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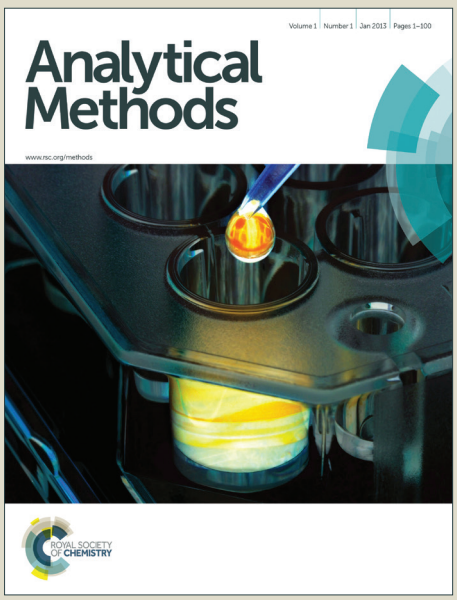

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Pipette tip-based molecularly imprinted monolith for selective micro-solid-phase extraction of methomyl in environmental water

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Abstract: A novel small molecular weight methomyl molecule-imprinted monolith (MIM) was prepared inside a polypropylene pipette tip by polymerization reaction. Then the pipette tip-based MIM micro solid-phase extraction (PT-MIM-μ-SPE) method was developed for selective extraction of methomyl in aqueous solution. The extraction parameters, such as the sample flow rate, sample volume and elution solvent were investigated. By combining with high performance liquid chromatography-ultraviolet detector, the PT-MIM-μ-SPE method showed a good linear range of 0.6-1000.0 μg L^{-1} with a low limit of detection 0.2 μg L^{-1}. The method was also applied for the pretreatment of methomyl in various environmental water samples. The relative recoveries were in the range of 84.9 to 105.1% with relative standard deviations less than 9.0 %. The results showed that methomyl could be selectively enriched and monitored from environmental water samples.

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Keywords: Molecularly imprinted monolith; Pipette tip; Micro-solid phase extraction; Methomyl; Environmental water.

1. Introduction

Methomyl whose trade name is Lannate belongs to carbamate pesticides. It is a systemic, broad spectrum insecticide and was registered for the use on more than 100 crops worldwide for control of pests on vegetables, soybeans, cotton, some fruit crops, and ornamentals owing to its broad spectrum of biological activity. Methomyl sprayed on croplands can easily migrate to environmental water. Hence, extensive use of methomyl may cause residues in environmental water. As an acetyl cholinesterase inhibitor, methomyl can cause nerve damage to people and animals, and is harmful to the environment and human health. In order to protect human health, the maximal residue limits (MRLs) of pesticides has been established in food and drinking water by the European Union and China, etc [1,2]. European Union requires the MRLs 0.1 μg L^{-1} for individual pesticide and of 0.5 μg L^{-1} for total pesticides in drinking water [1], while in China, the MRLs of pesticides in drink water are in the range of 0.01-10 μg L^{-1} (GB/T 5750.9-2006). Therefore, sensitive and selective methods are desirable in the determination of pesticides in environmental water.

For the sensitive detection of carbamate pesticides in water sample, high performance liquid chromatography (HPLC) and liquid chromatography-mass spectrometry (LC-MS) were often used due to the low thermal stability of carbamate pesticides, which were supposed to be sensitive, reliable and suitable [3-6].

Sample preparation is a crucial step during the whole analysis process especially in the analysis of trace level of pesticide residues from complicated matrix-based samples. Conventional extraction methods for the determination of pesticide residues

were based on liquid-liquid extraction (LLE) and solid phase extraction (SPE). Compared with LLE, SPE has the advantages of simplicity, rapidly and less consumption of organic solvents. However, the common nonselective sorbents used in SPE usually result in coextraction of many matrix components. Although immune affinity extraction (IAE) is capable of differentially adsorb target analytes, it still has some disadvantages such as lack of stability and high cost of antibody preparation. Molecular imprinting is a technique which can create the artificial receptor-like binding sites with a "memory" for the shape and functional group positions of the template molecule. So, molecularly imprinted polymers (MIPs) are good alternatives to biological substances. MIPs can be synthesized conveniently by a mixture of solution containing template molecule, porogenic reagent, functional monomer, cross-linker and initiator. After polymerization, template molecules are removed and polyporous materials with selectively functional binding sites are obtained. Due to the high stability, ease of preparation, and high sensitivity, MIPs have been used widely in different applications, such as chromatographic stationary phases [7,8], solid phase extraction (SPE) [9-12], catalysis and sensing [13-18]. MIPs-based SPE is one of the most successful and useful application. MIPs based SPE combines both the advantages of MIPs and SPE, and exhibits good extraction efficiency, reusability and selectivity to certain kinds of analytes [19], which is promising to selectively and effectively extract drugs in complicated matrix. The most widely used technique for preparing MIP materials is by conventional free-radical solution polymerization. In order to acquire particles with the appropriate size for HPLC and SPE, the bulk MIPs

have to be crushed, grounded and sieved. The particles produced in this time-consuming process are irregular in size and shape, resulting in significant loss in chromatographic performance [20]. In addition, some active sites are destroyed during the grinding process leading to lower MIP loading capacity. To overcome these disadvantages, the molecularly imprinted monolithic (MIM) columns were prepared by in situ polymerization directly inside a capillary or stainless steel or the tip of a pipette. This method could avoid the tedious grinding and sieving procedures as well as the problems of costly particle loss, particles in homogeneity, and molecular imprinted spots loss and could easily obtained a MIM with the ideal porous structure and low back pressure at a high flow rate [21]. To use the synthesized MIM directly as SPE sorbents is a promising method. Recently, Zheng et al. [22] prepared a MIM inside a fused-silica capillary and applied it in the extraction of fluoroquinolones from milk samples. Some research groups, including ours, prepared MIM in a pipette tip for the selective micro-solid phase extraction of residue level of drug and pesticide from complicated matrix [23-26]. Compared with SPE, the amount of sorbents and the volume of eluting solvents could be reduced greatly if the MIM prepared in a fused-silica capillary or a pipette tip, so the extraction efficiency could be increased as a result [27]. Besides, the amount of template molecule required during monolith preparation is much less than that of other methods [28]. Since the MIM that synthesized in a capillary was fragile, and required tedious pretreatment process, the pipette tip-based MIM microextraction is a promising technique for the selective extraction of target analyte residues in complicated matrice.

To the best of our knowledge, MIP sorbents using small molecular weight methomyl as the template molecule have not been reported, and no attention has been paid to make use of MIM as the sorbent for high selective extraction of methomyl from complex matrices. In this work, methomyl-MIM was synthesized in a pipette tip for the first time. The pipette tip could match to a syringe without any other treatment to perform the molecularly imprinted monolith micro-solid phase extraction (PT-MIM-μ-SPE). The MIM was applied for the selective extraction of methomyl. Various experimental parameters affecting the pipette tip based methomyl-MIM- μ-SPE were optimized. The optimized method based on PT-MIM-μ-SPE combined with HPLC was established and applied for the determination of methomyl in various environmental water samples.

2. Experimental

2.1. Instruments

The chromatographic analysis was carried out on an Agilent 1200 HPLC system (Agilent Technologies, Palo Alto, CA, USA), equipped with an auto injector and a diode array detector (DAD) . A reverse phase Agilent SB-C18 column (250 mm × 4. 6 mm i.d., 5 μm) was used for separation of the analytes. The mobile phase was methanol-water (40:60, v/v) at a flow rate of 1.0 mL min^{-1}. The column temperature was 30°C and the detection wavelength was set at 235 nm. The injection volume was

10 μL. Ultrasonic instrument KQ-100DE was purchased from Kunshan Ultrasonic Instrument Co., Ltd. (Jiangsu, China) and a pHS-3C digital pH meter (Shanghai Rex Instruments Factory, China) was employed for pH measurements.

2.2. Reagents and Chemicals

Ethylene glycol dimethacrylate (EGDMA, 98% pure) was purchased from Acros (New Jersey, USA). Methacrylic acid (MAA), Acrylamide (AM), 2,2'-bisisobutyronitrile (AIBN, AR), toluene (AR), dodecanol (AR), sodium hydroxide (AR) and hydrochloric acid (AR) were obtained from Tianjin Kermel chemical reagents development centre (Tianjin, China). methomyl, was purchased from Sigma-Aldirich (St louis, MO, USA), and its chemical structure is shown in Fig. 1. Methanol (HPLC grade) and acetonitrile (HPLC grade) were ordered from Tedia (Fair Lawn, New Jersey, USA). Sodium chloride was procured from Zhanyun Chemical Co, Ltd. (Shanghai, China). Ultrapure water was purified on a Mill-Q water purification system (Millipore Corporation, Billerica, MA, USA).

The stock standard solution of methomyl was prepared by weighing 2.5 mg methomyl dissolved in 50 mL HPLC-grade methanol. Then the stock standard solution at a concentration of 50 μg mL^{-1} was made and stored at 4 ℃ in a refrigerator. A series of standard solutions were daily prepared by an appropriate dilution from the stock solution with ultrapure water.

2.3. Sample preparation

Reservior water was collected from Danjiang Kou Reservior (Danjiang Kou, Hubei, China). South Lake water, farmland water and waste water were collected from Wuhan (Wuhan, China). All of them were kept at 4 ^{o}C and filtered through a 0.45 μm polyether sulfone membrane which was purchased from Wuhan Shenshi Chemical Industry Co. Ltd (Wuhan, China) prior to analysis.

2.4. Preparation of Methomyl-Imprinted Monolith

For the preparation of the methomyl-imprinted monolith, the template methomyl (0.05mmol) was dissolved in porogenic solvents (50 μL toluene, 450 μL 1-dodecanol) in a glass vial and mixed with MAA (0.20 mmol) as the functional monomer. The mixture was surged ultrasonically for 15 min. In order to make the template and the monomer assemble each other better, the mixture was placed in the dark for two hours. Then, 1.00 mmol of cross-linker EGDMA and 0.032 mmol (5.3 mg) of initiator AIBN were added and degassed by ultrasonication for about 30 min. Next, 60 μL of the homogeneous solution was filled into a pipette tip which had been sealed at one end. Subsequently, the other end of the pipette tip was sealed with silicon rubber. After polymerization at 65 ◦C for 24 h, the silicon rubber was removed. The resultant MIM was washed with methanol to remove the template molecules. A reference, non-imprinted monolith (NIM), was prepared simultaneously like the same

procedure, including washing, but in the absence of the template molecule.

2.5 PT-MIM-μ-SPE procedure

The prepared methomyl-imprinted monolith was applied for extraction of methomyl in aqueous solutions. As shown in Fig. 2, solutions were put in the syringe and loaded by a SN-50C6 syringe pump (Shengnuo Medical Equipment Co., Ltd., Shenzhen, China). For precondition, the MIM was washing with 1.0 mL methanol and 0.5 mL water, respectively. For extraction, an aliquot of 3.0 mL sample solution was loaded at a flow rate of 0.15 mL min^{-1}. Then, The MIM was washed with 0.5 mL water at a flow rate of 0.15 mL min^{-1} to remove the matrix interferences. Lastly, the analytes were eluted with 60 μL acetonitrile at a flow rate of 0.05 mL min^{-1}. The eluent solution in glass-lined pipe was injected into the HPLC system with an autosampler for analysis directly.

3. Results and discussion

In order to obtain the optimized extraction conditions, enrichment factor (EF) and Relative recovery (RR) were used to evaluate the extraction efficiency of MIM.

$$EF = \frac{C_{elu}}{C_0}$$

The EF was defined as the ratio between the analyte concentration in eluent (C_{elu}) and the initial concentration of analyte (C_0) within the sample solution.

$$RR\% = \frac{C_{found} - C_{real}}{C_{add}} \times 100\%$$

C_{found} represents the concentration of the analyte after adding a known amount of standard to the real sample, C_{real} is the concentration of the analyte in real sample, and C_{add} refers to the concentration of a known amount of standard that was spiked in the real sample.

The imprinting factor (IF) was used to evaluate the recognition abilities of the MIM:

$$IF = \frac{EF_{MIM}}{EF_{NIM}}$$

where the EF_{MIP} is the EF of methomyl extracted by MIM and EF_{NIP} is the EF of methomyl extracted by NIM monolith under the same conditions.

3.1. Preparation and evaluation of methomyl-imprinted monolith

3.1.1. Optimization of preparation conditions

Different functional monomers will construct different binding sites with template. To improve the recognition and selectivity property of MIM, two different functional monomers, including MAA and AM were investigated. The results showed that MAA has the higher specific recognition ability for methomyl compared with AM. To realize the better selectivity, MAA was chosen as the functional monomer. The ratio between monomer and cross-linker can affect the pore size and capacity of the

reticular structure of the polymer [16]. Increasing the amount of cross-linker can maintain the stability of the recognition sites and lead to high selectivity for the target. But, on the other hand, too more amount of cross-linker would result in large density and bad permeability of the polymer, which would decrease the extraction efficiency, therefore, the proper ratio is required. In this study, the molar ratios of the monomer to cross-linker ranged from 1:1 to 1:6 were investigated, respectively. The results showed when the ratio was lower than 1:3, the MIM showed bad recognition ability and the mechanical stability of the polymer was poor. However, when the ratio was higher than 1:5, the backpressure is too high to allow the mobile phase to flow through the monolith. So, 1:5 was chosen as the optimized ratio of the monomer and cross-linker, and it was selected for further optimization.

3.1.2. The characterization and specific evaluation of the MIM

The MIM morphological structure was investigated by scanning electron microscope (SEM). As can be seen in Fig. 3, there were many macropores and flow-through channels inlaid in the network skeleton of methomyl-imprinted monolith, which provided flow paths through the column. Due to the size and density of the macropore network, the monolith had a high internal porosity and, consequently, low column hydraulic resistance. The pores allowed the mobile phase to flow through with low flow resistance.

FT-IR was performed to testify the successful preparation of

methomyl-imprinted monolith. As shown in the supplementary material Fig. 1S, the infrared spectrogram of methomyl imprinted monolith was different from that of methomyl and MAA. The characteristic peak of MAA was around at 1690 and 1631 cm^{-1}, which were corresponding to the C=O and C=C stretching of MAA. Compared with the infrared spectrogram of MAA, the stretching vibration wide peak of 3000-3300 cm^{-1} and the peak of 1631 cm^{-1} became weak in the infrared spectrogram of the associated MIM and NIM complexes. The C=O stretch vibration peak of 1690 cm^{-1} shifted to that of 1720 cm^{-1}. These results showed that the polymers have been successfully synthesized.

In order to evaluate the selectivity of the MIM, imidacloprid and carbendazim were tested as non-analogues (the supplementary material for the structure detail, Fig. 2S). For sampling, methomyl, imidacloprid and carbendazim standard solutions were mixed and diluted using deionized water at a final concentration of 200 μg L^{-1}, 1.0 mL of the mixed solution was loaded on the MIM and NIM at a flow rate of 0.15 mL min^{-1}. 60 μL acetonitrile was used to elute analytes. The eluent was analyzed by HPLC directly. As shown in Fig. 3S, the results indicated that the MIM had a higher affinity for methomyl than NIM, where IF was 2.26. And MIM had weaker extraction ability for both imidacloprid and carbendazim than NIM monolith. All these results demonstrated MIM had the specific selectivity for methomyl.

3.1.3. Recognition mechanism of MIM to methomyl

Based on the above results, hydrogen bonds were expected to be formed among methomyl and monomers (MAA) as a key interaction force for binding site construction. The hydroxyl groups of MAA acted as hydrogen bond donors. The higher hydrogen-bonding ability of the hydroxyl group in MAA and methomyl enhanced the strength of the hydrogen bonding between methomyl and monomers and thus yielded imprinted polymers with better recognition properties. The illustration of the MIM and its molecular recognition was shown in Fig. 4S. Hydrogen bonds were formed between methomyl and MAA，which led to the formation of a self-assembled complex of methomyl and MAA. According to the structure information of MAA and methomyl, three MAA molecules would form three hydrogen bonds with one oxygen atom and two nitrogen atoms of methomyl. The ratio of methomyl/MAA was 1:3, which was in agreement with our result, in which a ratio of 1:4 was used. A bit more functional monomers were always required to ensure complete interaction between functional monomers and templates, because some functional monomers remained dissociative with the templates.

3.2. Optimization of PT-MIM-μ-SPE conditions

In order to obtain the best extraction efficiency of the PT-MIM-μ-SPE method, several parameters such as the flow rate, volume, pH value, and salt concentration of sample, and the type and volume of eluent were optimized in this study. Sample solutions were spiked with methomyl at 0.20 μg mL^{-1} to perform the experiments.

3.2.1. Effect of sample flow rate

Sample flow rate was an important parameter for MIM microextraction, which was possible to affect extraction efficiency of methomyl and the time of analysis. The sample flow rate was optimized in the range of 0.05-0.25 mL min^{-1}. The results indicated that no significant difference of peak areas among different flow rates, indicating that sample flow rate have little influence on extraction efficiency in this work. Considering the analysis time and monolith pressure, 0.15 mL min^{-1} was selected for further studies.

3.2.2. Effect of eluent type

The selection of an appropriate eluent is of high importance for the PT-MIM-μ-SPE process. Considering the consistency to the mobile phase used in liquid chromatography, the eluent is limited to solvents such as methanol, acetonitrile and purified water. 1.0 mL of 0.2 μg mL^{-1} methomyl standard solution was used in the PT-MIM-μ-SPE system, and then mobile phase (methanol/water (40/60; v/v)), acetonitrile and methanol as eluent were tested. The results indicated that acetonitrile as the eluent exhibited the highest peak area. Thus, acetonitrile was selected as the eluent in the following experiments.

3.2.3. Effect of sample volume

The effect of sample volume was monitored by loading methomyl standard solution (containing 0.2 μg mL^{-1} of the analyte) from 1.0 to 5.0 mL at a constant flow rate. The eluent volume (methanol) was 60 μL. The results showed that EF of methomyl increased with the increasing of sample volume from 1.0 to 5.0 mL. This indicates that the maximal extraction capacity was not achieved even when 5.0 mL of sample solution was loaded. However, RR began to decrease when the sample volume increased. To achieve satisfactory extraction efficiency within a short time, 3.0 mL of sample solution was selected in the PT-MIM-μ-SPE procedure.

3.2.4. Effect of eluent volume

In order to study the effect of eluent volume on the extraction efficiency, different volumes of eluent (acetonitrile) were tested. The experimental results showed that 60 μL eluent was sufficient to elute more than 90% analyte from the monolith. Moreover, further increasing the volume of the eluent was not preferred because EF decreased with the increasing of eluent volume. Thus, 60 μL of eluent volume was selected for subsequent work.

3.2.5. Effect of sample pH

Sample pH was one of most important parameters for PT-MIM-μ-SPE which may affect the molecule form of the analyte and closely relate to the interaction between analytes and the MIM. The effect of the sample pH on the extraction efficiency for methomyl was investigated using several buffer solutions with pH 2.0-9.0. The results showed that from pH 2.0 to 3.0, the peak area of methomyl increased along with the increase of pH, and decreased when pH increased. The low responses observed at low pH may be attributed to the protonation of methomyl molecules. These protonated charged molecules were disadvantageous for the formation of hydrogen bonds between MAA and methomyl which led to that the methomyl molecules could not be adsorbed by the polymer. The decrease of the peak area at higher sample pH could be explained by the deprotonation of carboxyl in imprinted sites and the deprotonation charged imprinted sites could not adsorb analyte effectively. Thus, pH 3.0 was chosen as the optimal pH of the sample.

3.2.6. Effect of salt concentration

The effect of salt concentration of the sample on the extraction efficiency was also investigated. The results indicated that EF and RR increased as the concentration of NaCl increased from 0% to 30% (w/v). Addition of salt into the sample solutions could lead to the salting-out effect, and more analyte molecules would be extracted onto the MIM. To obtain high extraction efficiency, 30% NaCl (w/v) was added in the sample solution in the following experiments.

3.3. Evaluation of the method

By coupling with HPLC, the established method was applied for determination of methomyl in environmental water samples. Analytical performance of the method was validated, including linear range, coefficient (R), the limit of detection (LOD), the limit of quantification (LOQ) and reproducibility. As listed in Table 1. Good linearity (R=0.9998) was obtained in the range of 0.6-1000.0 μg L^{-1}. LOD, which indicated the sensitivity of the analytical method, was evaluated and found to be 0.2 μg L^{-1} (S/N=3). LOQ was 0.6 μg L^{-1}. The reproducibility of the method was determined by the intra-day and inter-day precisions at the concentration of 0.2 μg mL^{-1} in spiked environmental water samples for methomyl, respectively. The results showed that the intra-day precisions (RSDs) was 3.4%, while the inter-day precisions (RSDs) was 4.1%, indicating good reproducibility of the method.

3.4. Real samples analysis

To evaluate its applicability and accuracy, the developed PT-MIM-μ-SPE -HPLC method was applied for the determination of methomyl in environmental water samples. The results were listed in Table 2, trace amounts of methomyl was detected in reservoir water and farmland water. To investigate the extraction recoveries, four kinds of water samples, all spiked at concentrations of 5 μg L^{-1}, 50 μg L^{-1}, and 500 μg

L^{-1} were extracted under the optimized conditions. The relative recoveries were in the range of 84.9 % and 105.1 %, with RSD less than 9.0% (n=3). The chromatograms of blank and spiked farmland water samples after treated by MIM-μ-SPE and NIM-μ-SPE were shown in Fig. 4. All the results demonstrated that the proposed method was effective and reliable for the pretreatment and determination of methomyl in environmental water samples.

3.5. Comparison of PT-MIM-μ-SPE-HPLC-UV with Other Methods

The efficiency of the presented PT-MIM-μ-SPE-HPLC-UV method for environmental water samples was compared with that of other reported methods. As listed in Table 3, PT-MIM-μ-SPE-HPLC-UV method was obviously cheaper than other reported methods, and the LOD by the proposed method are comparable to those reported in other papers. All these results revealed that the PT-MIM-μ-SPE was a sensitive, simple, and reproducible technique that could be used for preconcentration of methomyl in environmental water samples.

4. Conclusion

In this work, a novel methomyl-MIM has been synthesized for selective extraction of methomyl in aqueous samples. The monolith could be connected with syringes in different sizes simply without any other treatment to performμ-SPE process. The MIM showed high selectivity and enrichment ability for methomyl. The

PT-MIM-μ-SPE followed by HPLC-DAD was developed as an analytical method for the sensitive and selective determination of methomyl in environmental water samples. The experimental results revealed that this method had high selectivity, low organic solvent consumption, good extraction efficiency and linearity over the investigated concentration range. The performance of this procedure in the analysis of methomyl in environmental water sample was satisfactory.

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Figure captions

Fig. 1. The molecule structure of methomyl, MAA and EGDMA.

Fig. 2. Scheme of the PT-MIM-μ-SPE device.

Fig. 3. SEM image of MIM (magnification, 5000×).

Fig.4. The chromatograms of blank farmland water sample treated by MIM-μ-SPE and spiked farmland water samples treated by MIM-μ-SPE (B) and NIM-μ-SPE (C). Sample solutions of methomyl were spiked at 5 μg L^{-1}.

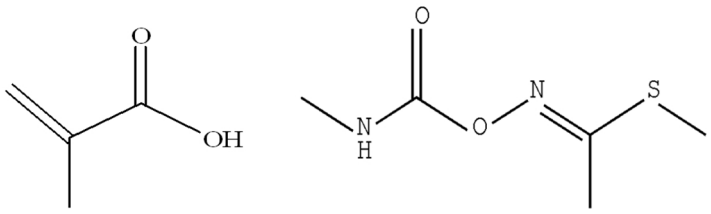
Table captions

Table 1 Analytical performance of PT-MIM-μ-SPE-HPLC method

Table 2 Recoveries, precisions of the PT-MIM-μ-SPE-HPLC method for methomyl in

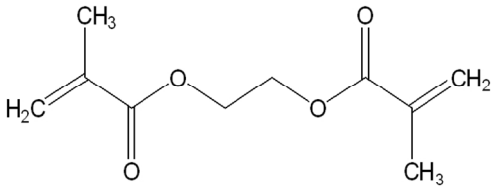
environmental water samples.

Table 3 Comparison of the proposed method with other reported methods



Methacrylic acid (MAA)

Methomyl



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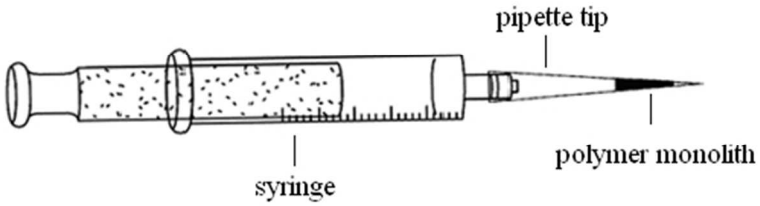

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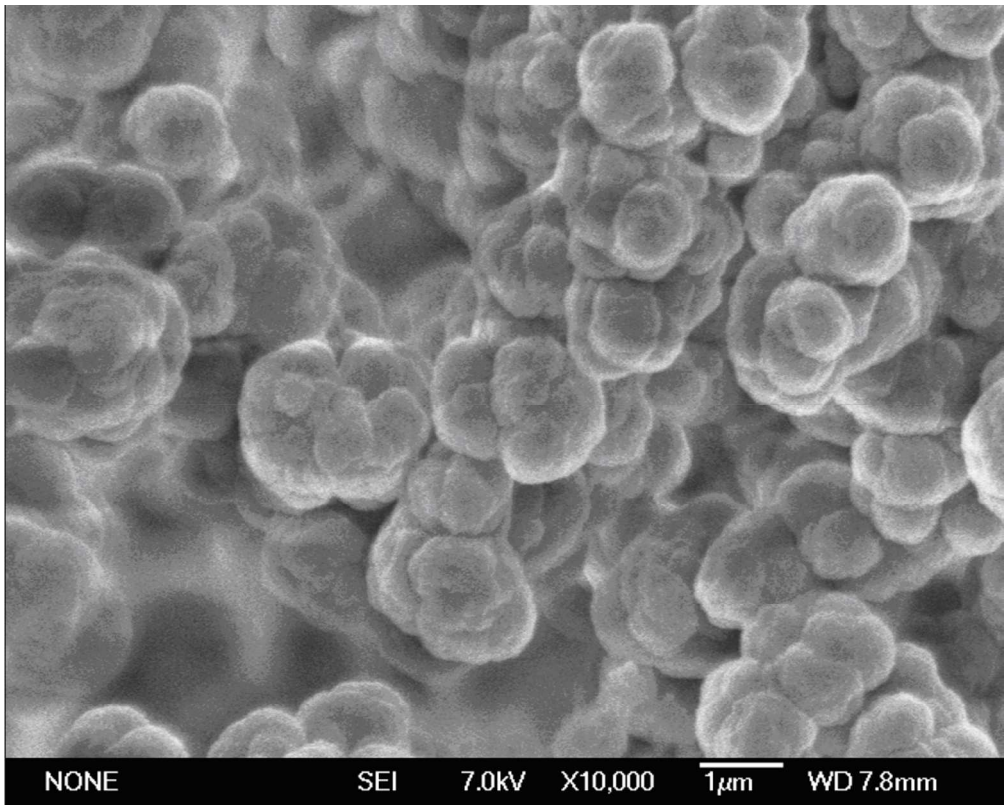
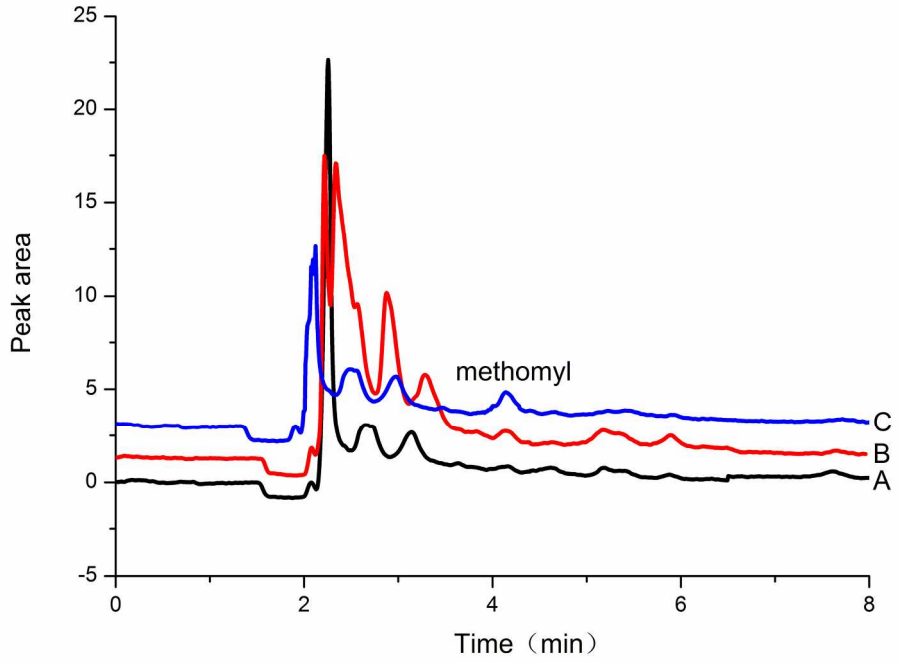


265x211mm (96 x 96 DPI)



207x160mm (300 x 300 DPI)

Table 1 Analytical performance of PT-MIM-μ-SPE-HPLC method

Analyte	Linear range ($\mu g\ L^{-1}$)	R	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	RSD (%)	
					Intra-day	Inter-day
methomyl	0.6-1000.0	0.9998	0.2	0.6	3.4	4.1

Table 2 Recoveries, precisions of the PT-MIM-μ-SPE-HPLC method for methomyl in environmental water samples.

Sample	Real ($\mu g\ L^{-1}$)	Added ($\mu g\ L^{-1}$)	Recovery (%)	RSD (%) (n = 3)
Reservoir water	0.7	5.0	98.6	9.0
		50.0	100.8	3.2
		500.0	105.1	4.8
South lake water	ND[a]	5.0	89.0	7.6
		50.0	91.4	3.0
		500.0	84.9	3.9
Farmland water	0.8	5.0	103.6	7.4
		50.0	90.6	5.6
		500.0	97.1	3.5
Waste water	ND[a]	5.0	93.7	4.7
		50.0	86.4	4.0
		500.0	91.2	6.1

ND[a]: not detected.

Table 3 Comparison of the proposed method with other reported methods

Method	Linear range ($\mu g\ L^{-1}$)	r^2	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	Reference
MASE-SPE-LC-MS	-	-	2.3	7.6	[3]
UASEME-UHPLC-MS/MS	0.31-100	0.998	0.11	0.31	[4]
MSPD-LC-MS	-	-	1.0	6.0	[5]
UHPLC-ESI-MS/MS	-	0.9916-0.9984	1.0-1.4	2.7-3.5	[6]
PT-MIM-μ-SPE-HPLC	1.0-1000.0	0.9998	0.2	0.6	This work