Analytical Methods

PAPER

View Article Online
View Journal | View Issue

Cite this: *Anal. Methods*, 2015, 7, 6411

Molecularly imprinted solid-phase extraction coupled with gas chromatography for the determination of four chloroacetamide herbicides in soil

Yan Wang,* Xiaoyang Jin, Dan Zhao, Xiaohong Guo and Ranhong Li

A molecularly imprinted solid phase extraction (MISPE) coupled with gas chromatography (GC) for the simultaneous separation and determination of four chloroacetamide herbicides, alachlor, acetochlor, pretilachlor and metolachlor, in soil was developed. Molecularly imprinted polymers (MIPs) with butachlor as the dummy template were synthesized *via* precipitation polymerization, where methacrylic acid (MAA) was used as the functional monomer, ethylene glycol dimethacrylate (EDMA) as the crosslinker and acetonitrile as the porogen. Fourier-transform infrared spectrometry (FTIR) and scanning electron microscopy (SEM) were used to characterize the polymers. Under the optimum SPE conditions, the polymer sorbents can selectively extract and enrich alachlor, acetochlor, pretilachlor and metolachlor. A comparison experiment also showed that the MISPE cartridges were better than the nonimprinted and C18 cartridges in terms of recovery. The mean recoveries of the four chloroacetamide herbicides from blank soil spiked at 0.1, 0.5, and 1 μg mL^{-1} ranged between 80.6 and 90.2% with relative standard deviations (RSD) of less than 8% ($n = 5$). The limit of detection (LOD) and the limit of quantification (LOQ) of the four analytes were in the range of 1.0×10^{-12} to 5×10^{-11} g and 0.0005–0.025 mg kg^{-1}, respectively. The presented MISPE-GC method exhibited highly selective separation and enrichment of trace chloroacetamide herbicides and could be potentially applied to the determination of chloroacetamide herbicides in soil.

Received 3rd February 2015
Accepted 20th June 2015

DOI: 10.1039/c5ay00281h

www.rsc.org/methods

1 Introduction

Chloroacetamide herbicides are a class of pre-emergent herbicide widely used in paddies and uplands. Due to the extensive use of chloroacetamide herbicides, they can cause a certain degree of pollution to the environment. Furthermore, their residues are also harmful to human health due to their ability to cause nasal turbinate tumors.[1] Consequently, it is of great significance to develop an effective and sensitive method for the rapid determination of trace chloroacetamide herbicide residues. Many methods have been developed for the determination of chloroacetamide herbicides. GC,[2] GC-MS[3] and LC-MS[4,5] are classical methods for this class of herbicide determination.

Generally, a preconcentration step is required for trace analysis from complex samples to reduce matrix interference and to enrich the target analytes. SPE is widely used for the extraction and preconcentration of analytes in various environmental, food and biological samples.[6] However, conventional SPE cartridges are silica and bonded silica such as C8 and C18, which suffer from non-specific selectivity in isolating targets. The lack of selectivity of these materials usually leads to the coextraction of several matrix components that can interfere in the analysis of targets.[7] Therefore, efficient cleanup methods with high selectivity are needed.

In recent years, molecular imprinting technology has been used for sample cleanup with higher selectivity to enrich the target molecules from complex matrices. MIPs are synthetic polymers usually obtained by the polymerization of functional and cross-linking monomers in the presence of a template molecule capable of forming complexes with the monomer.[8] The resulting polymers, following template removal, contain template-shaped cavities with a spatial distribution of functional groups complementary to the imprinted target.[9] These cavities have the potential to rebind the target molecule or related structural analogues. MIPs have the advantage of being inexpensive, chemically and thermally stable, and compatible with organic solvents.[10] Because of their unique performance, they have been widely used as SPE absorbents,[11] sensors,[12] and catalysts,[13] and for drug-controlled release[14] and chiral separation.[15]

There are various methods for the preparation of MIPs in the literature including bulk polymerization,[16] precipitation polymerization,[17] suspension polymerization[18] and swelling

College of Resources and Environment Science, Jilin Agricultural University, Changchun, Jilin, P. R. China. E-mail: wy62@163.com

polymerization.[19] However, MIPs prepared by bulk polymerization need grinding and sieving, which is a labor intensive and wasteful process.[20] Suspension and swelling polymerizations are more complicated processes and the use of additives (such as surfactants or stabilizers) is necessary.[21] Among the above methods, precipitation polymerization is probably the most facile synthetic method without the use of a surfactant. For these reasons, a precipitation polymerization method was used in the present work to prepare MIPs.

Since traditional MIPs are synthesized by using the target molecule as the template, the phenomenon of template bleeding from the resultant polymer may affect the accuracy and precision of detection results. In order to avoid the traditional major drawback of template bleeding associated with MIPs, a similar structure related to the target molecule was utilized as the template molecule, a so-called dummy molecularly imprinted polymer.

Several reported methods using MISPE for chloroacetamide herbicide cleanup are based on liquid chromatography.[22,23] In this work, MIPs were synthesized using butachlor as the dummy template and were applied as a SPE sorbent for the selective separation and quantitative determination of four chloroacetamide herbicide residues in soil.

2 Experimental

2.1 Materials and methods

Alachlor (99%), acetochlor (99%), pretilachlor (99%), butachlor (99%) and metolachlor (99%) were obtained from the national pesticide products quality supervision and inspection center (Nanjing, China). MAA and 2,2′-azobisisobutyronitrile (AIBN) were purchased from Beijing Chemical Reagent Factory (Beijing, China). EDMA was supplied by Aladdin (Shanghai, China). Inhibitors were removed from MAA and EDMA with an activated neutral aluminum oxide column. AIBN was recrystallized from methanol before use. All solvents were of analytical or HPLC grade and obtained from Beijing Chemical Factory (Beijing, China). Empty 1 mL SPE cartridges and polyethylene frits for MISPE were purchased from Biotage Company (Agilent, USA).

2.2 Apparatus

The gas chromatographic experiments were carried out on an Agilent 6890 gas chromatograph equipped with μECD detector and a 30 m × 0.25 mm ID, 0.25 μm film thickness HP-5MS GC column (Agilent, USA) was employed. The surface morphology of the polymers was observed by a SSX-550 SEM (Shimadzu, Japan). IR spectra of the obtained polymers were recorded on a FTIR Affinity-1 spectrometer (Shimadzu, Japan). SPE was performed with a Supelco (Bellefonte, PA, USA) 12-position SPE manifold equipped with a vacuum control valve and poly(tetrafluoroethylene) cartridge adapters.

2.3 Chromatographic conditions

The injector temperature was 260 °C, while the detector temperature was 280 °C. The GC oven was set to an initial temperature of 120 °C for 1 min, and the temperature program was set to increase from 120 to 280 °C at 15 °C min^{-1} and held at the maximum temperature for 2 min. Nitrogen flow was maintained at 1.5 mL min^{-1}.

2.4 Preparation of the polymers

During polymerisation, 1 mmol of butachlor and 4 mmol of MAA were dissolved in 100 mL of acetonitrile in a 100 mL Erlenmeyer flask. The mixture was allowed to equilibrate for 5 h, and then 4 mmol of EDMA and 0.0862 g of AIBN were added. Then the mixture was purged with nitrogen gas for 30 min. Polymerization was performed at 60 °C in a water bath for 24 h and the polymers were obtained by centrifuging at 4000 rpm for 10 min. Methanol–acetic acid (9 : 1, v/v) was used to remove the butachlor. As a reference, nonimprinted polymers (NIPs) were prepared following the same procedure but without the addition of butachlor.

2.5 Morphological characterization

The samples were prepared by wetting the slide glass with a small drop of the diluted particle dispersion. Prior to measurement, the samples were coated under vacuum with a thin layer of gold.

2.6 Structural characterization

IR spectra were recorded with KBr pellets using an accumulation of 32 scans and a resolution of 4 cm^{-1} in the range of 4000–400 cm^{-1}. Samples (20 mg) were thoroughly ground with KBr (180 mg) and the pellets were prepared using a hydraulic press.

2.7 Preparation of MIP and NIP cartridges

A 100 mg amount of MIP or NIP was packed into a 1 mL empty SPE cartridge between two frits. Before each use, the cartridges were conditioned with 4 mL of hexane. In the loading step, 1 mL of hexane standard solution (1 μg mL^{-1} with a mixture of alachlor, acetochlor, pretilachlor and metolachlor) was passed through the conditioned MIP and NIP cartridges. Then the MIP and NIP cartridges were washed with 4 mL of hexane. Finally, 6 mL of methanol was chosen as the eluting solvent. All of the fractions employed were collected separately and the amount of recovered compound was quantified by GC.

2.8 Sample preparation and solid-phase extraction

Freshly spiked soil samples were prepared by weighing 10.0 g of soil into a flask followed by spraying with 1 mL of different concentrations of the spiking solution (0.1, 0.5, 1.0 μg mL^{-1} of each of the four chloroacetamide herbicides). The spiked sample was allowed to stand overnight before extraction. A volume of 40 mL of acetonitrile was added to 10.0 g of a spiked soil sample, and the suspension was shaken for 1 h. The slurry was then filtered under vacuum. The extraction procedure was repeated three times, and the extracts were evaporated to dryness and redissolved in 1.0 mL of hexane.

For the soil sample MISPE process, the cartridge was preconditioned with 4 mL of hexane. After loading 1 mL of sample extract, the MISPE cartridge was washed with 4 mL of hexane

and eluted with 6 mL of methanol. The eluting fraction was collected and evaporated to dryness under a stream of N_2. The residue was redissolved in 1 mL of hexane and analyzed by GC.

2.9 SPE on commercial C18

The C18 cartridges were optimized by conditioning them sequentially with 4 mL hexane, loading with 1 mL of sample extract, washing with 4 mL of hexane, and eluting with 6 mL of methanol.

2.10 Selectivity experiments

The recognition selectivity of the polymers for chloroacetamide herbicides was investigated. The polymers (20 mg) were added into 5 mL of hexane solution containing 40 mg L^{-1} of the butachlor template or of the other four chloroacetamide herbicides, then the mixtures were incubated in a water bath at 25 °C for 24 h. The concentration of the solution after adsorption was measured by GC. The adsorbed amount of butachlor or other different analogues (mg g^{-1}) was calculated according to the following formula:

$$Q = \left(\frac{C_i - C_f}{M}\right) \times V \quad (1)$$

where Q, C_i, C_f, V, and M represent the binding capacity of the MIPs (mg g^{-1}), the initial solution concentration (mg L^{-1}), the final solution concentration (mg L^{-1}), the volume of the solution (mL) and the mass of dried polymer (mg), respectively.

The specific recognition property of the MIPs is evaluated by the imprinting factor (α). The imprinting factor of the template or analogue is calculated using the following formula:

$$\alpha = \frac{Q_{MIP}}{Q_{NIP}} \quad (2)$$

where Q_{MIP} and Q_{NIP} are the adsorption capacities of the template or analogue molecule on MIPs and NIPs, respectively.

The selectivity coefficient (β) of MIPs is calculated using the following formula:

$$\beta = \frac{\alpha_{tem}}{\alpha_{ana}} \quad (3)$$

where α_{tem} and α_{ana} are the imprinting factors of the template molecule and the analogue, respectively.

3 Results and discussion

3.1 MIP preparation

MAA is commonly used as a functional monomer for the preparation of MIPs because MAA is an acidic monomer and favorable for the formation of hydrogen bonds with the target molecules. In this work, hydrogen bonds are expected to form between butachlor and MAA, whereby the hydroxy group of MAA acts as a hydrogen bond donor interacting with the oxygen atom of butachlor. EDMA was selected as the cross-linker for synthesizing the MIPs as it can stabilize the network of MIPs and can maintain the complementary properties of the cavities towards the template after its removal.[24] Acetonitrile was selected as a porogen because of the good solubility of butachlor and the absence of disrupting interactions.

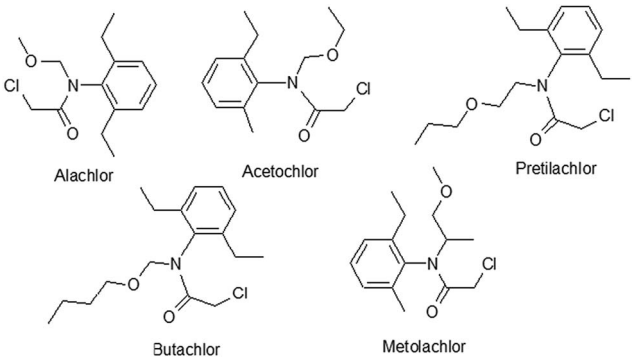

Fig. 1 The chemical structures of alachlor, acetochlor, pretilachlor, butachlor and metolachlor.

To overcome the problem of template bleeding, a structural analogue of the template can be used as a substitute when preparing the MIPs. Considering that butachlor and the other four herbicides are chloroacetamide herbicides with a similar structure (Fig. 1), butachlor was used as a dummy template to synthesize the MIPs by precipitation polymerization.

3.2 Morphological analysis

The microscopic characteristics of the MIPs and NIPs are shown in Fig. 2. The images show appreciable differences in the morphology of the polymers; the NIPs had highly agglomerated and irregular particles compared with the MIPs.

3.3 Structural analysis

The IR spectra of the NIPs (Fig. 3a), and the unleached (Fig. 3b) and leached MIPs (Fig. 3c) displayed similar characteristic peaks, indicating the similarity in the backbone structure of the different polymers. As shown in Fig. 3, the broad absorbance band observed around 3590 cm^{-1} can be associated with the O–H stretching vibration. This band for the leached MIPs appeared to be shifted downward in comparison to the unleached MIPs. The strong peaks at 2987 and 2953 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the C–H in the methyl groups, respectively. The features at 1735 cm^{-1} were attributable to the C=O groups. Two wave peaks at 1456 and 1388 cm^{-1} were associated with the asymmetric and symmetric deformation vibration of C–H in

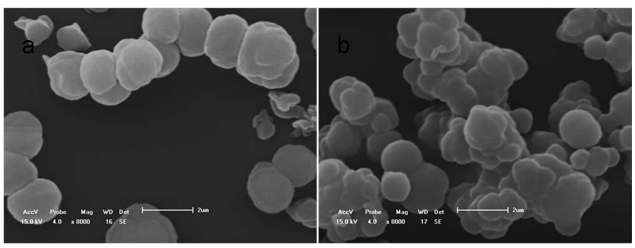

Fig. 2 SEM micrographs of the MIPs (a) and the NIPs (b).

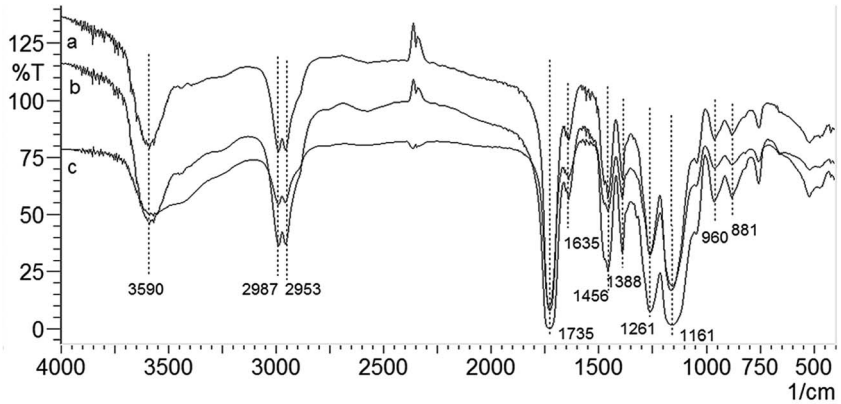

Fig. 3 FTIR spectra of the NIPs (a), the unleached MIPs (b) and the leached MIPs (c).

methylene, respectively. The wave peaks present at 1161 and 1261 cm^{-1} were attributed to the C–O–C asymmetric and symmetric stretching vibrations, respecitvely. The weak absorbance peak at 1635 cm^{-1} was assigned to the C=C stretching vibration, suggesting a low content of unreacted C=C. In addition, the peaks at 960 and 881 cm^{-1} were designated to the out of plane bending vibration and the out of plane wagging vibration of the vinylic C–H bonds, respectively.

3.4 Evaluation of MIP selectivity

In the present study, the imprinting factor (α) and the selectivity coefficient (β) were used as a measure of the selectivity of the MIPs for the template molecule and the analogue. The results in Table 1 clearly suggest that the MIPs possessed a high selectivity for the butachlor template and the other four chloroacetamide herbicides, perhaps due to their similar three-dimensional structures and side chain groups. The selectivity order for the other four chloroacetamide herbicides was acetochlor > alachlor > pretilachlor > metolachlor.

3.5 Optimization of MISPE from standard solutions

3.5.1 Selection of the loading solvent. To select an appropriate loading solvent, different polarity solvents such as hexane, toluene, acetonitrile and methanol were investigated. As shown in Fig. 4, chloroacetamide herbicides were strongly retained by MIP cartridges when non-polar solvents such as hexane and toluene were used as loading solvents, especially for hexane with 89–96% adsorption. However, the binding of chloroacetamide herbicides to MIPs was relatively low when using acetonitrile and methanol as loading solvents, especially for methanol with 61–70% adsorption. NIPs showed similar adsorption of chloroacetamide herbicides to MIPS from hexane and toluene solutions, while their binding in acetonitrile and methanol was reduced. These results were consistent with those reported in the literature which showed that the strength of the binding of the analyte to the MIPs increased as the polarity of the rebinding solvent decreased.[25,26] Therefore, hexane was selected as the loading solvent.

Table 1 The imprinting factors (α) and selectivity coefficients (β) of the MIPs

	α	β
Butachlor	2.05	—
Alachlor	1.90	1.08
Acetochlor	1.99	1.03
Pretilachlor	1.57	1.31
Metolachlor	1.84	1.11

3.5.2 Adsorption capacity of the MIP cartridge. The evaluation of the MIP capacity was performed by determining the maximum amount of chloroacetamide herbicide that could be retained on the polymer. Different loading volumes were used to evaluate the capacity of the MIP cartridges. The results in Fig. 5 showed that when 6 mL of standard solution was loaded onto the cartridge, the binding capacities of the MIP cartridges were 45.3 μg g^{-1} for alachlor, 45.9 μg g^{-1} for acetochlor, 43.9 μg g^{-1} for pretilachlor, and 44.6 μg g^{-1} for metolachlor.

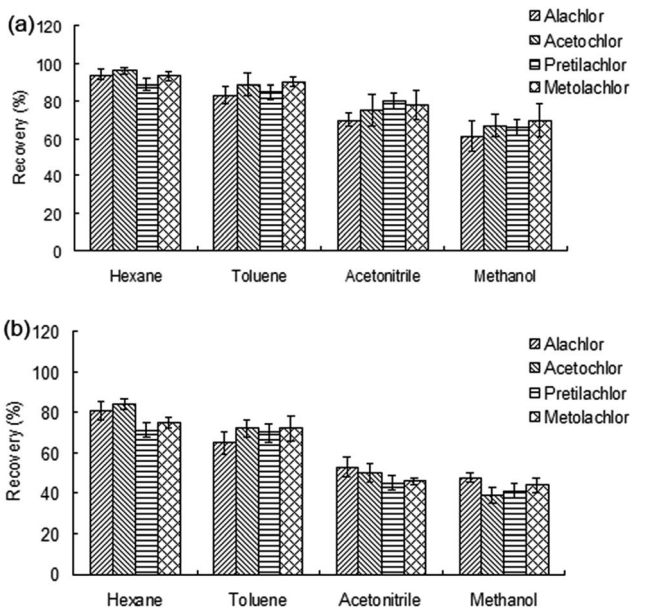

Fig. 4 Recoveries of the chloroacetamide herbicides for the MIPs (a) and the NIPs (b) with different loading solvents.

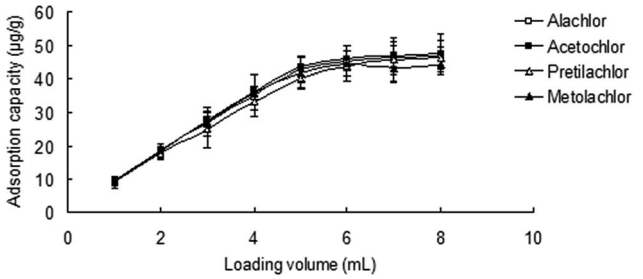

Fig. 5 Adsorption capacities of the MIP cartridges with different loading volumes.

3.5.3 Effect of the adsorption and desorption time. The adsorption and desorption processes of the chloroacetamide herbicides were performed in hexane and methanol, respectively. Different adsorption and desorption times were investigated and the results in Fig. 6 indicate that when the adsorption time is less than 2 min, the recovery of chloroacetamide herbicide will increase as the adsorption time increases. The recovery of chloroacetamide herbicide tended to stabilise when the adsorption time reached 4 min. Therefore, 4 min was selected as the optimal adsorption time. During the process of desorption, the recovery of chloroacetamide herbicide increased as the desorption time increased from 2 to 6 min. When the desorption time was more than 6 min, the recovery of chloroacetamide herbicide did not obviously increase. Therefore, 6 min was selected as the optimal desorption time.

3.5.4 Selection of washing solution. The washing step was the most crucial procedure to maximize the specific interactions between the analytes and binding sites, and to simultaneously reduce nonspecific interactions to discard interfering compounds in the polymers. After disrupting the nonspecific interaction between the MIPs and the interferents using a washing step, the specifically bound analytes were retained, and the analytes could then be quantitatively recovered in the following elution step.[27] To optimize the conditions of the washing step, different washing solvents such as hexane, chloroform, methylene chloride (DMC), ethyl acetate and acetone were investigated.

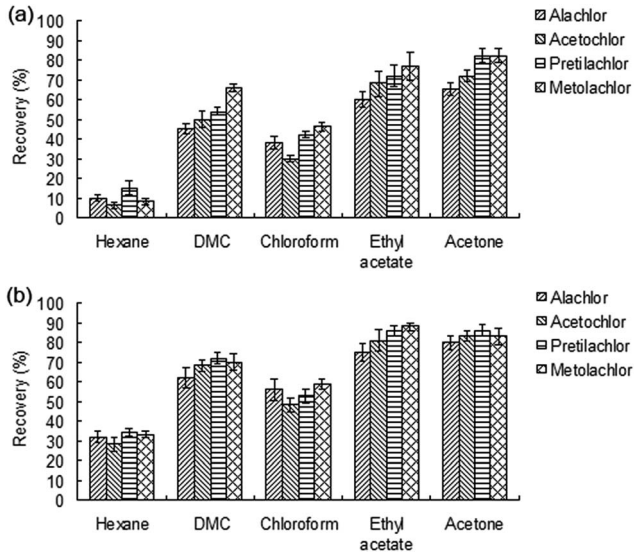

Fig. 7 Recoveries of the chloroacetamide herbicides on the MIPs (a) and the NIPs (b) with different washing solvents.

After loading 1 mL of standard solution on the MIP and NIP cartridges, 4 mL of each washing solvent was applied. The washing fractions of the solvent were collected and analyzed, and the results are shown in Fig. 7. It can be seen that all of the chloroacetamide herbicides underwent significant loss after washing with polar solvents, especially ethyl acetate and acetone which only gave about 25–30% adsorption. These

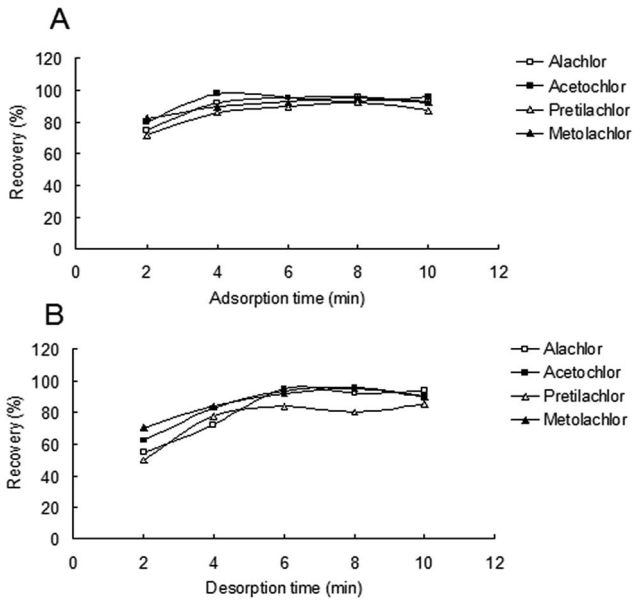

Fig. 6 Effect of the adsorption (A) and desorption time (B) on MISPE.

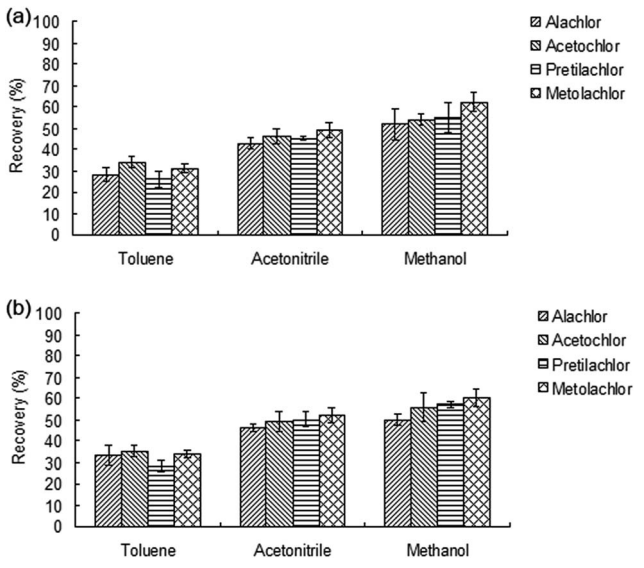

Fig. 8 Recoveries of the chloroacetamide herbicides on the MIPs (a) and the NIPs (b) with different elution solvents.

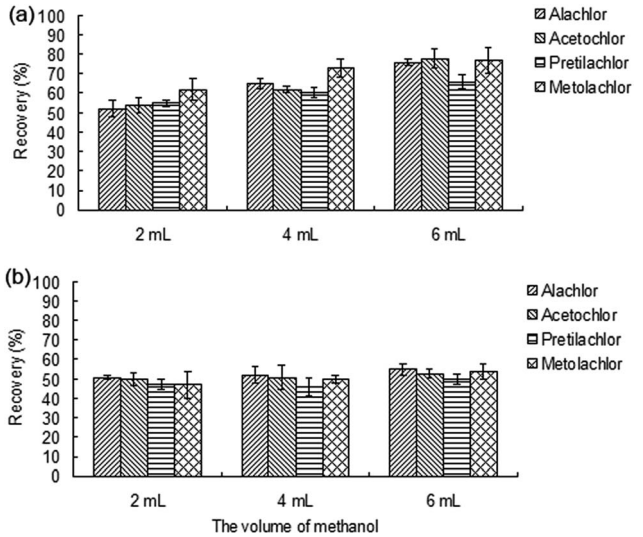

Fig. 9 Recoveries of the chloroacetamide herbicides on the MIPs (a) and NIPs (b) with different volumes of methanol.

results indicated that ethyl acetate and acetone were not suitable for the MIP washing process. About 40–70% of the chloroacetamide herbicide was removed from the cartridge after the washing step when using chloroform or DMC as the washing solvent. However, when using hexane as the washing solvent, a different result was observed. About 70–90% of all the chloroacetamide herbicides was selectively retained on the MIP cartridges when using hexane as the washing solvent. These results were consistent with those reported in the literature which showed that the strength of the binding of the analyte to the MIPs increased as the polarity of the rebinding solvent decreased.[28] As is shown in Fig. 7a and b, the recovery of NIP cartridges was higher than that of MIP cartridges under the same experimental conditions, which also proved that specific interactions between the specific sites and the analyte definitely existed. As a result, 4 mL hexane was selected as the optimum washing solution, since it minimises non-specific interactions without disturbing specific interactions in the imprinted polymer.

3.5.5 Selection of elution solution. The optimization of the elution step was performed using a series of elution solvents including toluene, acetonitrile and methanol. The results in Fig. 8 indicated that methanol provided the highest recoveries, due to it being easy to break the hydrogen-bonding between the chloroacetamide herbicides and the MIPs. The same results were observed in the NIP cartridges.

3.5.6 Volume of eluting solvent. The chosen volume of eluent must be just sufficient to elute the analyte from the sorbent. To optimize the volume of elution solvent, various volumes (2, 4, and 6 mL) of methanol were used to test the eluting efficiency. The recovery for each volume was calculated separately. As can be seen in Fig. 9, 6 mL of methanol can efficiently elute all the chloroacetamide herbicides from the MIP cartridges. Therefore, 6 mL of methanol was used to ensure a quantitative elution of the chloroacetamide herbicides from the sorbent.

3.6 Comparison of MISPE and C18-SPE from soil matrix

To determine the recoveries of the method, the soil samples were spiked with the four chloroacetamide herbicides at concentrations of 0.1, 0.5 and 1 μg mL^{-1}, and the results are given in Tables 2 and 3. The recoveries of the MIP cartridges were found to be 82.8–88% for alachlor, 85–90.2% for acetochlor, 84.8–87% for pretilachlor and 80.6–85% for metolachlor, with RSDs of 2.3–6.3% ($n = 5$). For the commercial C18 cartridge, the recoveries were found to be 75–83% for alachlor, 80.5–91% for acetochlor, 81–83.9% for pretilachlor and 74.9–86% for metolachlor, with RSDs of 3.3–7.6%. The selectivity

Table 2 Recoveries of the chloroacetamide herbicides in spiked soil samples using C18

Spiked level of analytes (μg mL^{-1})	0.1		0.5		1	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Alachlor	75	5.0	82	3.6	83	7.6
Acetochlor	80.5	7.2	88	3.3	91	3.4
Pretilachlor	81	4.9	82	5.0	83.9	6.1
Metolachlor	74.9	4.6	78.5	4.3	86	5.4

Table 3 Recoveries of the chloroacetamide herbicides in spiked soil samples using MISPE

Spiked level of analytes (μg mL^{-1})	0.1		0.5		1	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Alachlor	82.8	2.3	86	5.7	88	6.3
Acetochlor	85	3.4	90	3.4	90.2	4.6
Pretilachlor	84.8	3.4	85	3.6	87	5.5
Metolachlor	80.6	3.7	81	2.8	85	3.5

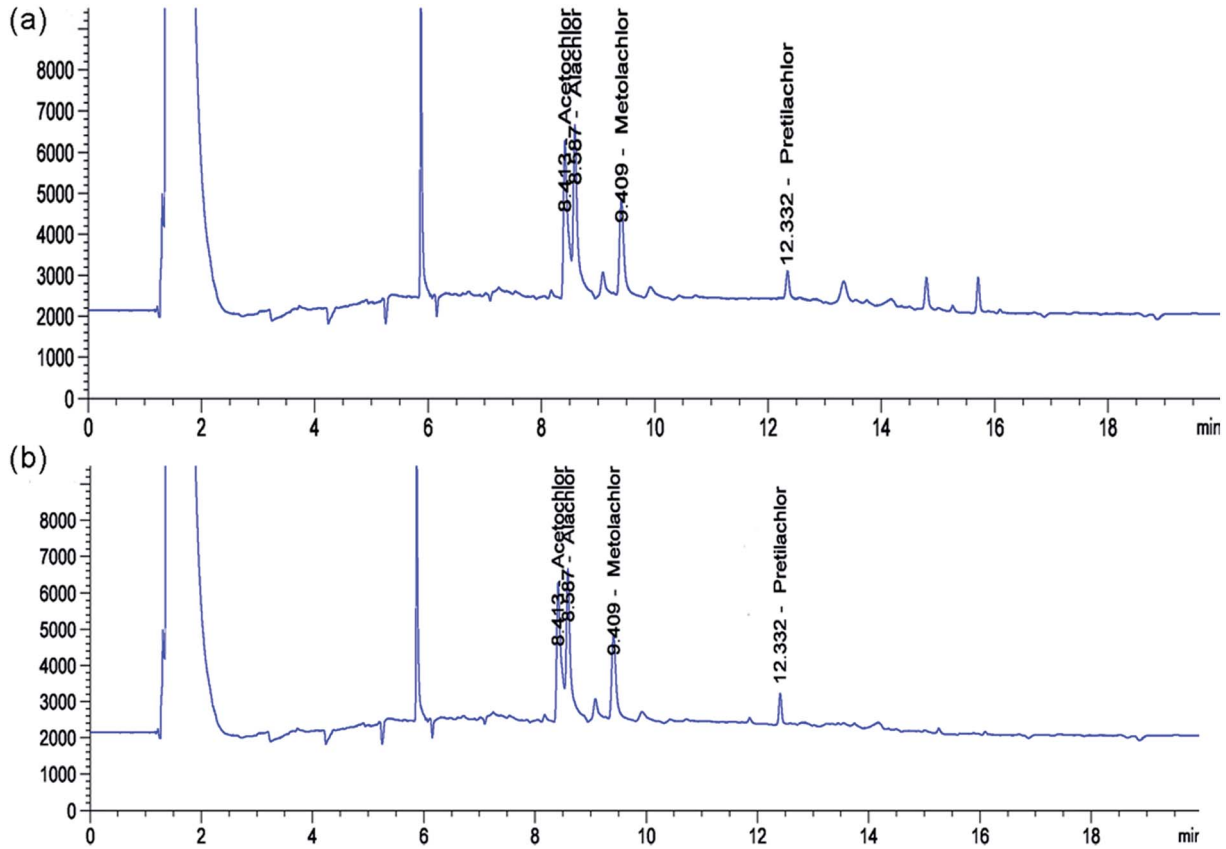

Fig. 10 Chromatograms of spiked soil samples with 1 μg mL^{-1} of chloroacetamide herbicide in hexane on C18 (a) and MIP (b) cartridges.

Table 4 Parameters of the MISPE-GC method

Analyte	Linear range	Regression equation	R^2	LOD (g)	LOQ (mg kg^{-1})
Alachlor	0.01–2 μg mL^{-1}	$Y = 209\,708X + 977.51$	0.9990	1.0×10^{-12}	0.0005
Acetochlor	0.01–2 μg mL^{-1}	$Y = 313\,164X + 4701.2$	0.9990	3.0×10^{-12}	0.0015
Pretilachlor	0.01–2 μg mL^{-1}	$Y = 117\,608X + 957.13$	0.9996	5.0×10^{-11}	0.025
Metolachlor	0.01–2 μg mL^{-1}	$Y = 236\,182X + 3728.3$	0.9999	1.0×10^{-11}	0.005

recoveries of commercial C18 samples were lower than that of the MIP cartridges, which is due to their lower affinities and their non-specific identification of the analytes. As shown in Fig. 10a and b, MIP extraction was much more effective than traditional C18 solid phase extraction. From all the results mentioned above, it is clear that the method proposed is reliable and applicable for the simultaneous determination of trace alachlor, acetochlor, pretilachlor and metolachlor in soil samples.

3.7 Validation of the MISPE-GC method

Calibration curves of the four chloroacetamide herbicides were constructed using the chromatographic peak areas *versus* the concentrations in the range of 0.01–2 μg mL^{-1}. Good linearity was obtained for all the chloroacetamide herbicides throughout the concentration range, and the regression equations are shown in Table 4. The limit of detection (LOD) and the limit of quantification (LOQ) at a signal-to-noise ratio of 3 were 1.0×10^{-12} to 5×10^{-11} g and 0.0005–0.025 mg kg^{-1}, respectively. The LOD and LOQ were lower than those reported in the literature.[22,23]

4 Conclusions

In this research, a sensitive and reliable method for the simultaneous determination of trace alachlor, acetochlor, pretilachlor and metolachlor in soil samples was developed. Satisfactory recovery, precision and sensitivity were achieved for the dummy template MISPE-GC method. These properties enabled the application of the dummy template MISPE method for selective extraction and sensitive screening of chloroacetamide herbicides in soil samples.

References

1 S. Coleman, R. Linderman, E. Hodgson and R. L. Rose, *Environ. Health Perspect.*, 2000, **108**, 1151–1157.
2 A. Balinova, *J. Chromatogr. A*, 1988, **455**, 391–395.
3 C. Rocha, E. A. Pappas and C. H. Huang, *Environ. Pollut.*, 2008, **152**, 239–244.
4 J. D. Vargo, *Anal. Chem.*, 1998, **70**, 2699–2703.
5 R. A. Yokley, L. C. Mayer, S. B. Huang and J. D. Vargo, *Anal. Chem.*, 2002, **74**, 3754–3759.
6 T. Madrakian, A. Afkhami, H. Mahmood-Kashani and M. Ahmadi, *Talanta*, 2013, **105**, 255–261.
7 H. Wang, H. Y. Yan, M. D. Qiu, J. D. Qiao and G. L. Yang, *Talanta*, 2011, **85**, 2100–2105.
8 R. D. Sole, A. D. Luca, M. Catalano, G. Mele and G. Vasapollo, *J. Appl. Polym. Sci.*, 2007, **105**, 2190–2197.
9 E. Moczko, A. Poma, A. Guerreiro, I. P. de Vargas Sansalvador, S. Caygill, F. Canfarotta, M. J. Whitcombe and S. Piletsky, *Nanoscale*, 2013, **5**, 3733–3741.
10 J. L. Cao, W. J. Kong, S. J. Zhou, L. H. Yin, L. Wan and M. H. Yang, *J. Sep. Sci.*, 2013, **36**, 1291–1297.
11 M. Javanbakht, A. M. Attaran, M. H. Namjumanesh, M. Esfandyari-Manesh and B. Akbari-adergani, *J. Chromatogr. B: Anal. Technol. Biomed. Life Sci.*, 2010, **878**, 1700–1706.
12 L. Q. Wang, F. Y. Lin and L. P. Yu, *Analyst*, 2012, **137**, 3502–3509.
13 V. Abbate, A. R. Bassindale, K. F. Brandstadt and P. G. Taylor, *J. Catal.*, 2011, **284**, 68–76.
14 G. Cirillo, F. Iemma, F. Puoci, O. I. Parisi, M. Curcio, U. G. Spizzirri and N. Picci, *J. Drug Targeting*, 2009, **17**, 72–77.
15 L. Sabourin, R. J. Ansell, K. Mosbach and I. A. Nicholls, *Anal. Commun.*, 1998, **35**, 285–287.
16 J. He, R. H. Lv, J. Zhu and K. Lu, *Anal. Chim. Acta*, 2010, **661**, 215–221.
17 J. F. Wang, P. A. G. Cormack, D. C. Sherrington and E. Khoshdel, *Angew. Chem., Int. Ed.*, 2003, **42**, 5336–5338.
18 P. Dramou, D. L. Xiao, H. He, T. B. Liu and W. Y. Zou, *J. Sep. Sci.*, 2013, **36**, 898–906.
19 L. Y. Zhang, G. X. Cheng and C. Fu, *Polym. Int.*, 2002, **51**, 687–692.
20 S. T. Wei, A. Molinelli and B. Mizaikoff, *Biosens. Bioelectron.*, 2006, **21**, 1943–1951.
21 M. Esfandyari-Manesh, M. Javanbakht, F. Atyabi, A. Mohammadi, S. Mohammadi, B. Akbari-Adergani and R. Dinarvand, *Mater. Sci. Eng., C*, 2011, **31**, 1692–1699.
22 L. Zhang, F. Han, Y. Y. Hu, P. Zheng, X. Sheng, H. Sun, W. Song and Y. N. Lv, *Anal. Chim. Acta*, 2012, **729**, 36–44.
23 X. G. Hu, G. M. Dai, J. J. Huang, T. T. Ye, H. J. Fan, Y. W. Tang, Y. Yu and Y. Liang, *J. Chromatogr. B: Anal. Technol. Biomed. Life Sci.*, 2010, **1217**, 5875–5882.
24 A. H. El-Sheikh, R. W. Al-Quse, M. I. El-Barghouthi and F. S. Al-Masri, *Talanta*, 2010, **83**, 667–673.
25 B. Sellergren and L. I. Andersson, *Methods*, 2000, **22**, 92–106.
26 I. Bakas, N. B. Oujji, E. Moczko, G. Istamboulie, S. Piletsky, E. Piletska, I. Ait-Ichou, E. Ait-Addi, T. Noguer and R. Rouillon, *Anal. Chim. Acta*, 2012, **734**, 99–105.
27 Y. P. Duan, C. M. Dai, Y. L. Zhang and L. Chen, *Anal. Chim. Acta*, 2013, **758**, 93–100.
28 B. Sellergren and L. I. Andersson, *Methods*, 2000, **22**, 92–106.

