

Electrochemical Sensing System for Determination of Heavy Metals in Seawater

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Abstract: A novel electrochemical flow sensing system for determination of heavy metals in seawater is described in this paper. Processes including on-line filtration, UV digestion, electrochemical enrichment, and ion-selective electrode potentiometric detection are involved in the system for sensitive, selective and rapid detection. For measurements of cadmium, lead and copper ions in seawater matrix, the linear response ranges are 1.0×10^{-9} – 1.0×10^{-7} M, 3.0×10^{-9} – 1.0×10^{-7} M and 1.0×10^{-9} – 1.0×10^{-7} M, respectively with the corresponding detection limits of 2.8×10^{-10} , 6.6×10^{-10} and 5.1×10^{-10} M. For six successive measurements, the system showed relative standard deviations of less than 5%. The whole analysis process could be completed within 25 min. The system was applied to determination of heavy metals in seawater and the results agreed with those obtained by stripping voltammetry. With advantages of simplicity, accuracy and low cost, the sensing system offers promising potentials for on-site analysis of heavy metals in seawater.

Key Words: Electrochemical sensors; Heavy metals; Seawater; Ion-selective electrodes; UV digestion; Electrochemical preconcentration

1 Introduction

Rapid and accurate monitoring of heavy metals in estuarine areas is of great importance for timely assessment and effective prevention of heavy metal pollution in coastal zones. Due to high levels of electrolyte background, complicated interferants and low concentrations of heavy metals, the determination of heavy metal elements in seawater samples requires high sensitivity and good selectivity. In recent years, various techniques have been reported for heavy metal detection, such as atomic absorption spectrometry^[1], atomic emission spectrometry^[2], inductively coupled plasma mass spectrometry^[3,4]. However, expensive apparatus and tedious procedures are always required for these methods. Electrochemical stripping voltammetry has been successfully used for determination of lead, cadmium and copper in

seawater with advantages of simple instrumentation, high sensitivity, and capability of simultaneously monitoring of a variety of heavy metals^[5]. Unfortunately, stripping voltammetry has low sensitivity in detection of the electrochemically irreversible metals, and may suffer from problems of interferences from instrument vibrations and dissolved oxygen in sample solution^[6,7].

Recent improvements in the detection limits of ion-selective electrodes (ISEs) yield potentiometric sensors for direct measurement of ions down to the subnanomolar level^[8,9]. ISEs can be used for monitoring trace levels of analytes in the presence of high concentrations of background electrolytes^[10,11]. In this paper, a flow sensing system was described for determination of heavy metal elements in seawater using solid contact polymeric membrane ISEs as detectors, which combined with online sample pretreatment

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and electrochemical preconcentration.

2 Experimental

2.1 Reagents

Ionophores *N,N,N',N'*-tetrabutyl-3,6-dioxaoctanedi (thioamide) (ETH 1062) and *tert*-butylcalix[4]arene-tetrakis(*N,N*-dimethylthioacetamide) (lead ionophore IV), the lipophilic cation-exchanger sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), the lipophilic salt tetradodecyl ammonium tetrakis(4-chlorophenyl)borate (ETH 500), poly(3-octylthiophene-2,5-diyl-co-3-decyloxythiophene-2,5-diyl) (POT), NaCl (99.999%) and HNO₃ (*Trace* SELECT) were purchased from Sigma. The methyl methacrylate-decyl methacrylate (MMA-DMA) copolymer matrix was synthesized as described before^[12].

2.2 Instrumentation

As shown in Fig.1, the processes involved in the electrochemical flow sensing of heavy metals in seawater include on-line filtration (0.45 μm), UV digestion, electrochemical preconcentration and potentiometric detection. The peristaltic pumps and switching valves were employed to deliver the solution through the flow system. Polytetrafluoroethylene (PTFE) tubing was used to connect all the components. The UV digestion unit was comprised of a UV lamp (200 W), a quartz spiral coil (2.5 m × 0.8 mm i.d., 5.2 cm in diameter) used as digestion reactor, a temperature control device with a small power fan and a reflection foil. The electrochemical accumulation cell had a three-electrode system with a bismuth-coated glass carbon (for Cd²⁺ and Pb²⁺) or a gold (for Cu²⁺) working electrode, an Ag/AgCl reference electrode (3 M KCl), and a platinum disk as counter electrode^[10]. The ISE indicator and Ag/AgCl disk electrodes were imbedded into the detection cell body face to face. Both the accumulation and detection cells were made of transparent plexiglass and had a volume of 60 μL.

2.3 ISE preparation

The Pb²⁺-ISE membrane was prepared by dissolving 200 mg of the membrane components in 2.0 mL CH₂Cl₂ and then subjected to ultrasonic treatment for 10 min. The membrane contained 1.1% Lead Ionophore IV, 0.5% NaTFPB, 10.0% ETH 500, and 88.4% copolymer MMA-DMA.

The Cd²⁺-ISE or Cu²⁺-ISE membrane was prepared by dissolving 200 mg of the membrane components in 2.0 mL CH₂Cl₂ and then ultrasounding for 10 min. The membrane contained 1.0% ETH 1062, 1.0% NaTFPB, 10.0% ETH 500, and 88.0% copolymer MMA-DMA.

A 10-μL of POT (25 mM with respect to the monomer in CHCl₃) was dripped on the electrode surface and left to dry. A 50-μL of the membrane solution was deposited on the top of the electrode and allowed to dry for 2–3 h.

The ISEs were conditioned in 1.0 mM of primary ions for one day and then in 1.0 nM of primary ions with 0.01 M NaCl for another day.

2.4 Preparation of bismuth film electrode

The bismuth film was prepared by immersing the polished glassy carbon electrode in 0.1 M acetate buffer (pH 4.6) containing 0.5 mM Bi(NO₃)₃. A deposition potential (−0.6 V) was applied to the glassy carbon electrode for 4 min while the solution was slowly stirred.

2.5 Determination procedure

(1) 10.0 mL of sample solution was adjusted to pH 2.0 with HNO₃ and then pumped by peristaltic pump 1 at a constant flow (typically 0.8 mL min^{−1}). After filtration and UV digestion, the solution was stored in a bottle. (2) The solution was delivered by peristaltic pump 2 at a constant flow (typically 0.5 mL min^{−1}), while the potential was held at some value to allow deposition of a primary ion. During this process, the remaining sample solution was directed to waste. (3) After the deposition step, the sample solution was exchanged by

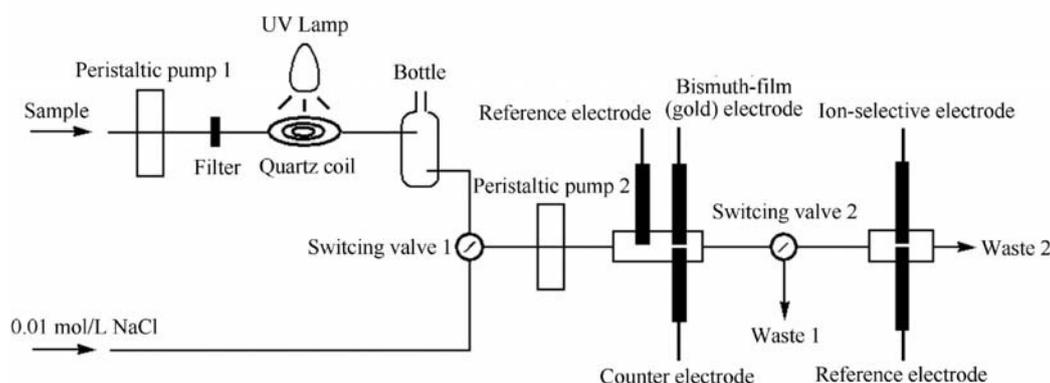


Fig.1 Schematic diagram of electrochemical flow sensing system for determination of heavy metals in seawater

0.01 M NaCl to wash the system for 1 min with the accumulation potential at the electrode. The electrodeposited primary ions were stripped into 0.01 M NaCl solution by scanning the potential linearly at a rate of 50 mV s^{-1} . (4) The detection solution containing the electrochemically released primary ions was directed to the potentiometric detection cell by changing the position of the valve. The potential was recorded for quantification after the signal was stable.

3 Results and discussion

3.1 UV digestion

In the flow system, the digestion efficiency was decreased with the flow rate increased. However, lower flow rates not only affected the analysis time, but could cause sample vaporization due to the high temperature in the flow path. The results showed that a flow rate of 0.8 mL min^{-1} could lead to relatively higher digestion efficiency and faster analysis. In addition, a large amount of CO_3^{2-} was produced in the digestion process, thus precipitations with Ca^{2+} and Mg^{2+} could form in seawater samples. To avoid the block of the flow line, the sample pH was adjusted to 2.0 using HNO_3 before UV digestion.

3.2 Electrochemical accumulation and release

Online electrochemical preconcentration was used to improve the performance of ISEs and eliminate the seawater matrix effect. Such matrix elimination was accomplished by replacing the original sample containing a high concentration of background electrolyte with a medium favorable to ISE detection. The parameters of electrodeposition were optimized. High responses were obtained when -1.0 , -0.8 and -0.3 V were used for deposition of Cd^{2+} , Pb^{2+} and Cu^{2+} , respectively with the corresponding stripping potentials were -0.7 , -0.5 , and $+0.4 \text{ V}$.

As shown in Fig.2, the influences of the deposition time were also examined over the range of 5–30 min. The potentiometric signal strongly increased with deposition time up to 15 min, and then leveled off. Therefore 15 min was chosen as the deposition time.

3.3 Solid contact ISEs

It was realized that primary ions could be transported through polymeric membranes of traditional ISEs under zero current. Such ion fluxes from the inner filling solution towards the sample solution may deteriorate the lower detection limit of ISEs. In this study, the detection limit was significantly improved by using a solid contact ISEs without inner filling solution. As shown in Fig.3, such electrodes offered subnanomolar detection limits of $4.5 \times 10^{-10} \text{ M}$, $8.2 \times 10^{-10} \text{ M}$

and $7.8 \times 10^{-10} \text{ M}$ for Cd^{2+} , Pb^{2+} and Cu^{2+} in the background of 0.01 M NaCl. Despite the extremely attractive detection limits of these electrodes, their application in real sample is still limited especially when high concentrations of interfering ions are present. For this reason, the potentiometric detection of heavy metals should be combined with an electrodeposition process, by which the original sample matrix can be replaced by a medium optimal for potentiometric detection.

3.4 Response time and detection limits

Cd^{2+} was chosen as a model heavy metal, and its potential responses are shown in Fig.4. The potential difference (ΔEMF) between the blank and the sample was used for quantification. Detailed experimental results revealed that there was a linear dependence of the ΔEMF on the concentrations of the heavy metals. The linear ranges were 1.0×10^{-9} – $1.0 \times 10^{-7} \text{ M}$ for Cd^{2+} , 3.0×10^{-9} – $1.0 \times 10^{-7} \text{ M}$ for Pb^{2+} , and 1.0×10^{-9} – $1.0 \times 10^{-7} \text{ M}$ for Cu^{2+} ($r > 0.99$) with the corresponding detection limits of $2.8 \times 10^{-10} \text{ M}$, $6.6 \times 10^{-10} \text{ M}$, and $5.1 \times 10^{-10} \text{ M}$ (3σ), respectively. The relative standard deviations ($n = 6$) were less than 5%, indicating a good reproducibility of the system. The results also showed that the bismuth-coated electrode could be continuously used for 1 d without significant changes in the response characteristics of the ISE, after the electrode was

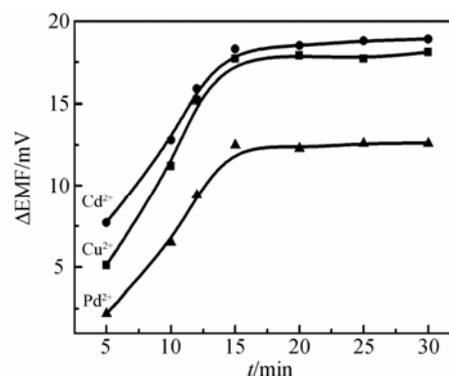


Fig.2 Effects of deposition time on potential changes for Cd^{2+} (●), Pb^{2+} (▲) and Cu^{2+} (■)

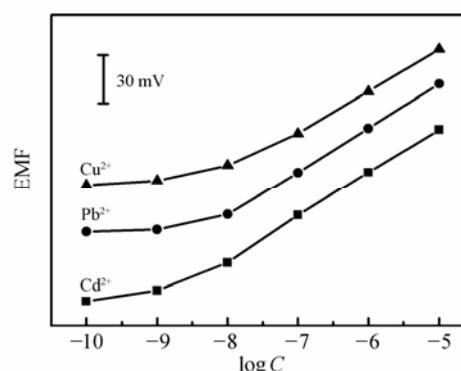


Fig.3 Potential responses of solid contact Cd^{2+} - (■), Pb^{2+} - (●), Cu^{2+} - (▲) selective electrodes

stored in 1.0 nM of the primary ion with 0.01 M NaCl for 1 month.

3.5 Interferences

For application in seawater samples, the interferences of some common inorganic ions were tested. As shown in Table 1, by coupling electrochemical preconcentration to the ISE detection, the interferences of Hg^{2+} , Pb^{2+} , Cd^{2+} and Cu^{2+} could be effectively circumvented.

3.6 Analysis of seawater sample

Five seawater samples were tested using the standard addition method. The results are listed in Table 2. It can be seen that the results obtained by the proposed method agree well with those by stripping voltammetry. The whole analysis process could be completed within 25 min, indicating a promising potential for on-site analysis of heavy metals in seawater.

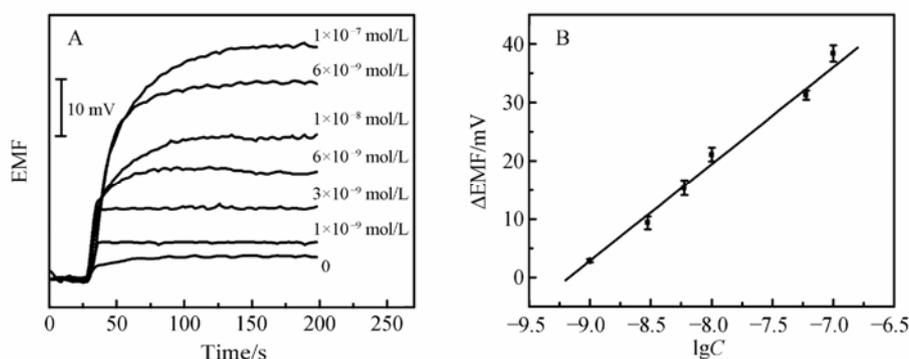


Fig.4 (A) Potentiometric responses of Cd^{2+} obtained by the proposed electrochemical sensing system. (B) The corresponding calibration curve

Table 1 Tolerable concentrations with respect to 1.0×10^{-8} M Cd^{2+} , Pb^{2+} and Cu^{2+} for some interfering ions

Interfering ions	Concentration (M) ^a		
	Cd^{2+}	Pb^{2+}	Cu^{2+}
K^+	0.1	0.1	0.1
Ca^{2+}	0.1	0.1	0.1
Mg^{2+}	0.5	0.5	0.5
Mn^{2+}	1.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}
Ni^{2+}	1.0×10^{-5}	1.0×10^{-5}	1.0×10^{-5}
Zn^{2+}	1.0×10^{-4}	1.0×10^{-4}	1.0×10^{-4}
Hg^{2+}	1.0×10^{-5}	5.0×10^{-6}	1.0×10^{-5}
Cu^{2+}	1.0×10^{-5}	1.0×10^{-4}	—
Pb^{2+}	5.0×10^{-5}	—	1.0×10^{-4}
Cd^{2+}	—	5.0×10^{-5}	1.0×10^{-5}

^a < 5% error

Table 2 Results of determination of heavy metals in seawater ($n = 3$)

Sample	Pb^{2+}		Cd^{2+}		Cu^{2+}	
	Present method ($\mu\text{g L}^{-1}$)	Stripping voltammetry ($\mu\text{g L}^{-1}$)	Present method ($\mu\text{g L}^{-1}$)	Stripping voltammetry ($\mu\text{g L}^{-1}$)	Present method ($\mu\text{g L}^{-1}$)	Stripping voltammetry ($\mu\text{g L}^{-1}$)
2	4.8 ± 0.1	4.6 ± 0.1	0.37 ± 0.03	0.40 ± 0.01	0.56 ± 0.05	0.31 ± 0.01
3	3.5 ± 0.1	3.2 ± 0.1	0.40 ± 0.02	0.37 ± 0.01	1.06 ± 0.06	0.78 ± 0.02
4	4.9 ± 0.3	5.2 ± 0.1	0.51 ± 0.04	0.48 ± 0.01	0.47 ± 0.01	0.40 ± 0.01
5	4.4 ± 0.4	4.5 ± 0.1	0.47 ± 0.02	0.46 ± 0.01	0.12 ± 0.04	0.15 ± 0.01

References

- Ning X A, Zhou Y, Liu J Y, Wang J H, Li L, Ma X G. *Spectroscopy and Spectral Analysis*, **2011**, 31(9): 2565–2568
- Guo P R, Mou D H, Wang C, Qiu R L, Du H. *Chinese J. Anal. Chem.*, **2009**, 37(11):1645–1650
- Rui Y K, Shen J S, Zhang F S. *Spectroscopy and Spectral Analysis*, **2008**, 28(10): 2421–2424
- Xu P, Sun Y L. *Chinese J. Anal. Chem.*, **2010**, 38(4): 581–584
- Liu D M, Jin Y, Jin Q H, Zhao J L. *Chinese J. Anal. Chem.*, **2011**, 39(11): 1748–1752
- Economou A, Clark A K, Fielden P R. *Analyst*, **2001**, 126(1): 109–113
- Achterberg E P, Holland T W, Bowie A R, Fauzi R, Mantoura C, Worsfold P J. *Anal. Chim. Acta*, **2001**, 442(1): 1–14
- Sokalski T, Ceresa A, Zwickl T, Pretsch E. *J. Am. Chem. Soc.*,

- 1997, 119(46), 11347–11348
- [9] Jagerszki G, Takacs A, Bitter I, Gyurcsanyi R E. *Angew. Chem. Int. Ed.*, **2011**, 123(7): 1694–1697
- [10] Chumbimuni-Torres K Y, Calvo-Marzal P, Wang J, Bakker E. *Anal. Chem.*, **2008**, 80(15): 6114–6118
- [11] Bedlechowicz-Sliwakowska I, Lingenfelter P, Sokalski T, Lewenstam A, Maj-Zurawska M. *Anal. Bioanal. Chem.*, **2006**, 385(8): 1477–1482
- [12] Qin Y, Peper S, Bakker E. *Electroanalysis*, **2002**, 14(19-20): 1375–138