem mass spectrometry (HPLC-MS/MS) in multiple reaction monitoring (MRM) mode could provide better sensitivity, selectivity and molecular weight information for exact identification, making this technique very suitable for the trace analysis of abamectin in complex food matrices. [2, 17, 19-21]

Nevertheless, due to the low concentration of abamectin and possible complex sample matrices in edible oils, sample pretreatment is unavoidable prior to instrumental analysis. Traditional liquid-liquid extraction (LLE) has limitations due to the time-consuming nature and the requirement of amount of organic solvents, some of which may be toxic and carcinogenic.[22] Solid phase extraction (SPE) is another popular sample pretreatment method, which has many advantages over traditional LLE in terms of selectivity, extracts, reproducibility and avoidance of emulsion

formation.[22] However, traditional SPE sorbents, such as C_{18} materials, show poor selectivity and only offer hydrophobic interaction for target compounds. Therefore, it is favorable to develop new materials with high selectivity as SPE sorbents to enrich and purify abamectin from edible oils.

In our previous reports, a novel SPE sorbent prepared by immobilization of humic acid on silica was developed and applied to the extraction of benzo[a]pyrene (BaP) from edible oil and Sudan dyes from hot chilli products.[23, 24] Owing to its peculiar structure, humic acid-bonded silica (HAS) could provide multiple interactions with target analytes, such as chelation, charge-transfer interactions, hydrophobic interactions, dipole-dipole interactions, ion exchange reactions, and hydrogen bonding.[25] In this paper, a HPLC-MS/MS coupled with HAS-based SPE method was proposed for the determination of abamectin in edible oils. Different parameters affecting the extraction process were studied and optimized in detail. To the best of our knowledge, this is the first time that SPE is used for the specific extraction of abamectin from edible oils.

2 Materials and methods

2.1 Reagents and materials

The irregular silica (50–74 μm) for preparing the SPE sorbent was purchased from Qingdao Haiyang Chemical Plant (Qingdao, China). 3-Aminopropyltrimethoxysilane (APTS) was obtained from the Chemical Plant of Wuhan University (Wuhan, China). Humic acid was supplied by Sinopharm Chemical

Reagents (Shanghai, China) and purified according to the method reported by Yang et al. before use. [26] Cleanert Florisil, Cleanert PSA and Cleanert ODS C18N cartridges were all purchased form Agela Technologies (Tianjin, China), and Oasis HLB cartridges was obtained from Waters (Milford, USA). Dichloromethane, n-hexane, ethyl acetate and ethanol were supplied by Sinopharm Chemical Reagents (Shanghai, China) and of analytical reagent grade. Methanol (HPLC grade) was obtained from Fisher Scientific (USA). Toluene, thionylchloride, N, N-dimethylformamide (DMF), and other solvents were purchased from the Shanghai Chemical Reagent Company (Shanghai, China) and were of analytical reagent grade. Water used throughout the study was purified using Milli-Q water system (Millipore, Billerica, MA, USA).

Individual standard solution (1 000 μg/mL) of abamectin (B1a) was purchased from Agro-Environmental Protection Institute, Ministry of Agriculture (Tianjin, China). The standard stock solution (10 μg/mL) was prepared in methanol and stored at -18 ℃. The working standard solutions were prepared daily. The sample solutions were spiked to the desired concentration for experiments.

2.2 Instrumentation

Liquid chromatography was performed using a Waters ACQUITY ultra-performance liquid chromatography (UPLCTM) system. The analytical column used was a Waters ACQUITY UPLC@BEH C18（50×2.1 mm, 1.7 μm）(Waters, Zellik, Belgium) with a flow rate of 0.3 mL/min. An aliquot of 5 μL sample extract was injected into the chromatographic system. Volumes of weak wash (10% MeOH) and strong wash (100% MeOH) solvents were 500 μL each. The column and sample

temperature were maintained at 40 ℃ and 10 ℃, respectively. Mobile phase was composed of MeOH/H_2O containing 0.01% HCOOH and 0.05% NH_4OH (95/5, v/v).

Tandem Mass spectrometry (MS/MS) was performed with a XevoTMTQ-S tandem quadrupole mass spectrometer (Waters, Milford, MA, USA). The MS was operated at electrospray ionization in positive mode (ESI+). For infusion experiments, 20 μg/L of abamectin standard dissolved in mobile phase was used at a flow rate of 10 μL/min. The capillary voltage was set at 3.5 kV. High pure nitrogen (N_2, 99.999%) was used as cone, nebulizing and desolvation gas. High pure argon (Ar, 99.999%) was used as Collision gas. The source temperature and desolvation temperature were set at 150 ℃ and 350 ℃, respectively. The cone and desolvation gas flow were maintained at 50 L/h and 700 L/h, respectively. Collision gas flow was set at 0.16 mL/min. Analysis of abamectin was performed in MRM mode. The most abundant product ion was selected for quantification and the second intense one for qualification. For data acquisition and processing, Masslynx and Quanlynx software 4.1 (Waters) was used.

2.3 Preparation of humic acid-bonded silica cartridges

HAS sorbent was prepared according to our previous work.[23] The HAS SPE cartridges were packed as followed: the resultant sorbent (500 mg) was packed into a 3-mL polypropylene syringe, and the material was retained by two polyethylene frits. Then SPE was performed on a Supelco 12-port model SPE Vacuum Manifold (Bellefonte, PA, USA).

2.4 Steps of SPE

0.50 g of oil sample was exactly weighed into a 10 mL centrifuge tube, and then the test sample was spiked with known amount of abamectin and incubated for 10 min at room temperature. Then the oil sample was diluted with 2 mL of n-hexane and vortexed for 1 min. Then, the mixture was loaded onto the HAS SPE cartridge which was sequentially preconditioned with 3 mL of acetone and 3 mL of n-hexane for activation. After the cartridge was rinsed with 10 mL of ethyl acetate/n-hexane (50:50, v/v), 2 mL of acetone was used for elution (at about 1 mL/min) and the eluate was collected into a centrifuge tube. The collected fraction was evaporated to dryness under a mild nitrogen stream at room temperature. The residue was dissolved in 1 mL of MeOH/H_2O (50:50, v/v) and the resulting solution was filtered through a deposable filter (0.45 μm pore) for HPLC-MS/MS analysis.

3 Results and discussion

3.1 Optimization of UPLC-MS/MS

In this study, UPLC system was used to analyze abamectin in edible oils, which resulted in a shorter peak width and higher signal-to-noise ratio. Furthermore, both the running time and between-sample column equilibration time were shortened considerably. To improve the sensitivity and stability for the determination of abamectin in edible oils, additives in mobile phase and MS parameters were optimized in details. It is reported that $[M+NH_4]^+$ adduct ion in ESI^+ mode was suitable for the detection of abamectin.[11] Thus a certain amount of HCOOH and NH_4OH was added to the mobile phase. The results indicated that mobile phase

composed of MeOH/water containing 0.01%HCOOH and 0.05% NH_4OH (95/5, v/v) could provide good and stable response of $[M+NH_4]^+$. Then the optimization of daughter ions as well as their collision energies and cone voltages was performed under the daughter scan mode to establish the MRM quantification method for quantification and confirmation. The quantification and qualification ion transitions of abamectin and the optimum collision energies and cone voltages were shown in **Table 1**.

3.2 Optimization of the SPE Conditions

The optimization of the SPE conditions was conducted on the blank oil samples spiked with 10 μg/kg abamectin. Various parameters such as the amount of sorbents, the loading solution, the washing solution, the desorption solution and the flow rates of sampling and eluting were investigated.

Optimization of the Amount of Sorbent. The different amounts of HAS sorbents (0.1 g, 0.3 g, 0.5 g and 1.0 g) was investigated in our study, and the recoveries of abamectin were 25.1%, 54.5%, 96.6%, 67.3% under the optimized conditions. It is diffcult to elute abamectin using 2 mL acetone from an excess of amount of HAS sorbent, leading to low recovery when 1.0 g of HAS sorbent was used. Therefore, 0.5 g of HAS sorbent was selected for the following experiment.

Optimization of the Sample Loading Conditions. The viscosity of oil samples is always very large. Therefore, it is necessary to select an appropriate solvent to dilute oil samples for extraction of abamectin by HAS-based SPE method. Dichloromethane and n-hexane were investigated in this study. The results are demonstrated in **Figure 2**.

It can be observed that the recovery of abamectin using n-hexane was about 100% while the recovery of abamectin using dichloromethane was lower than 30%. In the process of sample loading, the eluting ability of dichloromethane is stronger than that of n-hexane. Therefore, n-hexane was selected for further experiment.

Optimization of the Washing Conditions. After sample loading, cleanup procedure was essential, especially for the oil samples with complex sample matrices, which would seriously disturb the detection of target analytes. The cleanup step should meet the demand that the matrix interferences should be removed to the maximum extent while the loss of target analytes should be reduced to the minimum extent. Therefore different proportions of ethyl acetate to n-hexane were tested as the cleanup solution. The results are shown in **Figure 3**. With the increasing proportion of ethyl acetate to n-hexane, the recoveries of abamectin were gradually decreased. Ethyl acetate/n-hexane (50:50, v/v) was chosen as washing solution. We further optimized the volume of washing solution from 5 mL to 15 mL. As shown in **Figure 4**, 10 mL of washing solution was suitable for the high recovery of abamectin and removing of as much matrix interferences as possible.

Optimization of eluting solvents. We further optimized the eluting conditions. Different solvents such as methanol, acetonitrile, acetone and isopropanol were tested as eluents for the investigation of eluting efficiencies of abamectin. As shown in **Figure 5**, about 100% recoveries of abamectin could be achieved using methanol and acetone as eluents. Considering that acetone was much easier to concentrate for next analysis, acetone was selected as the eluting solvent. The effects of eluent volumes on

the recoveries were also investigated. We found that 2.0 mL acetone was enough for the effective elution of abamectin from HAS cartridge. Therefore, 2.0 mL acetone was selected as eluent at last.

Optimization of flow rates of sampling and eluting. The flow rates of sampling and eluting were also investigated. The results indicated that the rates in the range of 0.5 to 2 mL/min have no obvious influence on the recoveries of abamectin. In this study, the flow rates of sampling and eluting were adjusted to about 1 mL/min to obtain high recoveries and suitable analysis time.

Comparison of HAS sorbent with some commercial sorbents for the extraction of abamectin. Some commercial cartridges such as Cleanert Florisil, Cleanert PSA, Cleanert ODS C18N, and Oasis HLB were used to extract abamectin from oil samples under the conditions above. The recoveries of abamectin obtained by Florisil and PSA were 45.7% and 63.1%, respectively, while the recoveries of abamectin obtained by ODS and HLB were less than 10%. To further make a fair comparison, the extraction conditions for each cartridge were separately optimized. When ethyl acetate/n-hexane (10:90, v/v) was chosen as washing solution, the recoveries of abamectin obtained by Florisil and PSA were 72.4% and 84.3%, respectively, while the recoveries of abamectin obtained by ODS and HLB were also less than 10%. Low recoveries obtained by ODS and HLB were due to the hydrophobic retention mechanism as well as strong loading and washing solvents. Although the recoveries obtained by Florisil and PSA could meet the requirements of analysis method, there were some obvious oily matrix interferences after the eluting solution was evaporated to dryness, which

would influence the life time of the instrument and analytical stability. On the other hand, the recovery of abamectin obtained by HAS sorbent was 96.6% under the optimized conditons, and good cleanup performance could be achieved. Those results indicated good retention and selectivity of HAS sorbent for the extraction of abamectin in edible oils.

Figure 6 shows the typical chromatograms of the abamectin for blank and spiked oil samples. No interferences from sample matrix were observed after SPE under the optimized conditions.

3.3 Validation of the SPE-HPLC-MS/MS method

Calibration curves, detection limits, accuracy and precision. Matrix effects was always observed in HPLC-MS/MS with ESI mode due to the effect of matrix interferences on the ionization efficiencies of target analytes. Therefore, matrix-matched standard is necessary to correct for matrix effect for quantification analysis in HPLC-MS/MS. In this study, matrix-matched calibration solutions spiking in blank sample solutions at six concentration levels from 1 to 100 ng/mL were prepared to avoid the matrix effects. The calibration curves were established by plotting the peak areas of the analyte versus the concentrations of analyte. Limit of detection (LOD) and limits of quantification (LOQ) was calculated as the concentrations corresponding to a signal of 3 and 10 times the standard deviation of the baseline noise, respectively. Abamectin showed good linearity in the range of 0.5-100 μg/kg with satisfactory squared regression coefficients (R^2) 0.9996. The LOD and LOQ were found to be 0.16 μg/kg and 0.50 μg/kg, respectively.

To assay the accuracy of the method, recoveries were investigated on spiked oil samples at three different concentration levels of 1.0, 10.0 and 100.0 ng/mL. The recoveries were determined by comparing the calculated amounts of abamectin in the samples (using calibration curve) with the spiking amounts. The precision of the method was assessed by determining the intra- and inter-day relative standard deviations (RSDs) at three concentration levels. As listed in **Table 2**, the method recoveries at three different concentration levels of 1.0, 10.0 and 100.0 μg/kg were 101.8%, 94.0% and 91.7%, respectively. The intra-day and inter-day RSDs were below 4.4 % and 7.0%, respectively. Those results indicated that the proposed method was suitable for routine analysis.

Application of the proposed method for determination of the abamectin in edible oils products. The proposed SPE-HPLC-MS/MS method was successfully applied to the trace analysis of abamectin in five kinds of vegetable oils from market in Wuhan, China. The results are given in **Table 3**. No abamectin was detectable in those samples. The recoveries spiked at 10 μg/kg for abamectin were in the range of 102.3 to 118.6%, with RSDs less than 5.4 %.

Comparison with the previous method for abamectin determination in edible oils. The present HAS-based method was compared with the previous method based on liquid-liquid extraction (LLE) combined with low temperature purification (LTP) for analysis of abamectin in oil samples. As shown in Table 4, the LOD, recoveries and RSDs were comparable to this reported method. However, the reported method involved with a multi-step process of extraction and purification and required a lot of

time to freeze sample matrix. In this study, an effective one-step process of extraction and cleanup of abamectin from edible oils was achieved with the use of HAS-based SPE method, which uses less time and saves significant labor for analysis of abamectin in edible oils.

4 Conclusion

In this study, the feasibility of SPE based on HAS sorbent coupled to UPLC-ESI-MS/MS for confirmative as well as quantitative determination of abamectin residue in edible oils was demonstrated. The sampling, washing and eluting conditions were optimized to remove the matrix interferences as much as possible and obtain high recoveries of target analyte. Under the optimized conditions, the proposed SPE-UPLC-ESI-MS/MS platform was applied to determine abamectin residue in edible oils in five kinds of vegetable oils and no analyte was detectable among those samples. Recoveries of abamectin spiked in five kinds of vegetable oils were between 102.3 to 118.6% with RSDs less than 5.4%, indicating the good reliability and applicability of the proposed method for the analysis of different kinds of edible oils.

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Figure captions

Figure 1 Chemical structure of abamectin B_{1a}.

Figure 2 Effect of types of loading solvent on the recoveries of abamectin. The spiked samples with abamectin at 10 μg/kg were prepared with n-hexane and dichloromethane. Other SPE conditions were described in the experimental section.

Figure 3 Effect of the proportion of washing solvent (n-hexane/ethyl acetate, v/v) on the recoveries of abamectin. The HAS-based cartridges were washed with different proportions of washing solvent (n-hexane/ethyl acetate, v/v). Other SPE conditions were described in the experimental section.

Figure 4 Effect of the volume of washing solvent (n-hexane/ethyl acetate, 5/5) on the recoveries of abamectin. The HAS-based cartridges were washed with different volumes of washing solvent (n-hexane/ethyl acetate, 5/5) . Other SPE conditions were described in the experimental section.

Figure 5 Effect of eluting solvent types on the recoveries of abamectin. The HAS-based cartridges were eluted with different solvents. Other SPE conditions were described in the experimental section.

Figure 6 MRM chromatograms of a blank oil sample (a), as well as the sample spiked with abamectin at the concentration of 10 μg/kg (b). Retention time of abamectin: 0.66 min.

Tables

Table 1 Ion information of abamectin acquired by MS/MS

	Retention time (min)	Ion transition	Cone voltage (V)	Collision energy (ev)
Abamectin	0.66	890.5 > 305.2*	20	25
		890.5 > 567.3		15

Table 2 Precisions (intra- and inter-assay) and recoveries for the determination of abamectin in edible oils

Amount added (μg/kg)	Intra-assay (n = 4)			Inter-assay (n = 4)	
	Measured concentration (μg/kg)	Recoveries (%)	RSD (%)	Measured concentration (μg/kg)	RSD (%)
1.0	1.02	101.8	2.9	0.96	7.0
10.0	9.40	94.0	4.4	9.50	5.3
100.0	91.69	91.7	2.0	90.01	6.3

Table 3 Analytical results of abamectin in edible oils (n=4)

Samples	Sample A	Sample B	Sample C	Sample D	Sample E

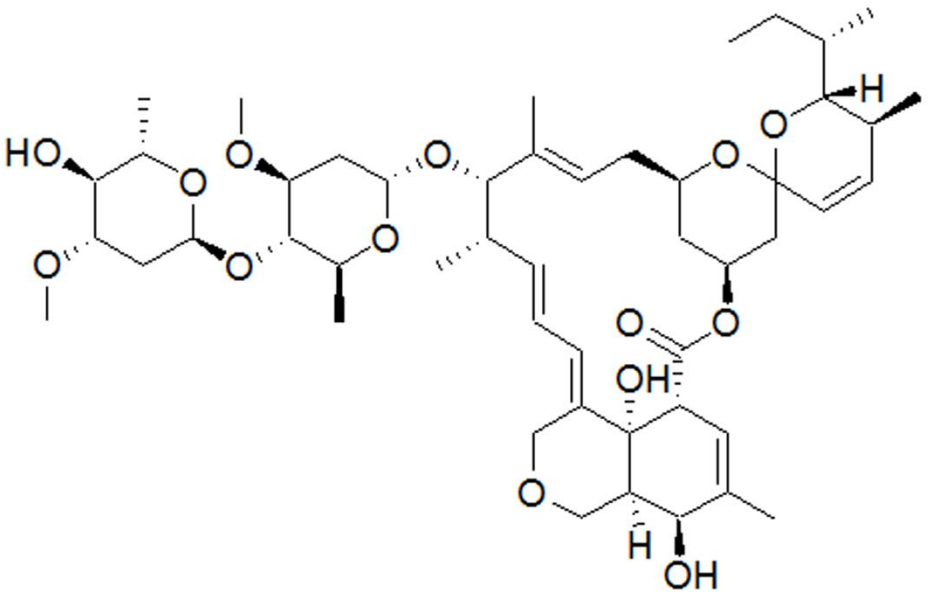
Mean concentration (μg/kg)	n.d. [a]	n.d.	n.d.	n.d.	n.d.
Added	10.0	10.0	10.0	10.0	10.0
Founded	10.71	11.86	11.32	10.23	11.86
Recovery (%)	107.1	118.6	113.2	102.3	118.6
RSDs (%)	5.4	0.6	3.9	0.2	4.8

[a] n.d referred to not detected.

Table 4 Comparison of method performance and analysis time with the previous method for detection of abamectin residue in edible oils

Sample preparation	Detection Method	Recoveries (%)	LOD (μg/kg)	RSD (%)	Analysis time (h) [a]	Reference
LLE+LTP	HPLC-MS/MS	85.9-119.3	0.16	3.2-10.3	17	14
SPE	HPLC-MS/MS	91.7-101.8	0.2-0.4	2.0-7.0	1	This paper

[a] Analysis time referred to the time of the whole analysis process for abamectin detection in edible oils, and was approximately estimated according to the literatures above.



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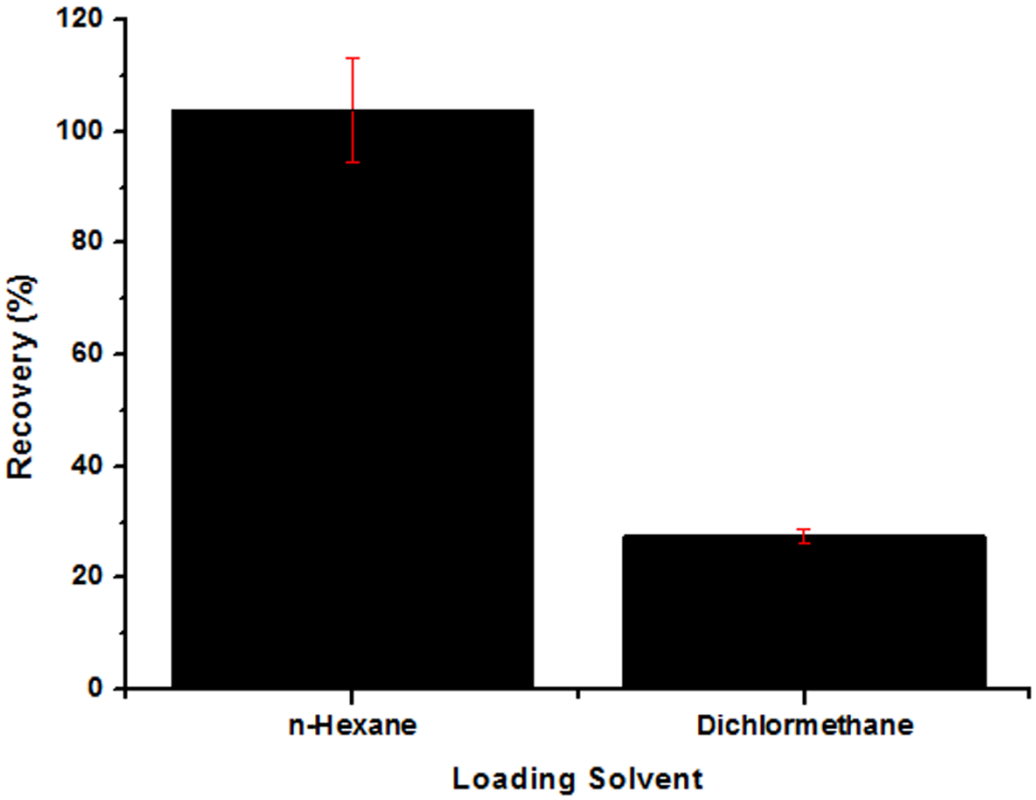
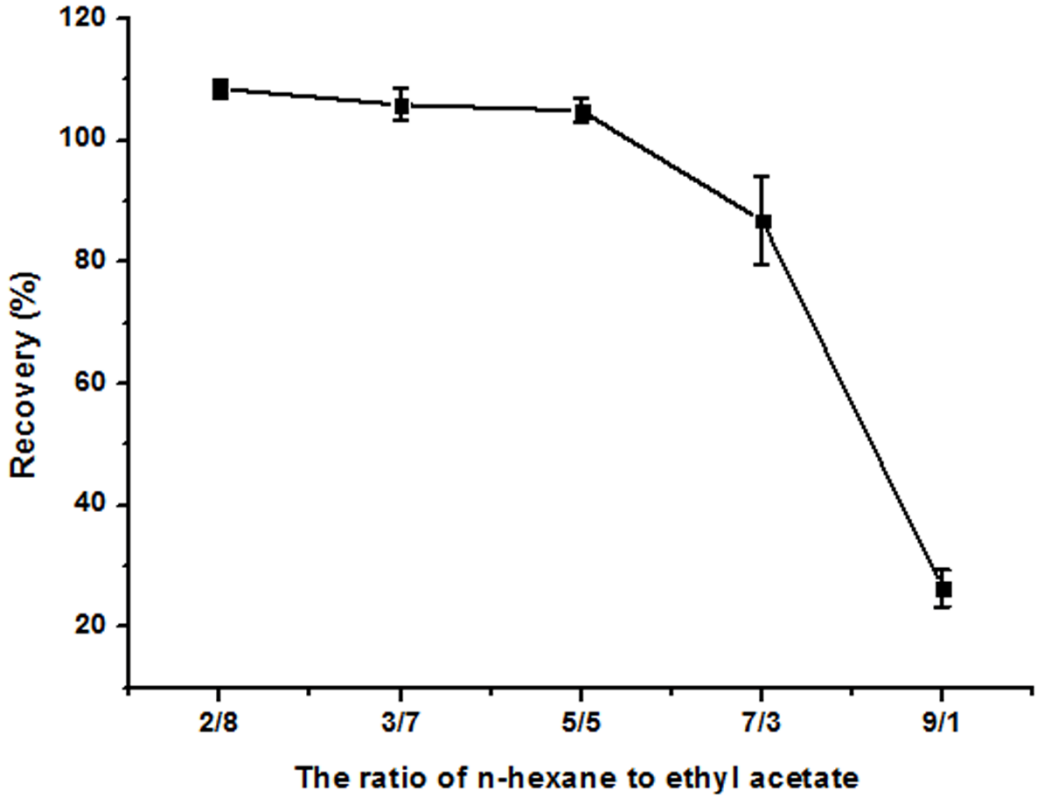


Figure 2 Effect of types of loading solvent on the recoveries of abamectin. The spiked samples with abamectin at 10 μg/kg were prepared with n-hexane and dichloromethane. Other SPE conditions were described in the experimental section.



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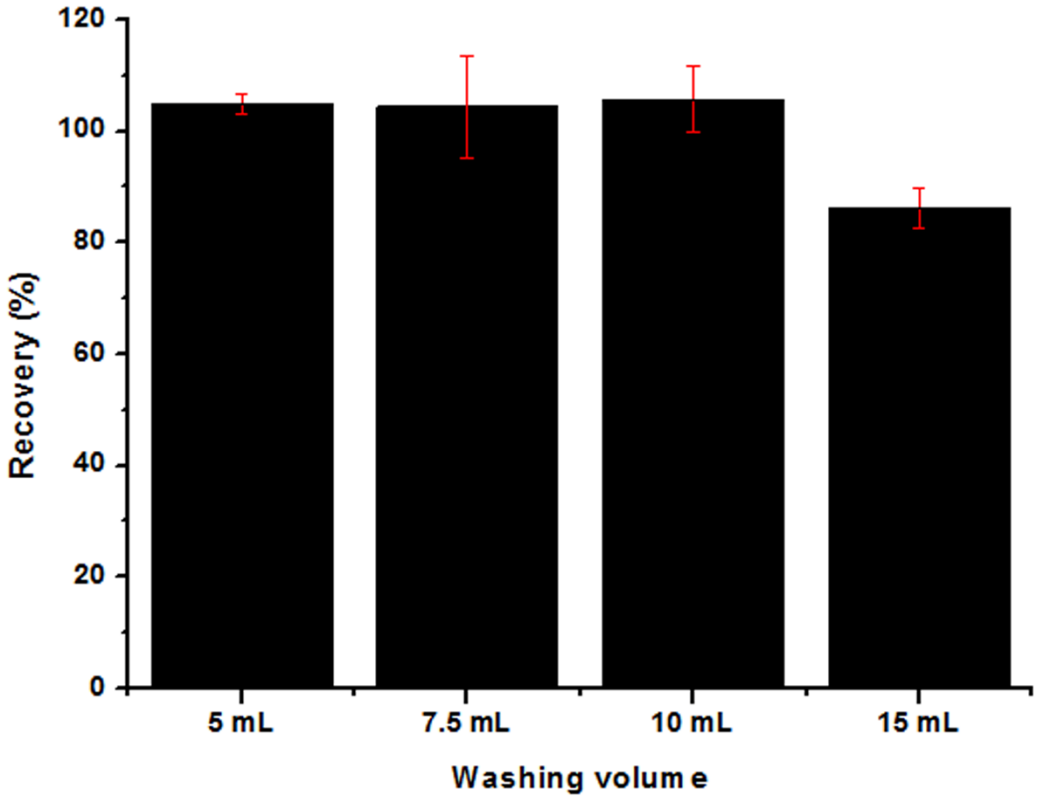

Figure 4 Effect of the volume of washing solvent (n-hexane/ethyl acetate, 5/5) on the recoveries of abamectin. The HAS-based cartridges were washed with different volumes of washing solvent (n-hexane/ethyl acetate, 5/5). Other SPE conditions were described in the experimental section.

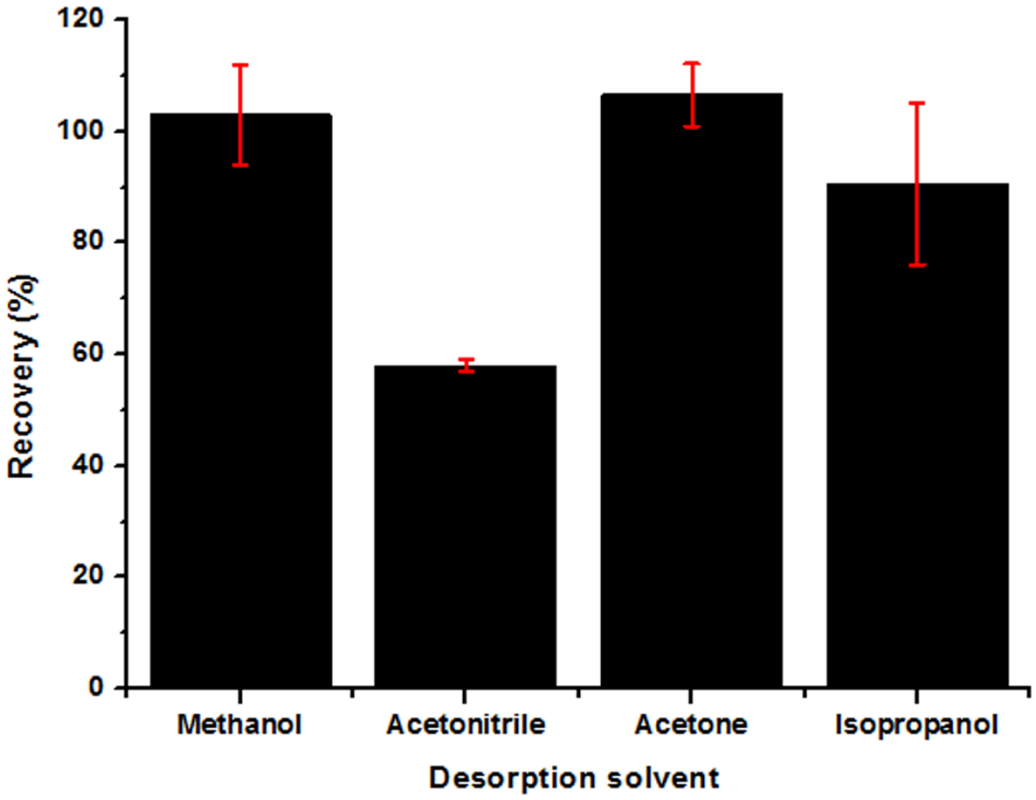

Figure 5 Effect of eluting solvent types on the recoveries of abamectin. The HAS-based cartridges were eluted with different solvents. Other SPE conditions were described in the experimental section.

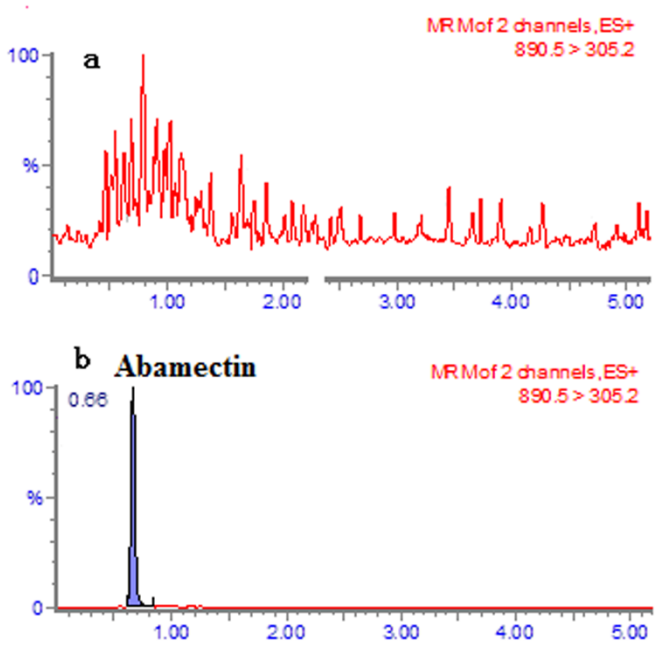

Figure 6 MRM chromatograms of a blank oil sample (a), as well as the sample spiked with abamectin at the concentration of 10 μg/kg (b). Retention time of abamectin: 0.66 min.