Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.708557

50 (2012) 125–131
December

Taylor & Francis
Taylor & Francis Group

Application of large molecular weight poly (4-styrenesulfonate) as a binding phase of the diffusive gradients in thin films technique

Hong Chen[a], Yu-jing Liu[a], Yu-hua Jiang[b], Jia-Li Gu[a], Ting Sun[c,*]

[a]*Department of Chemistry, Bohai University, Jinzhou 121013, China*
[b]*Department of Applied Chemistry, Liaoning Petrochemical Vocational Technology College, Jinzhou 121001, China*
[c]*Department of Chemistry, Northeastern University, Shenyang 110004, China*
Tel. +86 24 83684786; email: sunlth@163.com

Received 23 February 2012; Accepted 9 May 2012

ABSTRACT

As the replacement of previously recommended poly (4-styrenesulfonate) (PSS) with $M_w \sim 7 \times 10^4$ (PSS-7E4) for measuring metal ions by diffusive gradients in thin films (DGT), a relatively large molecular weight PSS with $M_w \sim 1 \times 10^6$ (PSS-E6) was used as binding phase in the liquid-type DGT device (PSS-E6 DGT). The binding capacities of PSS-E6 DGT for metals and the stability constants of PSS-E6 with metals were also investigated. The heavy metal speciations measured by PSS-E6 DGT in spiked river water (Cu^{2+}: 26.01 ± 2.59%, Cd^{2+}: 42.96 ± 2.56%, Co^{2+}: 16.41 ± 1.66%, and Ni^{2+}: 18.24 ± 1.96%) and in spiked domestic wastewater (Cu^{2+}: 10.35 ± 1.29%, Cd^{2+}: 20.31 ± 1.25%, Co^{2+}: 8.04 ± 0.89%, and Ni^{2+}: 8.86 ± 0.98%) were consistent with those measured by PSS-7E4 DGT in spiked river water (Cu^{2+}: 26.91 ± 2.82%, Cd^{2+}: 40.88 ± 3.04%, Co^{2+}: 14.83 ± 1.84%, and Ni^{2+}: 16.65 ± 1.83%) and in spiked domestic wastewater(Cu^{2+}: 9.76 ± 1.17%, Cd^{2+}: 19.36 ± 1.49%, Co^{2+}: 7.65 ± 0.92%, and Ni^{2+}: 7.83 ± 1.03%), respectively. Compared with PSS-7E4, PSS-E6 was more suitable as binding phase in the DGT device for its lower pretreatment depletion rate, lower cost, and lower pollution.

Keywords: Diffusive gradients in thin films; Binding phase; Poly (4-styrenesulfonate); Heavy metals

1. Introduction

Monitoring trace metals in water is essential since it enables predicting their impact on the environment. However, the toxicity of metals in aquatic systems is considerably dependent on the nature of the metal species present, and the most important factor is the biological availability of the metal species. Hence, chemical speciation of metals is important to determine water quality.

The relatively recent technique of diffusive gradient in thin films (DGT) represents a new approach for *in situ* determination of labile metal species in the aquatic systems [1]. In the last years, DGT is being increasingly used for the determination of metal speciation in a wide variety of media such as natural waters [2–6], soils [7,8], and sediments [9,10]. Some papers have been published on the monitoring of wastewater treatment plants [11,12] and waterworks producing drinking water using DGT devices [13]. The DGT technique combines the processes of mass transport through a diffusive layer and accumulation within a binding layer during deployment [1,3]. The diffusive layer allows solute species below a selected size threshold to pass from the bulk solution into the DGT device [2]. The binding layer rapidly and irreversibly accumulates the soluble analyte species. A

---

*Corresponding author.

diffusive gradient is thereby maintained within the diffusive layer between the bulk solution and the interface with the binding layer [1]. The analyte concentration in the bulk solution can thus be calculated using the DGT equation by measuring the mass of analyte accumulated in the binding layer after a particular deployment time [2,14].

Two types of DGT devices, including solid-type DGT device and liquid-type DGT device, have been developed for the measurement of labile soluble metal species. For solid-type DGT devices, the diffusive layer is a thin (0.2–2 mm thick) polyacrylamide hydrogel (>95% water) covered with a 0.45-μm pore size membrane at the interface with the bulk solution [2]; the binding layer is a layer of polyacrylamide hydrogel impregnated with Chelex-100 cation exchanger [1]. A new liquid-type DGT device employing poly (4-styrenesulfonate) (PSS) with a relatively low molecular weight of 7×10^4 (PSS-7E4) aqueous solution as the binding phase and a cellulose dialysis membrane as the diffusive layer (PSS-7E4 DGT) was recently reported [15,16]. The homogeneous mobile liquid binding phase provides an excellent contact between the binding phase and the diffusive layer. The advantages of the modified DGT device include a theoretically ideal mass transport and accumulation, good reproducibility, a well-defined reproducible diffusive layer, and no need for elution corrections [17–19]. The new DGT device has been used for the measurement of heavy metals in natural waters [15,16]. However, the high loss rate of PSS-7E4 in the process of pretreatment prevents its practical application. It is necessary to find a higher molecular weight PSS, to be used as binding phase, which presents a reduced loss of reagent and meet the requirements of liquid-type DGT device.

In this study, PSS with a relatively high molecular weight of 1×10^6 (PSS-E6) was used as the binding phase in the liquid-type DGT device (PSS-E6 DGT). The pretreatment depletion rate of PSS-E6 was investigated in the range of 1–10 d. The binding properties of PSS-E6 DGT for Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} were tested. The accuracy of PSS-E6 DGT and PSS-7E4 DGT for the measurement of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} in a synthetic solution—spiked Ling river water (Jinzhou, China) and spiked domestic wastewater (Jinzhou, China)—was assessed.

2. Experimental

2.1. Pretreatments

Cellulose acetate dialysis membranes ($M_w \sim 12{,}000$ or greater retain; Sigma, USA) were pretreated following the procedures recommended by Li et al. [15] and were stored in deionized water.

The purification of PSS with a $M_w \sim 1 \times 10^6$ (PSS-E6) was treated as described by Li et al. [15]. A 25.5 g portion of PSS-E6 was dissolved in 100 mL of deionized water. The solution was then transferred into a pretreated cellulose acetate dialysis bag which was placed in deionized water for 72 h with the water frequently replenished. After purification, the concentration of PSS-E6 was determined gravimetrically and a PSS-E6 stock solution of 0.10 M (concentration of sulfonic groups) was prepared. The pretreatment depletion rates of PSS-E6 and PSS-7E4 were investigated in the range of 1–10 d. The pretreatment depletion rate was defined as the ratio of the mass loss during purification to the total mass added before purification.

2.2. Measurement of diffusion coefficients of metals in the dialysis membrane

The diffusion coefficients (Dm) of metals (Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+}) through the dialysis membrane in various synthetic solutions (synthetic river water and synthetic domestic wastewater) were determined using a specifically designed diffusion cell with two perspex compartments [20,21], each with an interconnecting 2.0 cm diameter opening. A 3.0 cm diameter and 85 μm thickness disk of freshly pretreated dialysis membrane was placed on the openings between the compartments, ensuring that the membrane was the only mass transport medium. Fifty milliliter of carrier solution containing the diffusing ion of interest were introduced into the source solution compartment, and 50 mL of the same carrier solution with an experimentally optimized concentration of PSS solution were introduced into the receptor solution compartment [15]. Both compartments were continuously stirred during the experiment using an overhead stirrer at a constant speed. Samples were taken from both compartments at 0.5 h intervals up to 3 h and measured by flame atomic absorption spectrometry (FAAS). All experiments were carried out in a temperature controlled laboratory. Variation in temperature was no more than ±1℃. The average concentration at the sampling intervals was used to correct concentration changes in the source compartment.

2.3. Binding properties of PSS-E6 DGT for metals

The concentration of PSS-E6 in the device was optimized by examining the binding capacities of several devices with varying PSS-E6 concentrations of 0.005, 0.010, 0.015, 0.020, 0.030, and 0.040 M in a solution containing 2.0 μg mL^{-1} Cd^{2+} for 48 h.

The binding capacities of PSS-E6 DGT for metals (Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+}), the stability constants of PSS-E6 with metals, and the effects of varying pH (2–11 in 10 increments) and $NaNO_3$ concentration (0.0001, 0.001, 0.01, 0.1, and 1.0 M) on the binding capacities of PSS-E6 DGT were investigated (e.g. [15]). The pH values were adjusted using 2% HCl or NaOH. The ionic strength of the solution was adjusted with the appropriate addition of $NaNO_3$ at pH ~ 7.

2.4. Validation of PSS-E6 DGT

The DGT-labile fractions (Ψ) of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} were measured by PSS-E6 DGTs and PSS-7E4 DGTs. The devices were deployed in triplicate in a 30 L (sufficient volume of the sampled solution was used to ensure that depletion of metal ions by the DGT devices was negligible) well stirred 0.1 mg L^{-1} solutions (i.e. the synthetic river water, the spiked Ling river water, and the spiked domestic wastewater). Aforementioned metals were measured over periods of time from 24 to 96 h. The river water (Jinzhou, China) and domestic wastewater (Jinzhou, China) were collected on 15 July 2011 and on 18 October 2011, respectively. The 30 L of river water and domestic wastewater (individually) were immediately prefiltered under vacuum through qualitative filter papers before filtering through a 0.45 μm cellulose nitrate membrane in the laboratory. The parameters of Ling river water and domestic wastewater are shown in Table 1. The Ψ of metals was defined as follows:

$$\Psi = \frac{\text{DGT labile metal ion concentration}}{\text{total concentration of metal ion in bulk solution}} \tag{1}$$

2.5. Apparatus and reagents

The concentrations of metal and metal–PSS complexes solutions were determined by FAAS (AA-700, PE) after appropriate dilutions. All the reagents were analytical grade, and purchased from Sinopharm Chemical Reagent Co., Ltd, China.

3. Results and discussion

3.1. Comparison of depletion rate of PSS-E6 and PSS-7E4

The pretreatment depletion rates of PSS-7E4 and PSS-E6 in the range of 1–10 d were investigated. Fig. 1 shows that the pretreatment depletion rates increase almost linearly with time at the beginning until it reaches the maximum, and then remains unchanged in the later stage. The pretreatment time of PSS-E6 (3 d) was less than half that of PSS-7E4 (7 d). The average pretreatment depletion rates ($n = 5$) of PSS-7E4 and PSS-E6 were 70.33 ± 1.22 and 15.18 ± 0.87%, respectively. The use of PSS-E6 could reduce the loss of reagent. PSS-E6 owned lower pretreatment depletion rate, lower reagent cost, and shorter pretreatment time, which complied with the requirements of green analytical chemistry [22].

3.2. Diffusion coefficients of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+}

According to the DGT equation [23,24], the diffusion coefficients of metals in synthetic river water (Cu^{2+}: 1.25 ± 0.05 μcm^2 s^{-1}, RSD% = 3.31%; Cd^{2+}: 1.38 ± 0.10 μcm^2 s^{-1}, RSD% = 2.58%; Co^{2+}: 1.08 ± 0.08 μcm^2 s^{-1}, RSD% = 3.57%; and Ni^{2+}: 0.92 ± 0.04 μcm^2 s^{-1}, RSD% = 2.96%) and in synthetic domestic wastewater (Cu^{2+}: 1.18 ± 0.06 μcm^2 s^{-1}, RSD% = 4.25%; Cd^{2+}: 1.29 ± 0.09 μcm^2 s^{-1}, RSD% = 3.08%; Co^{2+}: 1.00 ± 0.11 μcm^2 s^{-1}, RSD% = 4.61%; and Ni^{2+}: 0.89 ± 0.09 μcm^2 s^{-1}, RSD% = 3.99%) were obtained.

3.3. The binding properties of PSS-E6 DGT

The binding capacities of DGT devices with different PSS-E6 concentrations (0.0050–0.040 M) were 29.78, 56.32, 71.58, 95.76, 96.27, and 93.38 μM, respectively. The accumulated mass of metal in the binding phase increased with the enhancement of PSS-E6 concentration between 0.0050 ~ 0.020 M and reached a plateau in the range 0.020 ~ 0.040 M. So the 0.020 M PSS-E6 solution was used as the binding phase of DGT technique. In addition, the viscosities (21℃) of PSS-E6 solutions of 0.0,050, 0.010, 0.020, 0.030, and 0.040 M were 3.95, 8.41, 12.5, 16.4, and 19.3 mpa s, respectively,

Table 1
Major cation concentration (mM), dissolved organic carbon (DOC, mg C L^{-1}), and pH of the Ling river water and the domestic wastewater[a]

Parameters	$[K^+]$	$[Na^+]$	$[Ca^{2+}]$	$[Mg^{2+}]$	DOC	pH
River water	0.25	1.45	0.85	1.10	10.30	6.9
Wastewater	0.30	3.52	1.62	1.35	44.34	7.6

[a] Major cation concentrations were measured by FAAS after appropriate dilution.

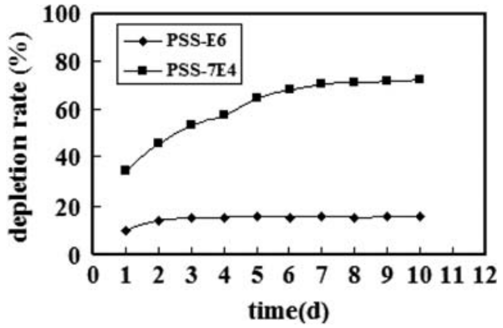

Fig. 1. Depletion rates of PSS-7E4 and PSS-E6 with pretreatment time.

and increased with the enhancement of its concentration. It was found that this concentration was relatively easy to handle due to less viscosity and less bubbles between the dialysis membrane and the solution of the binding phase.

The stability constants (log*K*) of PSS-E6 with Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} were 8.5, 9.4, 8.6, and 8.3, respectively. According to references [15], the log*K* of PSS-7E4 with Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} were 8.1, 9.0, 8.07, and 8.04, respectively. The results showed that PSS-E6 could combine with Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} as firmly as PSS-7E4.

The binding capacities of PSS-E6 DGT to Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} were 9.9, 10.6, 10.1, and 9.8 μM, respectively, which are similar to those observed for PSS-7E4 [15].

The changes in binding capacity of PSS-E6 DGT for Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} with pH are shown in Fig. 2. The binding capacity of PSS-E6 DGT increased rapidly from pH 1 to 4, probably as a result of the increase in proportion of base form of the sulfonic acid groups [15,25]. From pH 4 to 7, the binding capacity for metal ions remained quite constant. The Cu^{2+} binding capacity decreased rapidly at pH > 7, the Co^{2+} and Ni^{2+} binding capacity decreased rapidly at pH > 9, and the Cd^{2+} binding capacity decreased rapidly at pH > 10 as a result of the change of metal speciation (i.e. the formation of insoluble hydroxide forms) [15,25,26].

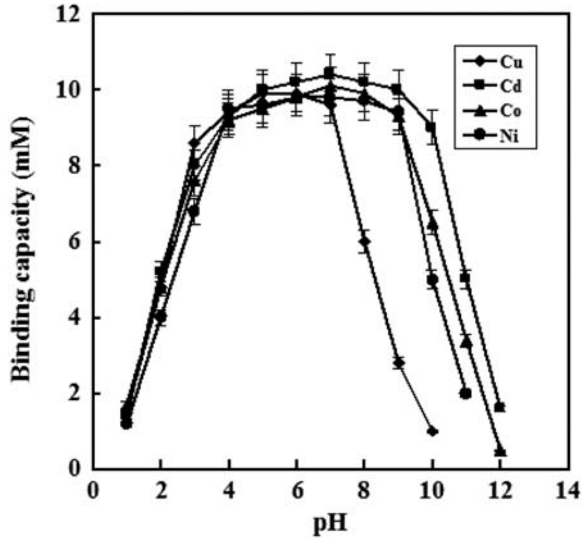

Fig. 2. Effect of pH on the binding capacities of PSS-E6 DGT for metals: Concentration of Cu^{2+} = 1.3 mM, Cd^{2+} = 1.3 mM, Co^{2+} = 1.3 mM, and Ni^{2+} = 1.3 mM, deployment time = 48 h, temperature = 20℃.

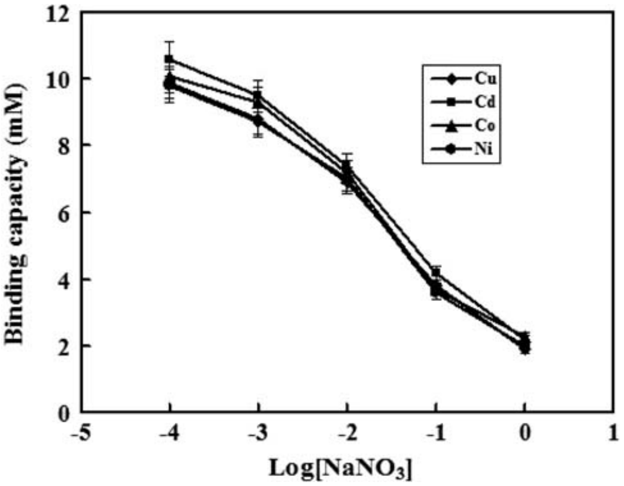

Fig. 3. Effect of ionic strength (presented as logarithmic concentration of $NaNO_3$) on the binding capacity of PSS-E6 DGT for metals: Concentration of Cu^{2+} = 1.3 mM, Cd^{2+} = 1.3 mM, Co^{2+} = 1.3 mM, and Ni^{2+} = 1.3 mM, deployment time = 48 h, temperature = 20℃.

The changes of binding capacity of PSS-E6 DGT for Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} with increasing ionic concentration are shown in Fig. 3. The binding capacities of PSS-E6 DGT for aforementioned metals decreased with an increase in the ionic concentration (as $NaNO_3$) that increases from 0.0001 to 1.0 M. A similar trend has been reported for PSS-7E4 DGT [15]. This was due to the competition of Na^+ with above metals [27,28]. However, the effect of the ion concentration may be various for different DGT devices, even for the same DGT device at different pH. In the presence of major environmental ions, $D_{\mathrm{As}}{}^{\mathrm{V}}$-Nafion is ~20% higher than $D_{\mathrm{As}}{}^{\mathrm{V}}$-Nafion measured in $NaNO_3$/sodium acetate at the same pH [29]. Panther and coworkers attributed this increase in diffusion coefficient to two factors. Most importantly, specific interactions between Mg^{2+} and Ca^{2+} and sulfonate groups within the Nafion membrane may decrease electrostatic repulsions for the negatively charged species, promoting faster diffusion of $H_2AsO_4^-$. A lesser contributing factor may be partial complexation of As^V by Ca^{2+} and Mg^{2+} to form uncharged complexes which diffuse more rapidly through the Nafion membrane [29]. For Chelex-DGT at pH 5.0, C_{DGT}/C_{Sol} ratios between 0.85 and 1.07 were obtained across the ionic strength range (0.001−0.7 $mol\,L^{-1}$ NaNO3) in the measurement of Al [30]. However, at pH 8.4, C_{DGT}/C_{Sol} decreased as ionic strength increased. For the deployment times at pH 8.4 (where $Al(OH)^{4-}$ accounts for > 99.9% of total dissolved Al forms), ionic strength significantly affects the uptake of Al by Chelex-DGT. These results clearly demonstrate that the measurement of Al by Chelex-DGT is critically dependent on both pH and ionic strength and that the Chelex-DGT method may not be applicable to all natural waters, especially seawater, for the measurement of Al [30].

3.4. Performance of PSS-E6 DGT

The DGT devices were validated by testing the relationship between the mass of analyte accumulated in the binding layer (*M*) and the deployment time (*t*) in a solution of known concentration (Fig. 4). The uptakes of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} by PSS-E6 DGT increased linearly with time up to 96 h ($r^2 = 0.987$ for Cu^{2+}, $r^2 = 0.995$ for Cd^{2+}, $r^2 = 0.983$ for Co^{2+}, and $r^2 = 0.991$ for Ni^{2+}). The Ψ of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} in the synthetic solution were 96.5 ± 2.21% (RSD% =

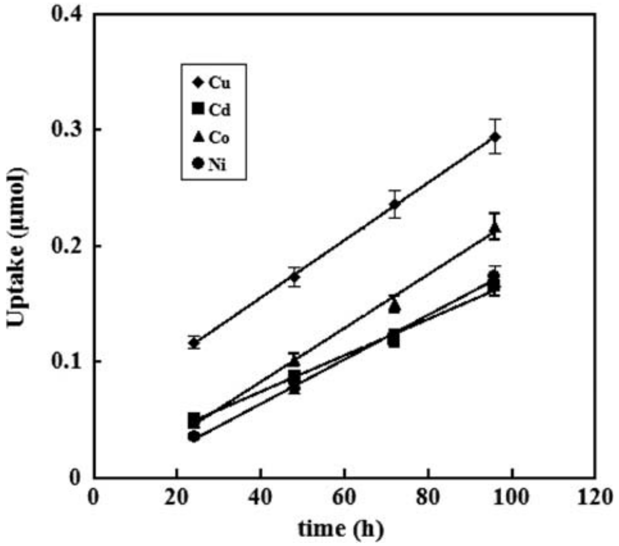

Fig. 4. The uptake of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} by PSS-E6 DGT in a synthetic solution: $Cu^{2+} = 0.1\,mg\,L^{-1}$, $Dm = 1.25\,\mu cm^2\,s^{-1}$; $Cd^{2+} = 0.1\,mg\,L^{-1}$, $Dm = 1.38\,\mu cm^2\,s^{-1}$; $Co^{2+} = 0.1\,mg\,L^{-1}$, $Dm = 1.08\,\mu cm^2\,s^{-1}$; and $Ni^{2+} = 0.1\,mg\,L^{-1}$, $Dm = 0.92\,\mu cm^2\,s^{-1}$. $\Delta g = 85\,\mu m$, $A = 3.14\,cm^2$, temperature = 20℃.

Table 2
The measurements of DGT-labile Cu^{2+}, Cd^{2+} Co^{2+}, and Ni^{2+} by PSS-E6 DGT and PSS-7E4 DGT in spiked river water and spiked domestic wastewater ($n = 3$)

Metals	Spiked river water				Spiked domestic wastewater			
	PSS-E6 DGT		PSS-7E4 DGT		PSS-E6 DGT		PSS-7E4 DGT	
	Ψ (%)	RSD%	Ψ (%)	RSD%	Ψ (%)	RSD%	Ψ (%)	RSD%
Cu^{2+}	26.01±2.59	4.01	26.91±2.82	4.23	10.35±1.29	5.01	9.76±1.17	4.81
Cd^{2+}	42.96±2.56	2.12	40.88±3.04	3.20	20.31±1.25	2.48	19.36±1.49	3.10
Co^{2+}	16.41±1.66	4.11	14.83±1.84	5.01	8.04±0.89	4.51	7.65±0.92	4.82
Ni^{2+}	18.24±1.96	4.32	16.65±1.83	4.43	8.86±0.98	4.47	7.83±1.03	5.30

3.28%), 97.5 ± 1.45% (RSD% = 3.62%), 96.7 ± 3.11% (RSD % = 4.19%), and 95.6 ± 2.86% (RSD% = 3.85%), respectively. The results indicated that PSS-E6 DGT could measured accurately Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} in synthetic river water and meet the requirements of DGT binding phase [31].

Ψ of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} in the spiked Ling river and spiked domestic wastewater are shown in Table 2. The measurement results of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} using the two DGT devices (PSS-E6 DGT and PSS-7E4 DGT) were no significant deferent with t test both in the spiked Ling river ($t = 1.00 < t_{0.95,4} = 2.78$ for Cu^{2+}, $t = 2.26 < t_{0.95,4} = 2.78$ for Cd^{2+}, $t = 2.72 < t_{0.95,4} = 2.78$ for Co^{2+}, and $t = 2.54 < t_{0.95,4} = 2.78$ for Ni^{2+}) and in the spiked domestic wastewater ($t = 1.48 < t_{0.95,4} = 2.78$ for Cu^{2+}, $t = 2.10 < t_{0.95,4} = 2.78$ for Cd^{2+}, $t = 1.31 < t_{0.95,4} = 2.78$ for Co^{2+}, and $t = 2.37 < t_{0.95,4} = 2.78$ for Ni^{2+}). However, Ψ of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} in the spiked Ling river and spiked domestic wastewater were much lower than those in the synthetic river water, and Ψ of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} in the spiked domestic wastewater were also much lower than those in the spiked Ling river. This was because of the presence of DOC which would have complexed a significant fraction of the added metal ions [16], and higher DOC ($44.34\,\mathrm{mg\,C\,L^{-1}}$) in the spiked domestic wastewater made Ψ of Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} much lower than those in the spiked Ling river ($10.30\,\mathrm{mg\,C\,L^{-1}}$).

4. Conclusions

The PSS-E6 DGT could measure accurately Cu^{2+}, Cd^{2+}, Co^{2+}, and Ni^{2+} in synthetic solutions. There were no difference between the speciation measurements of PSS-E6 DGT and PSS 7E4 DGT for above heavy metals in spiked Ling river water (Jinzhou, China) and spiked domestic wastewater (Jinzhou, China). PSS-E6 is a green and environment-friendly binding phase of DGT with the lower pretreatment depletion rate, lower cost, and lower pollution. It is feasible to use PSS-E6 instead of PSS 7E4 as the binding phase of liquid-type DGT device. The *in situ* measurements of heavy metals with PSS-E6 DGT in natural waters or wastewaters will be further investigated further in subsequent papers.

Acknowledgment

This study was supported by a grant from Engineering and Technology Research Center of Food Preservation, Processing and Safety Control of Liaoning Province, and Food Safety Key Lab of Liaoning Province (LNSAKF2011038).

References

[1] W. Davison, H. Zhang, *In situ* speciation measurements of trace components in natural waters using thin-film gels, Nature 367 (1994) 546–548.

[2] H. Zhang, W. Davison, Performance characteristics of diffusion gradients in thin films for the *in situ* measurement of trace metals in aqueous solution, Anal. Chem. 67 (1995) 3391–3400.

[3] M.C.A.-D.L. Torre, P.-Y. Beaulieu, A. Tessier, *In situ* measurement of trace metals in lakewater using the dialysis and DGT techniques, Anal. Chim. Acta 418 (2000) 53–68.

[4] N. Odzak, D. Kistler, H.B. Xue, *In situ* trace metal speciation in a eutrophic lake using the technique of diffusion gradients in thin films (DGT), Aquat. Sci. 64 (2002) 292–299.

[5] W. Li, F. Wang, W. Zhang, D. Evans, Measurement of stable and radioactive cesium in natural waters by the diffusive gradients in thin films technique with new selective binding phases, Anal. Chem. 81 (2009) 5889–5895.

[6] R.J.K. Dunn, P.R. Teasdale, J. Warnken, M.A. Jordan, J.M. Arthur, Evaluation of the *in situ*, time-integrated DGT technique by monitoring changes in heavy metal concentrations in estuarine waters, Environ. Pollut. 148 (2007) 213–220.

[7] B. Nowack, S. Koehler, R.A. Schulin, Use of diffusive gradients in thin films (DGT) in undisturbed field soils, Environ. Sci. Technol. 38 (2004) 1133–1138.

[8] T. Huynh, H. Zhang, W. Laidlaw, B. Singh, A. Baker, Plant-induced changes in the bioavailability of heavy metals in soil and biosolids assessed by DGT measurements, J. Soil Sediment. 10 (2010) 1131–1141.

[9] J.L. Roulier, S. Belaud, M. Coquery, Comparison of dynamic mobilization of Co, Cd and Pb in sediments using DGT and metal mobility assessed by sequential extraction, Chemosphere 79 (2010) 839–843.

[10] S. Tankere-Muller, H. Zhang, W. Davison, N. Finke, O. Larsen, H. Stahl, R.N. Glud, Fine scale remobilisation of Fe, Mn, Co., Ni, Cu and Cd in contaminated marine sediment, Mar. Chem. 106 (2007) 192–207.

[11] J. Sondergaard, *In situ* measurements of labile Al and Mn in acid mine drainage using diffusive gradients in thin films, Anal. Chem. 79 (2007) 6419–6423.

[12] T. Yapici, I.I. Fasfous, J. Murimboh, C.L. Chakrabarti, Investigation of DGT as a metal speciation technique for municipal wastes and aqueous mine effluents, Anal. Chim. Acta 622 (2008) 70–76.

[13] A. Díaz, R. Arnedo, R. Céspedes-Sánchez, R. Devesa, J. Martin-Alonso, Monitoring of (bio)available labile metal fraction in a drinking water treatment plant by diffusive gradients in thin films, Environ. Monit. Assess. 184 (2012) 539–548.

[14] A.J. Peters, H. Zhang, W. Davison, Investigation of the application of DGT devices for measurement of trace metals in low ionic strength fresh waters, Anal. Chim. Acta 478 (2003) 237–244.

[15] W. Li, P.R. Teasdale, S. Zhang, R. John, H. Zhao, Application of a poly(4-styrenesulfonate) liquid binding layer for measurement of Cu^{2+} and Cd^{2+} with the diffusive gradients in thin-films technique, Anal. Chem. 75(11) (2003) 2578–2583.

[16] W. Li, H. Zhao, P.R. Teasdale et al., Trace metal speciation measurements in waters by the liquid binding phase DGT device, Talanta 67 (2005) 571–578.

[17] H.-T. Fan, Y.-Q. Bian, D.-P. Sui, G.-F. Tong, T. Sun, Measurement of free copper (II) ions in water samples with polyvinyl alcohol as a binding phase in diffusive gradients in thin-films, Anal. Sci. 25 (2009) 1345–1349.

[18] H.-T. Fan, T. Sun, W. Li, D.-P. Sui, S. Jin, X.-J. Lian, Sodium polyacrylate as a binding agent in diffusive gradients in thin-films technique for the measurement of Cu^{2+} and Cd^{2+} in waters, Talanta 79 (2009) 1228–1232.

[19] H. Chen, J. Dong, Y.-X. Niu, T. Sun, Determination of Ni^{2+} in waters with sodium polyacrylate as a binding phase in diffusive gradients in thin-films, Chem. Res. Chinese U. 27 (2011) 703–707.

[20] L.Y. Chang, W. Davison, H. Zhang, M. Kelly, Performance characteristics for the measurement of Cs and Sr by diffusive gradients in thin films (DGT), Anal. Chim. Acta 368 (1998) 243–253.

[21] H. Zhang, W. Davison, Diffusional characteristic of hydrogels used in DGT and DET techniques, Anal. Chim. Acta 398 (1999) 329–340.

[22] S. Armenta, S. Garrigues, M. de la Guardia, Green analytical chemistry, Trends Anal. Chem. 27 (2008) 497–511.

[23] H. Zhang, W. Davison, Direct *in situ* measurements of labile inorganic and organically bound metal species in synthetic solutions and natural waters using diffusive gradients in thin films, Anal. Chem. 72 (2000) 4447–4457.

[24] H. Chen, T. Sun, D.-P. Sui, J. Dong, Effective concentration difference model to study the effect of various factors on the effective diffusion coefficient in the dialysis membrane, Anal. Chim. Acta 698 (2011) 27–35.

[25] H.-T. Fan, T. Sun, Selective removal of iron from aqueous solution using ion imprinted cyanato-functionalized silica gel sorbents, Sep. Sci. Technol. 47 (2012) 1–6.

[26] W.W. Bennett, P.R. Teasdale, J.G. Panther, D.T. Welsh, D.F. Jolley, Speciation of dissolved inorganic arsenic by diffusive gradients in thin films: selective binding of As^{III} by 3-mercaptopropyl-functionalized silica gel, Anal. Chem. 83 (2011) 8293–8299.

[27] J.H. Chen, H. Lin, Z.H. Luo, Y.S. He, G.P. Li, Cu(II)-imprinted porous film adsorbent Cu-PVA-SA has high uptake capacity for removal of Cu(II) ions from aqueous solution, Desalination 277 (2011) 265–273.

[28] H.-T. Fan, T. Sun, H.-B. Xu, Y.-J. Yang, Q. Tang, Y. Sun, Removal of arsenic (V) from aqueous solutions using 3-[2-(2-aminoethylamino)ethylamino]propyl-trimethoxysilane functionalized silica gel adsorbent, Desalination 278 (2011) 238–243.

[29] J.G. Panther, K.P. Stillwell, K.J. Powell, A.J. Downard, Perfluorosulfonated ionomer-modified diffusive gradients in thin films: Tool for inorganic arsenic speciation analysis, Anal. Chem. 80 (2008) 9806–9811.

[30] J.G. Panther, W.W. Bennett, P.R. Teasdale, D.T. Welsh, H. Zhao, DGT measurement of dissolved aluminum species in waters: Comparing Chelex-100 and titanium dioxide-based adsorbents, Environ. Sci. Technol. 46 (2012) 2267–2275.

[31] W. Li, H. Zhao, P.R. Teasdale et al., Preparation and characterisation of a poly (acrylamidoglycolicacid-co-acrylamide) hydrogel for selective binding of Cu^{2+} and application to diffusive gradients in thin films measurements, Polymer 43 (2002) 4803–4809.