Int. J. Electrochem. Sci., 10 **(2015)** 1393 - 1403

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Potentiometric Detection of Trace-Level Chlorpyrifos in Seawater Using a Polymeric Membrane Electrode Coupled with on-line Molecularly Imprinted Solid-Phase Extraction

Sixia Li[1,2], *Rongning Liang*[2,*] , *Wei Qin*[2], *Ruiqing Yao*[1,*]

[1] School of Chemical Engineering, Northwest University, Xi'an 710069, China
[2] Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences(CAS); Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong 264003, P. R. China
[*]E-mail: rnliang@yic.ac.cn (R.N. Liang); yrqnwu@sina.com (R.Q. Yao)

Received: 17 October 2014 / *Accepted:* 14 November 2014 / *Published:* 16 December 2014

Potentiometric sensors have evolved to be a promising tool for environmental trace analysis and potentiometric biosensing. However, the applications of potentiometric sensors are restricted to measurements of samples without complex matrixes. A new potentiometric detection system for detection of trace-level chlorpyrifos (CPF) in real samples is described in this paper. By using on-line molecularly imprinted solid-phase extraction (MISPE), interferences from sample matrixes can be effectively eliminated. Numerous key variables including affecting the extraction recovery of MISPE have been optimized. The proposed detection system offers a low detection limit of 0.027 nmol L^{-1} and exhibits excellent selectivity over other organicphosphate pesticides such as parathion-methyl, phoxim and dipterex. The practical application of the proposed system has been carried out for detection of CPF at trace levels in real seawater samples.

Keywords: Sample matrix elimination, Potentiometric sensor, Chlorpyrifos, Molecularly imprinted solid-phase extraction, Seawater

1. INTRODUCTION

In recent years, tremendous fundamental advances have led to dramatic improvements in the development and application of potentiometric sensors. In particular, the discovery of lowering the detection limit of ion-selective electrodes (ISEs) [1-3] allows potentionmetric measurements at subnanomolar levels [4]. Currently, ISEs have evolved to be a promising technique for environmental trace analysis [5-8] and potentiometric biosensing [9,10]. However, it should be noted that ISEs may

not be suitable for direct measurements of complex matrix samples such as seawater [11,12]. Indeed, a high saline background may strongly deteriorate the detection limit of ISEs due to the occurrence of the ion-exchange process [7]. In addition, natural organic matter may be extracted to the polymeric ISE membrane and interfere with the ISE response [12].

For ISE applications for complex matrix samples, an approach based on on-line electrochemically modulated preconcentration and matrix elimination has been reported [12]. By coupling the potentiometric detection to an efficient on-line electrochemical accumulation step, the proposed method offers potentiometric detection down to low parts per billion levels in samples containing 0.5 M NaCl background electrolyte. Although this approach opens new opportunities for applications of ISEs in marine environments, it needs more sophisticated instrumentation [13].

Molecularly imprinted solid-phase extraction (MISPE), as an efficient approach for sample separation and preconcentration, has attracted much attention for applications in environmental, clinical, and food analyses owing to its attractive features including excellent selectivity, low cost, ease of use, and high reliability [14-20]. Molecularly imprinted polymers (MIPs) as highly selective materials are tailor-made by polymerization of a selected monomer and crosslinker in the presence of a target analyte, acting as the template for assembly of its own recognition sites [20]. After polymerization and subsequent template removal, rigid polymeric materials with recognition sites specific for the template molecules can be obtained. Recently, MIPs have been used as sorbents packed in the SPE cartridges for efficient separation and preconcentration of analytes from complex matrixes [15,18].

The aim of this work is to demonstrate that on-line MISPE can be used for sample enrichment and matrix elimination so that potentiometric detection at trace levels becomes possible for seawater samples. Chlorpyrifos (CPF), a representative organophosphorus pesticide, is chosen as a model of environmental pollutants, which reserves potential risks of behavioral deficits both in animals and children [21,22]. The CPF imprinted polymer is synthesized by bulk polymerization and used as an on-line MISPE sorbent for selective extraction of CPF from seawater samples. The extracted CPF can be quantitatively detected by the CPF potentiometric sensor [23]. For the first time, this paper reports on the combination of on-line MISPE with ISE for elimination of detrimental sample matrix effects.

2. EXPERIMENTAL

2.1. Regents and materials

Methacrylic acid (MAA), 2,2'-azobisisobutyronitrle (AIBN), and tetrahydrofuran (THF) were purchased from Tianjin Kermel Chemical Reagent Co., Ltd. Sodium chloride, sodium phosphate dibasic, potassium dihydrogen phosphate were obtained from Guoyao Chemical Reagent Co., Ltd. (Shanghai, China). Tridodecylmethylammonium chloride (TDMAC), ethylene glycol dimethacrylate (EGDMA), 2-nitrophenyloctylether (*o*-NPOE), 3,5,6-trichloro-2-pyridyloxy-acrtic acid, chlorpyrifos, high molecular weight poly(vinyl chlorid) (PVC), and Amberlite XAD-2 resin were obtained from Sigma-Aldrich. Methanol (MeOH) and acetonitrile (ACN) of high performance liquid chromatography

(HPLC) grade were purchased from Shanghai ANPEL Scientific Instrument Co., Ltd (Shanghai, china). A stock solution of 10^{-3} M chlorpyrifos was made by dissolving 3.50 mg chlorpyrifos in 10 mL acetonitrile. A stock solution of 10^{-2} M 3,5,6-trichloro-2-pyridyloxy-acrtic acid was made by dissolving 25.7 mg 3,5,6-trichloro-2-pyridyloxy-acrtic acid in 10 mL acetonitrile. Aqueous solutions were prepared with double-deionized water (resistivity 18.2 MΩ cm) obtained with a Pall Cascada laboratory water system. The phosphate buffer solution (PBS, pH 7.4) was prepared with freshly deionized water. MAA, EGDMA, THF were distilled in vacuum prior to use. Other chemicals were of analytical grade and used as received.

2.2. Synthesis of the CPF imprinted polymer for solid-phase extraction

The CPF MIP was synthesized by the bulk method as described elsewhere [24]. Briefly, 1 mmol chlorpyrifos and 4 mmol MAA were mixed in a 40 mL glass tube for 1 h pre-complexation. Then, 28 mmol EGDMA, 20 mL porogenic solvent (ACN), and 0.43 mmol initiator (AIBN) were added. The polymerization mixture was sonicated for 3 min, purged with gentle flow of nitrogen for 10 min to remove the dissolved oxygen thoroughly and sealed under nitrogen atmosphere. Polymerization was carried out by submerging the tube in an oil-bath pan. The temperature was increased from room temperature to 75 ^{o}C within 30 min and maintained at 75 ^{o}C for 24 h. The obtained polymer was grounded in a mortar and sieved. Fines were discarded by repeated sedimentation in acetonitrile, and the resulting 25~50 μm particles were collected. The template CPF was removed by successive washing steps in a Soxhlet extractor with methanol-acetic acid (9:1, v/v) and acetonitrile, until the template could not be detected at 228.7 nm by high performance liquid chromatography (HPLC). Nonimprinted polymer (NIP) was prepared following the same procedure in the absence of the template molecules.

2.3. Preparation of the MISPE cartridge

The obtained CPF MIP was dried in a vacuum chamber for 24 h at 45 ^{o}C. Then MIP particles of 50 mg were packed into a polypropylene SPE cartridge (2.5 mL, Shanghai ANPEL), with PTFE frits (porosity 25 μm, ANPEL) placed at both ends.

2.4. Preparation of CPF potentiometric sensor and potentiometric detection of CPF

The CPF potentiometric sensor was prepared as described before [23]. Briefly, the CPF potentiometric sensor based on uniform-sized MIP beads as receptors was firstly immersed in the diluted elute solution obtained from the on-line MISPE step for the molecular recognition and simultaneous preconcentration of CPF. After 10 min incubation with a rotation speed of 3000 rpm, the proposed sensor was washed and then transferred to a separate electrochemical cell containing 0.05 M PBS of pH 7.4 for subsequent potentiometric detection. A fixed amount of indicator ion, 3,5,6-

trichloro-2-pyridyloxy-acrtic acid, was finally added to indicate the potential change induced by the CPF incubation [23].

2.5. General procedure

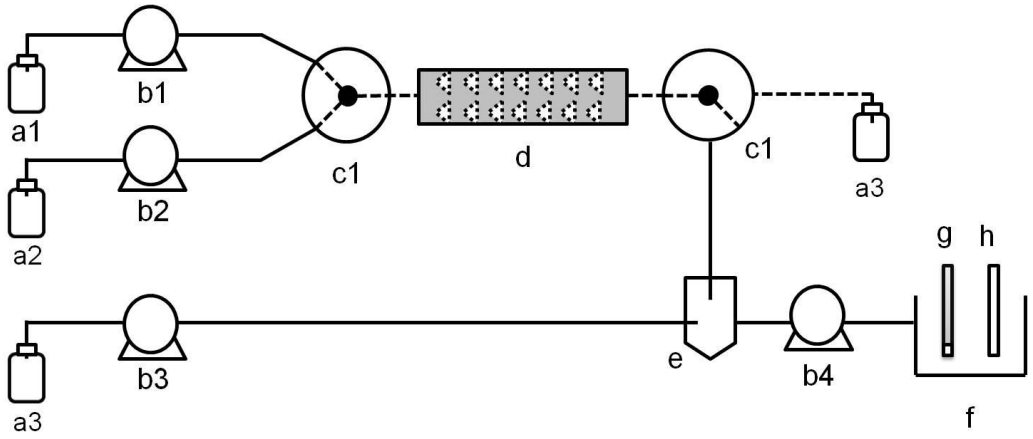

Figure 1. Schematic diagram of the on-line system for detection of CPF in seawater samples: (a1) conditioning solution or sample; (a2) cleaning solution or eluent; (a3) deionized water; (a4) waste; (b1), (b2), (b3), (b4) peristaltic pump; (c1), (c2) switching valve; (d) MISPE cartridge; (e) preconcentration cell; (f) detection cell; (g) indicator electrode; (h) reference electrode

The apparatus manifold employed is shown in Figure 1. The MISPE cartridge (d) was treated with 10 mL of deionized water and 10 mL of ACN via the pump (b1) prior to the extraction. Using the same pump, 100 mL of sample was then introduced to the MISPE cartridge at a flow rate of 30 mL/min. The effluents, in both cases, were delivered to waste through the valve (c2). CPF was retained in the MISPE cartridge while interferents passed the cartridge, thus eliminating the sample matrix effect. After extraction, the MISPE cartridge was washed with 10 mL of 10^{-2} M NaOH solution and then 10 mL of deionized water delivered by the pump (b2) at 5 mL/min to remove the nonspecifically bound compounds (e.g., humic acids) from the MIP. The retained CPF was eluted with 10 mL of ACN by using the pump (b2). The resulting eluant was delivered into the preconcentration cell (e) and evaporated with a gentle stream of nitrogen to 1 mL. Then, 4 mL of deionized water was added to the cell by the pump (b3). In this case, an enrichment factor of 25 was obtained. The resulting solution was delivered to the detection cell (f).The concentration of CPF was finally quantified by the CPF potentiometric sensor.

2.6. Recovery measurements

The recovery measurements of MISPE for CPF were carried out by using a reversed-phase HPLC system which consisted of a AIIiance e2695 (Waters, U.S.) pump, a photo-diode array (PDA) detector (Waters 2695-2998, U.S.), and a Waters C-18 column (SunFire, 5 μm 4.6 × 250 mm).

ACN/H_2O (80/20, v/v) was used as mobile phase with a flow rate of 1.0 mL/min and the column temperature was 40 ^oC.

2.7. Gas chromatograph-mass spectrometric (GC-MS) analysis

Seawater samples were collected from estuaries and filtered using a glass fiber filter (0.45 μm) and then passed through a self-packed Amberlite XAD-2 glass column. The retained analytes were eluted by 100 mL of hexane. The eluted samples were dried by anhydrous granulated sodium sulfate, and then evaporated to a final volume of 300 μL under a stream of nitrogen. 2,2',6,6'-Tetrachlorobiphenyl (PCB 54) was added as internal standard. The resulting samples were analyzed with an Agilent GC/MS-system (7890A GC/5975 MSD) in the negative chemical ionization mode (NCI), using methane as ionization gas and equipped with an DB-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific) [25].

3. RESULTS AND DISCUSSION

Polymeric membrane ISEs are most widely used chemical sensors in clinical diagnostics, process control and environmental monitoring. Currently, such electrodes routinely offer detection limits in the nanomolar or lower concentration range without any accumulation step. Despite the extremely attractive detection limits of these electrodes, their practical use is limited when high salt and organics concentrations are present, as in seawater samples. For this reason, we explore a novel potentiometric detection system for detection of trace-level CPF in seawater following a MISPE step for sample matrix elimination. In this case, potentiometric detection of CPF at trace level in seawater samples becomes possible by preceding the measurement by the MISPE step.

3.1. Optimization of extraction parameters

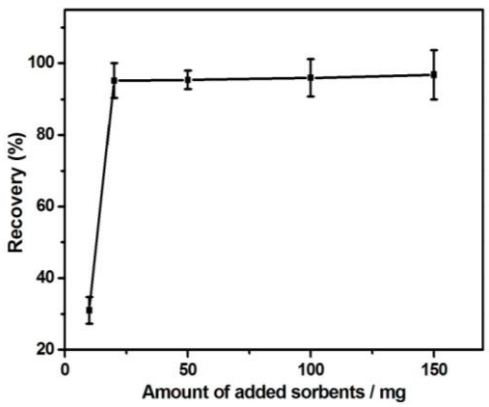

Figure 2. Effect of the amount of MIP sorbent on the recovery of CPF. Conditioning solution, 10 mL ACN and 10 mL deionized water; sample volume, 100 mL; washing solution, 10 mL 10^{-2} M NaOH solution and 10 mL of deionized water; eluent solution, 10 mL ACN. Each data point represents a mean value ± relative standard deviation for three measurements.

In order to achieve a high-efficiency extraction of CPF, we firstly tested the effect of the amount of MIP sorbent in the range of 10-150 mg on the recovery of the target analyte. The results are shown in Figure 2. It can be seen that the recovery of CPF increases with increasing the amount of MIP sorbent up to 20 mg, which is attributed to the increase in the number of binding sites of the MIP sorbent for selective extraction of CPF from sample solution. However, further increase in the amount of MIP sorbent would not significantly improve the recovery. Although 20 mg of MIP sorbent could guarantee the complete extraction, better reproducibility was obtained by the cartridge with 50 mg MIP sorbent. Therefore, 50 mg of MIP sorbent was employed for subsequent experiments.

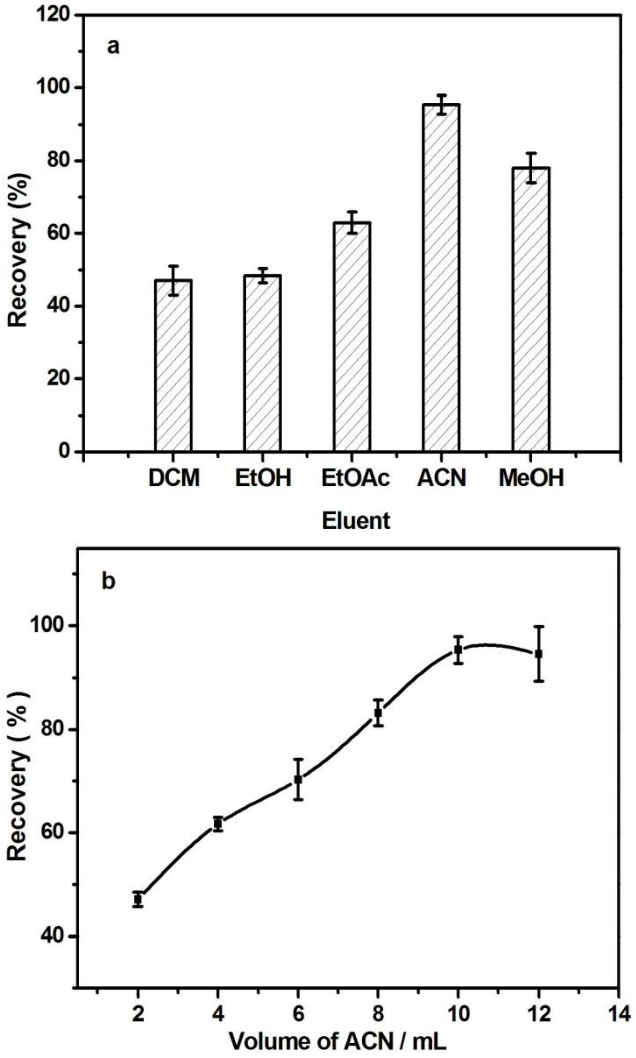

Figure 3. Effects of eluent (**a)**, the eluting volume (**b)**, and the eluting flow rate (**c)** on the recovery of CPF. Each data point represents a mean value ± relative standard deviation for three measurements. Other conditions as in Figure 2.

Studies were undertaken to determine the effect of various eluent reagents on the recovery of CPF. It has been well established that the retained CPF can be eluted from the MISPE cartridge by polar organic solvents [26, 27]. The elution characteristics of several different polar eluents including

dichloromethane, ethylacetate, ethanol, methanol and ACN have been investigated (Figure 3a). The results show that ACN is the best eluant with the highest recovery, which is in correspondence with the literature [28]. Thus, ACN was selected as the suitable eluent. Since the sample extraction efficiency also depends on the volume and flow rate of the eluent which determine the extraction time and sample recovery [29], the effects of the volume and flow rate of ACN were also evaluated. As shown in Figure 3b, the recovery of CPF increases upon increasing the volume of the eluent up to 10 mL, which is due to the fact that larger amounts of eluent could release more CPF from the MISPE cartridge. Figure 3b also shows that further increasing the eluent volume cannot increase the detection sensitivity. Therefore, a volume of 10 mL of ACN was selected for the eluting step. Figure 3c shows the effect of the flow rate of ACN on the recovery of CPF. It can be seen that higher flow fates result in lower sample recoveries which are due to the fact that the short elution period may be not enough to wash the residual CPF sufficiently. However, lower flow rates could prolong the detection procedure. Considering a compromise between higher recovery and shorter analysis time, a flow fate of 10 mL/min was employed.

3.2. Selectivity of MISPE cartridge

The extraction recovery of the MIPSPE cartridge for CPF can be affected by other related organicphosphate pesticides. These compounds may occupy available binding sites in the MIP sorbent and thus decrease the CPF recovery [26]. The selective extraction of CPF in the presence of other organicphosphate pesticides such as parathion-methyl, phoxim and dipterex by the proposed MIPSPE cartridge was performed. CPF and other organic pesticides were prepared individually with a concentration of 1.0×10^{-8} M.

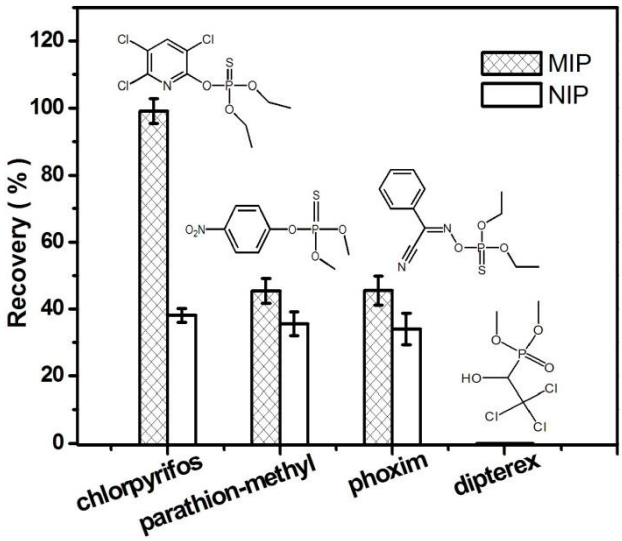

Figure 4. Recoveries of CPF by the MIP and NIP cartridges in the presence of parathion-methyl, phoxim and dipterex. Other conditions as in Figure 2.

Figure 4 shows the recoveries of CPF, parathion-methyl, phoxim and dipterex on the MISPE cartridge packed with MIP and NIP sorbents. As can be seen, the recoveries of CPF and other organic pesticides with the MIP are higher than that of the NIP, indicating that the MIP possesses better affinities to the template and other pesticides. These affinities are mainly caused by the hydrogen bonding interactions between carboxylic groups in the MIP and phosphate groups in organophosphate pesticides [30]. Notably, the recovery of CPF obtained by the MISPE cartridge is much higher than that of other pesticides, which suggests the specific recognition of the target analyte by using the MIP as the sorbent of MISPE cartridge. However, parts of parathion-methyl and phoxim can be retained in the MISPE cartridge with the recoveries of 45.4% and 45.5%, respectively. It should be noted that the retained organicphosphate pesticides could not influence the downstream potentiometric detection since it has been proven by our previously reported work that the proposed CPF potentiometric sensor showed an excellent selectivity over these pesticides [23].

3.3. Matrix effect elimination

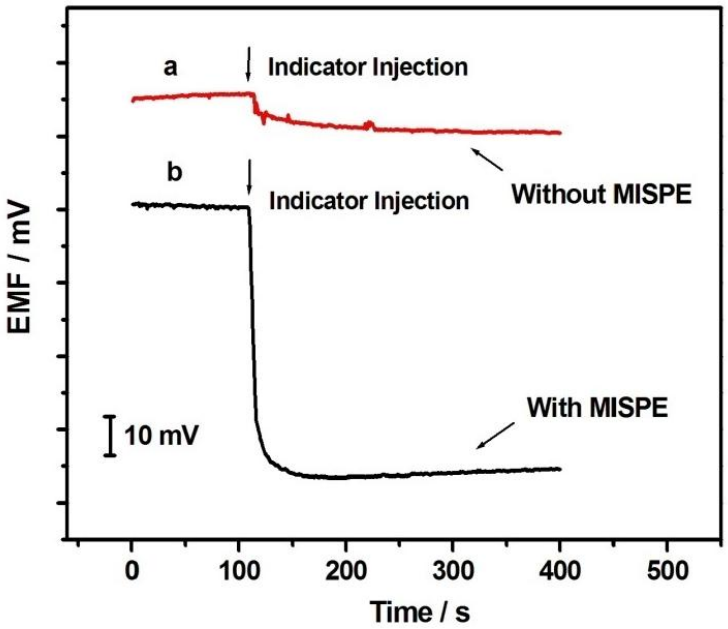

Figure 5. Potential responses of the detection system without (a) and with (b) the MISPE cartridge. Concentration of indicator ion, 3×10^{-5} M; sample, 0.5 M NaCl and 10 mg/L fluvic acid. Other conditions as in Figure 2.

Seawater samples usually contain rather high concentrations of electrolytes (e.g., NaCl) and dissolved organic compounds (e.g., humic acids) [31]. Therefore, it is necessary to employ the MISPE cartridge to eliminate the interferences of interfering ions and organic compounds prior to the potentiometric detection. The effect of the MISPE cartridge for detection of CPF in a background containing 0.5 M NaCl and 10 mg/L fluvic acids is shown in Figure 5. It can be seen that the CPF potentiometric sensor with the MISPE cartridge indeed exhibits much larger potential response to 3×10^{-5} M indicator as compared to that without the cartridge. This is probably due to the fact that,

without MISPE cartridge, the hydrophobic fluvic acids can be adsorbed onto the surface of the polymeric membrane based MIP sensor and render the polymeric membrane insensitive to the indicator ions. These results indicate that seawater sample components that are commonly detrimental to potentiometric measurements can be effectively eliminated by the proposed on-line MISPE cartridge.

3.4. Calibration curve of the proposed detection system

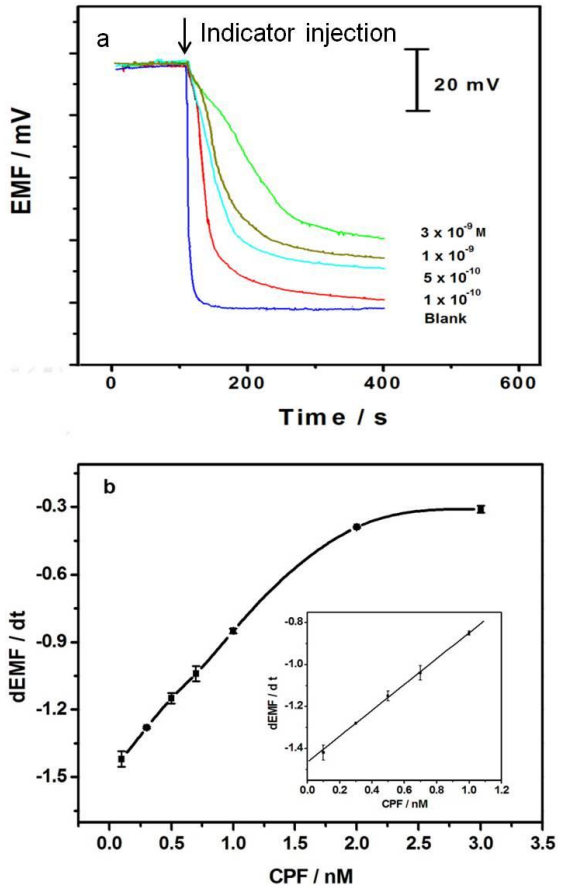

Figure 6. a Potentiometric responses to 3×10^{-5} mol/L indicator after incubation of the proposed sensor with increasing concentrations of CPF from 0.1 to 3 nM in 0.5 M NaCl and 10 mg/L fluvic acid sample following enrichment by the MISPE cartridge. **b** The initial slopes of the EMF changes over the concentration range 0.1 to 3 nM and the inset shows the initial slopes of the EMF changes over the concentration range 0.1 to 1 nM. Data represent an average ± standard deviation for three measurements. Other conditions as in Figure 2.

The proposed detection system of CPF involves two steps: the first is the extraction of CPF through the selective interaction between CPF in the sample solution and the MIP binding sites in the MISPE cartridge; the second is the potentiometric detection of CPF.

The detection system was explored for the measurements of CPF at trace levels. Figure 6 shows the ISE potential responses to 3×10^{-5} M indicator after incubation with CPF at different

concentrations in the eluant which was previously enriched by the MISPE cartridge. As can be seen, the potential response to the indicator anion can be largely inhibited by incubation of the MIP based ISE membrane with CPF in the eluant which causes less binding sites available in the membrane phase. Detailed experimental results reveal that there is a linear dependence of the initial slope of the EMF change, which was evaluated by a numeric fit of initial part of the EMF change (< 5 mV) to a first-order polynomial, on the concentration of CPF in the range of 0.1-1 nmol L^{-1} (γ = 0.999) with a detection limit of 0.027 nmol L^{-1} (3σ). This detection limit is three orders of magnitude lower than those reported by other researchers [32, 33]. The high sensitivity of the proposed detection system offers promising potential for trace-level potentiometric detection of CPF in seawater samples.

3.5 Analysis of real seawater samples

In order to evaluate the feasibility of the proposed system for practical analysis, measurements of trace CPF in real seawater samples were carried out. 1000 mL of seawater samples were filtered through a standard 0.45 μm filter, enriched by a factor of 250 and potentiometrically analyzed with the present system. The results are given in Table 1.

Table.1 Comparison of the results obtained by the proposed detection system and GC-MS for determination of CPF in real seawater samples.

Samples	the proposed method (10^{-11} mol/L) [a]	GC-MS method (10^{-11} mol/L) [a]
Seawater 1	4.7 ± 0.3	2.9 ± 0.8
Seawater 2	nd [b]	2.2 ± 0.3
Seawater 3	5.1 ± 0.8	4.4 ± 0.2
Seawater 4	3.5 ± 0.1	3.1 ± 0.3

a. Average value of three determinations ± standard deviation.
b. nd means not detected.

It can be seen that the data obtained by coupling the potentiometric detection to the selective on-line matrix elimination cartridge agree well with those obtained by the GC-MS method, indicating that the proposed potentiometric detection system has promising potential for trace-level analysis of CPF in seawater samples.

4. CONCLUSIONS

A novel potentiometric detection system for the determination of trace-level CPF in seawater based on on-line MISPE for sample matrix elimination has been described. The proposed system shows excellent selectivity and high sensitivity for CPF detection with a low detection limit of 0.027 nmol L^{-1}. Since many MIPs have been extensively exploited in analytical chemistry, this methodology is promising to develop the potentiometric detection system based on MISPE for trace-level measurements of other organic compounds.

ACKNOWLEDGEMENT
This work was financially supported by the Instrument Developing Project of the Chinese Academy of Sciences (YZ201161), the National Natural Science Foundation of China (41206087, 20977073), and the Taishan Scholar Program of Shandong Province (TS20081159).

References

1. E. Bakker, D. Diamond, A. Lewenstam, E. Pretsch, *Anal. Chim. Acta*., 393 (1999) 11.
2. E. Pretsch, *Trends Anal. Chem*., 26 (2007) 46.
3. T. Sokalski, A. Ceresa, T. Zwickl, E. Pretsch, *J. Am. Chem. Soc*., 119 (1997) 1134.
4. E. Bakker, E. Pretsch, *Anal. Chem*., 74 (2002) 420A.
5. G. Hanrahan, D. G. Patil, J. Wang, *J. Environ. Monitor*., 6 (2004) 657.
6. A. Ceresa, E. Bakker, B. Hattendorf, D. Gunther, E. Pretsch, *Anal. Chem*., 73 (2001) 343.
7. R. De Marco, G. Clarke, B. Pejcic, *Electroanal*ysis, 19 (2007) 1987.
8. S. Rodriguez-Mozaz, M. J. Lopez de Alda, D. Barcelo, *Anal. Bioanal. Chem*., 386 (2006) 1025.
9. J. Langmaier, E. Samcova, Z. Samec, *Anal.Chem*., 79 (2007) 2892.
10. M. E. Meyerhoff, B. Fu, Bakker E, J.H. Yun, V.C. Yang, *Anal. Chem*., 68 (1996) A168.
11. C. Zuliani, D. Diamond, *Electrochim. Acta*, 84 (2012) 29.
12. K.Y. Chumbimuni-Torres, P. Calvo-Marzal, J. Wang, E. Bakker, *Anal. Chem*., 80 (2008) 6114.
13. W. Qin, R. Liang, X. Fu, Q. Wang, T. Yin, W. Song, *Anal. Chem*., 84 (2012) 10509.
14. A. Martín-Esteban, *Trends Anal. Chem*., 45 (2013) 169.
15. A. Beltran, F. Borrull, P. A. G. Cormack, R. M. Marce, *Trends Anal. Chem*., 29 (2010) 1363.
16. W. J. Cheong, S. H. Yang, F. Ali, *J. Sep. Sci*., 36 (2013) 609.
17. X. Shen, C. Xu, L. Ye, *Ind. Eng. Chem. Res*., 52 (2013) 13890.
18. C. He, Y. Long, J. Pan, K. Li, F. Liu, *J. Biochem. Bioph. Meth*., 70 (2007) 133.
19. J. K. Awino, Y. Zhao, *J. Am. Chem. Soc*., 135 (2013) 12552.
20. L. Chen, S. Xu, J. Li, *Chem. Soc.Rev*., 40 (2011) 2922.
21. T. Caceres, W. He, R. Naidu, M. Megharaj, *Water Res*., 41(2007) 4497.
22. J. F. Sandahl, D. H. Baldwin, J. J. Jenkins, N. L. Scholz, *Environ. Toxicol. Chem*., 24 (2005) 136.
23. R. Liang, D. Song, R. Zhang, W. Qin, *Angew. Chem. Int. Ed*., 49 (2010) 2556.
24. E. Turiel, A. Martín-Esteban, P. Fernández, C. Pérez-Conde, C. Cámara, *Anal. Chem*., 73 (2001) 5133.
25. G. Zhong, Z. Xie, M. Cai, A. Moeller, R. Sturm, J. Tang, G. Zhang, J. He, R. Ebinghaus, *Environ. Sci. Technol*., 46 (2012) 259.
26. Q. Lu, X. Chen, L. Nie, J. Luo, H. Jiang, L. Chen, Q. Hu, S. Du, Z. Zhang, *Talanta*, 81 (2010) 959.
27. I. M. Baldim, M. C. de Oliveira Souza, J. C. J. da Cunha Souza, E. C. Figueiredo, I. Martins, *Anal. Bioanal. Chem*., 404 (2012) 1959.
28. T. B. Jordan, D. S. Nichols, N. I. Kerr, *Anal. Bioanal. Chem*., 394 (2009) 2257.
29. F. Du, G. Ruan, S. Liang, F. Xie, H. Liu, *Anal. Bioanal. Chem*., 404 (2012) 489.
30. X. Zhu, J. Yang, Q. Su, J. Cai, Y. Gao, *J. Chromatogr. A*, 1092 (2005) 161.
31. X. A. Álvarez-Salgado, A. E. J. Miller, *Mar. Chem.*, 62 (1998) 325.
32. J. W. Wong, M. G. Webster, C. A. Halverson, M. J. Hengel, K. K. Ngim, S. E. Ebeler, *J. Agric. Food Chem.*, 51 (2003) 1148.
33. C. G. Xie, H. F. Li, S. Q. Li, J. Wu, Z. P. Zhang, *Anal. Chem.*, 82 (2010) 241.