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Application of poly (ethyleneimine) solution as a binding agent in DGT technique for measurement of heavy metals in water

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ABSTRACT

A 0.050 mol L^{-1} solution of poly (ethyleneimine) (PEI), had been used as a novel binding agent of diffusive gradients in thin-films (DGT) technique (PEI-DGT) for measuring the concentrations of labile Cu^{2+}, Cd^{2+} and Pb^{2+} in waters. The binding capacities of the PEI-DGT for Cu^{2+}, Cd^{2+} and Pb^{2+} were 11.8, 10.2 and 10.6 μmol L^{-1}, respectively. The performance of PEI-DGT was independence of pH in the range of 4–8 and ionic strength in the range from 1×10^{-4} to 0.1 mol L^{-1} (as $NaNO_3$). PEI-DGT could measure $104.7\pm5.2\%$ of the total concentration of Cd^{2+} (0.500 mg L^{-1}), $95.2\pm4.3\%$ of the total Cu^{2+} (0.500 mg L^{-1}) and $99.2\pm3.4\%$ of the total Pb^{2+} (0.500 mg L^{-1}) in synthetic solution. Effects of the ligands on the measurement of labile metals were also investigated in synthetic solutions containing the various concentrations of EDTA and humic acid. In EDTA solution, the concentrations of labile metals measured by PEI-DGT showed good agreement with the theoretical concentrations of free metal ions. In humic acid solution, the concentrations of labile metals measured by PEI-DGT decreased with the increase of the concentrations of humic acid. Several DGT devices with various binding agents, including PEI, sodium polyacrylate and poly(4-styrenesulfonate) solution, were used for the measurement of labile fractions of Cu^{2+}, Cd^{2+} and Pb^{2+} in the spiked waters and in mine wastewaters. The results showed that the concentrations of labile metal measured by DGT devices with different binding agents could be significantly different, indicating that the labile fractions of metals were dependent on the binding strength of the binding agents with metals. By choosing binding agents, the useful information on the speciation and bioavailability of the analytes can be provided.

1. Introduction

Most heavy metal ions are detrimental to the environment due to their nonbiodegradable and persistent nature when these metals exist in or are discharged into various water resources [1,2]. Heavy metals can be accumulated in living tissues through the food chain and present a threat to human health due to their toxic or carcinogenic [3,4]. With respect to its toxicity or availability, it is generally recognized that the ecotoxicological significance of heavy metals can be determined by its physicochemical forms in environment rather than by the total dissolved concentrations [5–7].

There is a clear need for rapid, effective and low-cost integrated methods which can directly monitor the fate and concentrations of pollutants in the environment, and evaluate effects and hazards of pollutants for the environment [8,9]. Diffusive gradients in thin-films (DGT) technique which has been proposed by Davison and Zhang has become one of the most promising in situ sampling and trace metal measurement techniques in natural waters, soils and sediments [10–12]. DGT has been used as a tool for the measurement of labile metals species including free metal ions, inorganic complexes and fraction of organic complexes [13]. In the first DGT device, the metal species are diffused across a diffusion layer comprising a polyacrylamide hydrogel which allows solute species below a size threshold to pass, and then trapped in a binding layer comprising a chelex-100 resin in its Na-form which can irreversibly bind the soluble analytes diffused through diffusion layer and make the concentrations of analytes effectively zero at the interface between diffusion layer and binding layer [13].

With the development of DGT technique, Li et al. reported a new type DGT device which uses a cellulose acetate dialysis membrane as the diffusion layer and 0.02 mol L^{-1} solution of poly (4-styrenesulfonate) as the binding layer for the measurement of copper and cadmium in waters [14,15]. The homogeneous mobile liquid binding agent provides the excellent contact between the binding layer and the diffusive layer [14,15]. The advantages of the new DGT device include a theoretically ideal mass transport and accumulation, good reproducibility, a well-defined reproducible

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diffusive layer and no need for elution corrections [14,15]. More recently, several liquid binding agents (such as sodium polyacrylate solution [16], polyvinyl alcohol solution [17] and thiol-polyvinyl alcohol solution [18]) have been developed. Some researches suggest that the DGT labile metal fractions should be dependent on binding strength of the binding agent with analytes and it is possible to use these different DGT devices to measure the speciation and bioavailability of metals in the environment by choosing binding agents [19–21]. However, only a few researches on the liquid binding agents with different chelating functional groups have been reported [16–18].

Poly (ethyleneimine) (PEI) is a typical alkaline water-soluble functional macromolecular which contains a large quantity of N-donor atoms and can react with heavy metals [22–25]. The molecules of commercial PEI often have branch chains (branched PEI), and contain primary, secondary and ternary amino groups in a ratio of approximately1:2:1 [26].

In this study, we investigated the feasibility of PEI solution as a liquid binding agent of DGT device (PEI-DGT) for measuring copper, cadmium and lead in waters. The influence of a range of pH (2–9) and electrolyte concentrations (0.0001–0.7 mol L^{-1} $NaNO_3$) on PEI-DGT were also investigated. The validation of PEI-DGT device was evaluated under laboratory conditions and then deployed in various waters. Effects of ligands (EDTA and humic acid) on the concentrations of labile metals were tested. Finally DGT devices with different binding agents for determining DGT labile fractions of heavy metals were investigated.

2. Experimental

2.1. Pretreatment

Cellulose acetate dialysis membranes (12, 000 MWCO, <5 nm pore size, USA) were pretreated according to the procedures recommended [14]. The PEI had an average M_w 60,000 (Sigma, USA). A 10% solution of PEI was transferred into a cellulose acetate dialysis bag which was placed in deionized water for 10 days with the water frequently replenished. The PEI with lower molecular weight which can pass through the dialysis membrane was removed after the process. The solution of PEI still in the bag was then filtered with a cellulose nitrate filter membrane with 0.45 μm pore size to remove any undissolved particles. After purification, the concentration of amino groups of PEI was determined by acid–base titration [27,28] and a 0.10 mol L^{-1} stock solution of PEI (the concentration of monomer) was prepared.

2.2. The measurements of diffusion coefficients

The diffusion coefficients, D_m, of Cu^{2+}, Cd^{2+} and Pb^{2+} through the dialysis membrane in synthetic solutions (synthetic lake water and synthetic industrial wastewater) were determined using a specially designed diffusion cell as described by Davison [29,30]. The cell comprised two compartments, each with an interconnecting 2 cm diameter opening. A 3 cm diameter disc of dialysis membrane was placed on the opening. The dialysis membrane of known thickness ($\Delta g = 50$ μm) provided the only connection for mass transport between two compartments. One compartment (A, source) contained 10 mmol L^{-1} of heavy metal ions in 75 mL of synthetic solutions as the carrier solution. The other compartment (B, receiving) was filled with synthetic solutions with an experimentally optimized concentration of binding agents in a 75 mL solution of the same matrix. The solutions of binding agents were capable of reducing the interfacial free ion concentration to zero over the deployment time used; therefore a gradient of diffusive fluxes was maintained. Both compartments were stirred continuously using an overhead stirrer. Samples were taken from both compartments and measured by An AA-6300c flame atomic absorption spectrometer (FAAS, Shimadzu Corporation, Japan) at 20 min intervals up to 120 min. In addition, average concentration at the sampling intervals was used to correct the changes of concentrations in the source compartment [14].

2.3. Optimization of PEI concentration

The opening of the polyethylene tube containing purified binding agent solution was covered smoothly and sealed tightly with a pretreated cellulose acetate dialysis membrane of 50 μm thickness. The devices were deployed with membrane side facing down to ensure the contact of membrane and binding agent solution.

To estimate the optimal concentration of PEI solution, the DGT devices with various concentrations of PEI solutions (0.010, 0.020 0.030, 0.040, 0.050, 0.060 and 0.070 mol L^{-1}) were immersed in the solutions which contained 1 mmol L^{-1} of Cd^{2+}, Cu^{2+} or Pb^{2+} (individually) at pH 6 for 10 days with stirring. The sufficient time can make the binding agent saturate.

2.4. The binding Properties of PEI-DGT

The effect of pH on the binding of PEI-DGT for metals was assessed in solutions containing 0.500 mg L^{-1} metal ions with varying pH (2–9 in eight increments). The pH values of solutions were adjusted using 0.1 mol L^{-1} HCl or NaOH solution. The influence of various electrolyte concentrations on PEI-DGT responses was carried out in solutions containing various concentrations of $NaNO_3$ or NaCl ranging from 1.0×10^{-4} to 0.7 mol L^{-1} at pH 6. The effects of various concentrations of Ca^{2+} and Mg^{2+} on PEI-DGT responses were investigated in solutions containing various concentrations of $CaCl_2$ or $MgCl_2$ ranging from 1×10^{-4} to 0.2 mol L^{-1} at pH 6.

2.5. DGT performance

In order to investigate the validity of PEI-DGT for the measurement of Cd^{2+}, Cu^{2+} and Pb^{2+}, the devices were carried out in a synthetic solution containing 0.500 mg L^{-1} of metals according to a composition described by Li [14]. The assembly was deployed in a well-stirred solution for different time periods, up to 120 h. At each sampling time, three of DGT units were taken from the solution, and the amounts of metals were measured by FAAS.

2.6. Influence of ligands on the measurement of labile metals fractions

Metals species were detected by the PEI-DGT in synthetic solutions (deionized water and 0.01 mol L^{-1} $NaNO_3$) at pH 6 with additions of EDTA at molar ratios of 2.0:1.0, 1.0:1.0 and 1.0:2.0 with the metal ions, and humic acid (HA, molecular weight 13,000, Aldrich) at the mass ratios of 1:8, 1:15 and 1:30 with the metal ions [31].

2.7. Measurement of labile metals in spiked water

To measure labile metals in water, PEI-DGT devices were deployed with 24 h intervals from 0 to 120 h in 50 L of three kinds of spiked waters with 0.500 mg L^{-1} Cu^{2+}, Cd^{2+} and Pb^{2+}, including a river water collected from the surface of Hun River (Shenyang, China) on May 12, 2012, a artificial lake water collected from the surface of Nan lake (Shenyang, China) on May 30, 2012 and a treated industrial wastewater collected from the surface of local industrial wastewater canal on July 12, 2012. The DGT devices

Table 1
Major cation concentrations, dissolved organic carbon and pH value of the Hun river water, Nan lake water, treated wastewater and untreated mine wastewater[a].

Measured parameters	Hun river water	Nan lake water	Treated wastewater	Untreated mine wastewater
$[K^+]$/mg L^{-1}	0.20 ± 0.02	0.12 ± 0.02	0.23 ± 0.04	0.18 ± 0.02
$[Na^+]$/mg L^{-1}	1.5 ± 0.1	1.7 ± 0.2	3.4 ± 0.3	2.2 ± 0.2
$[Ca^{2+}]$/mg L^{-1}	1.4 ± 0.1	1.1 ± 0.1	2.7 ± 0.2	3.2 ± 0.2
$[Mg^{2+}]$/mg L^{-1}	0.59 ± 0.04	0.64 ± 0.06	0.97 ± 0.08	0.43 ± 0.05
$[Cu^{2+}]$/mg L^{-1}	N.D.[b]	N.D.	N.D.	0.32
$[Cd^{2+}]$/mg L^{-1}	N.D.	N.D.	N.D.	0.22
$[Pb^{2+}]$/mg L^{-1}	N.D.	N.D.	N.D.	5.58
[DOC]/mg C L^{-1}	7.8 ± 0.5	11.6 ± 0.8	35.8 ± 1.5	19.7 ± 1.1
pH	7.4 ± 0.2	7.9 ± 0.1	7.8 ± 0.1	5.6 ± 0.2

[a] Major cation concentrations were measured by FAAS after appropriate dilution. Data presented here are the mean values of three replicates.

[b] N.D. means not detected.

with different liquid binding agents containing different chelating functional groups, such as PA and PSS solution were also deployed in above waters at the same time.

2.8. Deployment of PEI-DGT in mine wastewater

The performance of PEI-DGT for measuring labile Cu^{2+}, Cd^{2+} and Pb^{2+} was tested by applying it to a filtered untreated mine wastewater which contained the high concentrations of above ions and was collected from the surface of wastewater canal (Nanpiao, Liaoning, China) on September 25, 2012. PEI-DGT devices were deployed in the filtered mine wastewater for 24-h interval over a 5-day period.

60 L of each above water samples was immediately pre-filtered under vacuum through a glass microfibre filter (Whatman GF/B) in the laboratory before filtering through a 0.45 μm cellulose nitrate membrane (Whatman). The concentrations of major cation, dissolved organic carbon (DOC) and pH of collected waters were described in Table 1. The concentration of DOC was measured using a TOC analyzer (Dohrmanne DC-190, GE, USA). In order to avoid the effect of water-insoluble substances in water samples on the DGT measurements, then and to permit a more direct comparison with other DGT device, the filtered water samples were used for the performance of DGT [32]. DGT assemblies were copiously rinsed with deionized water immediately after retrieval. The volume of solution was sufficiently large (50 L) to avoid a significant depletion of metal concentration. During the experiment, the concentration of metals in the test solution was controlled and the average concentrations of metals at the sampling intervals were used to correct the changes of metal concentration. Unless stated all the experiments were performed in triplicate and stirred by an aquarium pump with a rate of 10 L min^{-1} at room temperature [33].

In addition, all the reagents were of analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) unless noted otherwise. Solutions were prepared with deionized water. Glassware was acid-washed before use.

3. Results and discussion

3.1. The diffusion coefficients of metal ions

DGT directly measured a flux, namely, the rate of supply from solution depended on the kinetics of solution exchange. Here, an experimentally determined value of the diffusion coefficient, D_m, was measured according to the procedure described above. The diffusion coefficients were calculated using quantitative equation of DGT (Eq. (1)) as the procedures recommended [14].

$$D_m = M\Delta g / ACt \tag{1}$$

The mass of ions, M, that is accumulated in the binding agent from a solution with analyte concentration (C), after passing through a diffusive layer of area (A) and thickness (Δg), over a deployment time (t).

Diffusion coefficients for Cu^{2+}, Cd^{2+} and Pb^{2+} in the dialysis membrane are determined from the uptake of metals with time and rearrangement of Eq. (1). The values measured of the diffusion coefficients were obtained (D_m=1.59 μcm^2 s^{-1} for Cu^{2+}, D_m=3.01 μcm^2 s^{-1} for Cd^{2+} and D_m=2.23 μcm^2 s^{-1} for Pb^{2+}). The lower values for dialysis membrane compared with polyacrylamide hydrogel (6.25 μcm^2 s^{-1} for Cu^{2+}, 5.36 μcm^2 s^{-1} for Cd^{2+} and 9.91 μcm^2 s^{-1} for Pb^{2+}) [34] were due to a lower porosity and lower water content of the dialysis membrane (ca. 50%) than that of the polyacrylamide hydrogel (ca. 95%) [13].

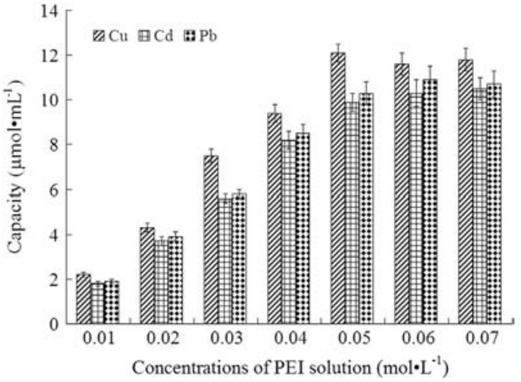

Fig. 1. Optimal concentration of PEI solution in well-stirred solutions containing 1 mmol L^{-1} of Cd^{2+}, Cu^{2+} or Pb^{2+} (individually) at pH 6 for 10 days at 25 °C. Mean values and ranges (bars) of triplicate measurements are given.

3.2. Optimal concentration of PEI solution

To investigate the optimal concentration of PEI solution for the binding agent, the DGT devices with various concentrations (0.010–0.070 mol L^{-1}) of PEI solution were deployed in a well-stirred solution of Cu^{2+}, Cd^{2+} and Pb^{2+} ions. The mass of metals accumulated by PEI solution is plotted against the concentrations of PEI solution in Fig. 1. The mass of metals accumulated increased with the increase of concentration of PEI solution to 0.050 mol L^{-1} and then reached a plateau in the range from 0.050 to 0.070 mol L^{-1}. Due to the high concentrations of PEI solution with strong alkaline, hydroxides of metals were easy to form and hinder the diffusion of the ions. So the 0.050 mol L^{-1} PEI solution was used as the binding agent of DGT technique. The binding capacities of PEI-DGT for Cu^{2+}, Cd^{2+} and Pb^{2+} were 11.8, 10.2 and 10.6 μmol mL^{-1}, respectively.

3.3. Effect of pH

The pH of the solution affects the speciation and solubility of transition metals and the charge of the binding functional groups of PEI. The ratio of the concentrations measured by the DGT technique (C_{DGT}) to the concentrations measured directly by FAAS (C_{FAAS}) in solution is plotted versus pH in Fig. 2. Ratios of 1 were obtained for the pH ranges from 4 to 8 for Cu^{2+}, Cd^{2+} and Pb^{2+}. The low ratios were observed when the solution pH was below 4. This was because the protonated forms of amino groups were much less capable of forming the complexes than the neutral form [25]. The ratios decreased at high pH due to a significant change in the speciation of the metals from the free metal ion to the metal hydroxide which was usually much less soluble [35]. The pH range of solution for sampling Cu^{2+}, Cd^{2+} and Pb^{2+} by PEI-DGT was 4–8. This pH range was suitable for PEI-DGT applications in natural waters.

3.4. Effect of ionic strength

Influence of ionic strength on the binding ability of PEI-DGT was studied since natural waters contain a range of major cations and anions (shown in Fig. 3). The ratios of C_{DGT}/C_{FAAS} by PEI-DGT were close 1 in the ranges of $NaNO_3$ concentration from 1×10^{-4} to 0.1 mol L^{-1} and decreased slightly at $NaNO_3$ concentration of 0.7 mol L^{-1} (Fig. 3a). Similar experiments were performed using NaCl to adjust the ionic strength of solutions at pH 6 from 1×10^{-4} to 0.1 mol L^{-1} (Fig. 3b). When NaCl concentration was below 0.1 mol L^{-1}, the ratio of C_{DGT}/C_{FAAS} was close to 1. At 0.7 mol L^{-1} solution of NaCl, the lower value was obtained. The measurements of PEI-DGT for the metals were unaffected by adding $NaNO_3$ or NaCl in range of 1×10^{-4}–0.1 mol L^{-1}. The results showed that the measurement of PEI-DGT was independent of ionic strength in range of 1×10^{-4}–0.1 mol L^{-1}.

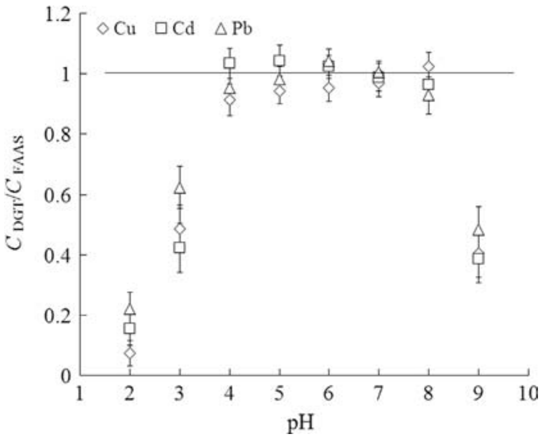

Fig. 2. Effect of pH on performance of PEI-DGT for the measurement of Cu^{2+} (◇) Cd^{2+} (□) and Pb^{2+} (△) in well-stirred synthetic solutions containing 0.500 mg L^{-1} of Cd^{2+}, Cu^{2+} and Pb^{2+} for 120 h with a interval of 24 h at 25 °C. Mean values and ranges (bars) of triplicate measurements are given.

3.5. Effect of Ca^{2+} and Mg^{2+}

To assess the effect of Ca^{2+} and Mg^2 on the ratios of C_{DGT}/C_{FAAS}, PEI-DGT assemblies were immersed in solutions containing various concentrations of Ca^{2+} and Mg^{2+} ranging from 1×10^{-4} to 0.2 mol L^{-1}. The ratios of C_{DGT}/C_{FAAS} are plotted against the concentrations of Ca^{2+} or Mg^2 in Fig. 4. The ratios of 1 within the concentrations of Ca^{2+} or Mg^{2+} in the range of 1×10^{-4}–5×10^{-2} mol L^{-1} were obtained, while the values were lower when $[Ca^{2+}]$ or $[Mg^{2+}] > 0.1$ mol L^{-1}. The results showed that the PEI-DGT response was independent of concentrations of Ca^{2+} or Mg^{2+} in range of 1×10^{-4}–5×10^{-2} mol L^{-1}.

3.6. Validation of PEI-DGT

The PEI-DGT are validated by testing the relationship between the mass of analyte accumulated in the binding layer (M) and the deployment time (t) with a solution of known concentration. The mass of metals, M, that is accumulated in the binding agent from a solution with analyte concentration (C), after passing through a diffusive layer of area (A) and thickness (Δg), over a deployment time (t), can be predicted by the DGT equation

$$M = D_m ACt/\Delta g \tag{2}$$

The validation of the DGT measurement is assessed in two ways [36]. Firstly, from Eq. (2), a linear relationship is expected between measured mass, M and deployment time, t, if the device acts according to theory. Secondly, the ratios (> 90%) of the concentrations measured by the DGT technique to the concentrations measured directly by FAAS are desirable with DGT [36].

Fig. 5 shows the mass taken by the PEI-DGT at different time intervals. The uptake of Cu^{2+}, Cd^{2+} and Pb^{2+} increased linearly with time up to 120 h ($r^2 = 0.9805$ for Cu^{2+}, $r^2 = 0.9972$ for Cd^{2+} and $r^2 = 0.9908$ for Pb^{2+}). PEI-DGT measured $104.7 \pm 5.2\%$

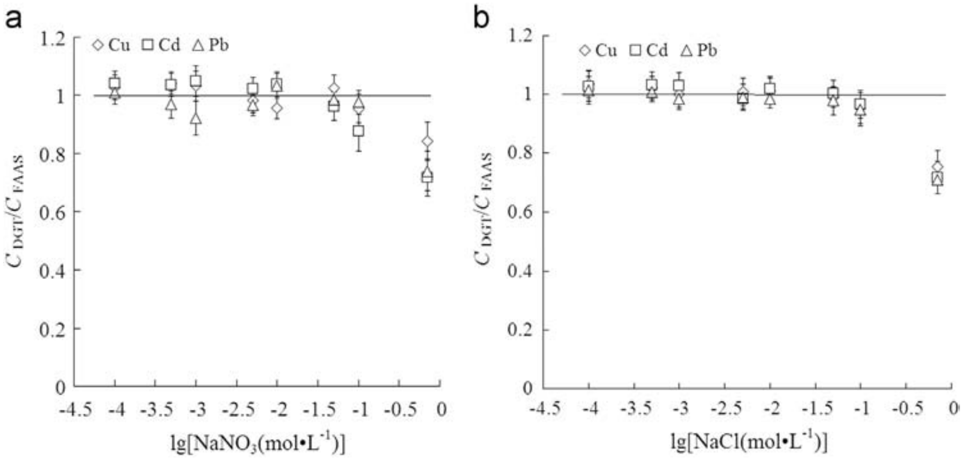

Fig. 3. Effect of ionic strengths (presented as the concentrations of $NaNO_3$ (a) and NaCl (b)) on performance of PEI-DGT for the measurement of Cu^{2+} (◇) Cd^{2+} (□) and Pb^{2+} (△) in well-stirred synthetic solutions containing 0.500 mg L^{-1} of Cd^{2+}, Cu^{2+} and Pb^{2+} with variously added $NaNO_3$ or NaCl at pH 6 for 120 h with a interval of 24 h at 25 °C. Mean values and ranges (bars) of triplicate measurements are given.

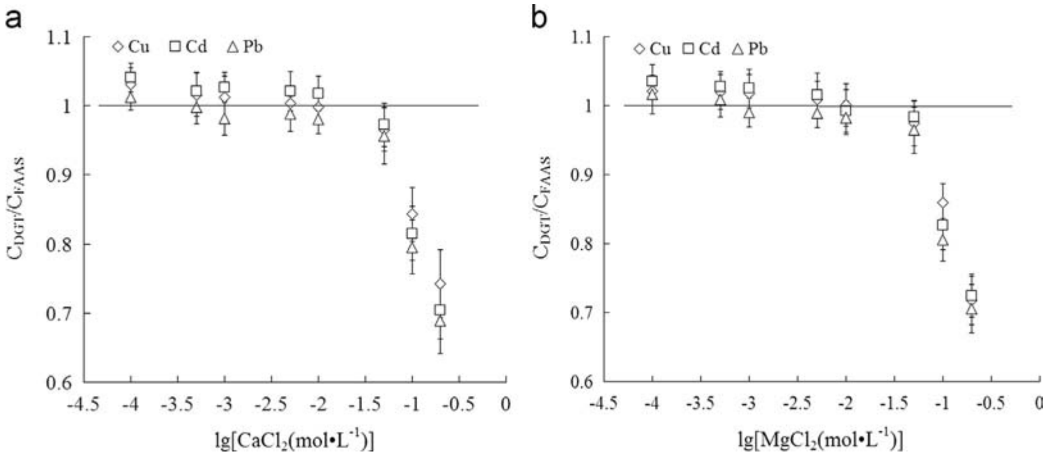

Fig. 4. Effect of Ca^{2+} (a) and Mg^{2+} (b) on performance of PEI-DGT for the measurement of Cu^{2+} (◇) Cd^{2+} (□) and Pb^{2+} (△) in well-stirred synthetic solutions containing 0.500 mg L^{-1} of Cd^{2+}, Cu^{2+} and Pb^{2+} with variously added $CaCl_2$ or $MgCl_2$ at pH 6 for 120 h with a interval of 24 h at 25 °C. Mean values and ranges (bars) of triplicate measurements are given.

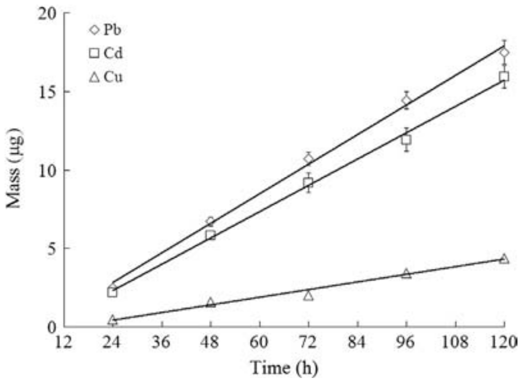

Fig. 5. The uptake of Cu^{2+}, Cd^{2+} and Pb^{2+} (as the measured mass on PEI) by DGT units (diffusive layer with surface area of 3.14 $cm^2$and thickness of 50 μm) vs. time. The experiments were carried out in well-stirred synthetic solution containing 0.500 mg L^{-1} of Cd^{2+}, Cu^{2+} and Pb^{2+} at pH 6 for 120 h with a interval of 24 h at 25 °C. Solid lines are the theoretical lines calculated by Eq. (2). Mean values and ranges (bars) of triplicate measurements are given.

(mean ± standard deviation (SD)) of the total concentration of Cd^{2+}, 95.2 ± 4.3% of the total Cu^{2+} and 99.2 ± 3.4% of the total Pb^{2+} in synthetic solution. These results indicated that the configuration of PEI-DGT was close to an ideal as described by the DGT equation, and confirmed that the 0.050 mol L^{-1} PEI solution was suitable as a binding agent of DGT technique for the measurement of Cu^{2+}, Cd^{2+} and Pb^{2+} in aqueous solution.

3.7. *Effect of ligands*

3.7.1. *Labile metals in the presence of EDTA*

EDTA is a strong chelating agent which can form very stable and soluble complexes with many metal ions. It is a common synthetic organic ligand often found in natural waters due to its widespread use and resistance to degradation [37]. In order to evaluate the influence of EDTA on the measurement of labile metals, PEI-DGT devices were deployed in synthetic solution with the different molar ratios of metal ions/EDTA. The theoretical concentration of free metal ions is effectively equal to the concentrations of metal ions minus the concentration of EDTA. From Table 2, it can be observed that the percentages of labile metals dramatically decreased with reducing of the molar ratios of metal ions/EDTA. It was found that the percentages values of 49.50 ± 2.84% for Cu^{2+}, 53.92 ± 4.12% for Cd^{2+}, and 52.45 ± 3.86% for Pb^{2+} were very close to the theoretical values for 2:1 M ratios of metals/EDTA, respectively. However, the percentages of labile metals were virtually zero at metal/EDTA ratios≤1. The drop of the percentages of labile metal by PEI-DGT was due to the increasing non-liability of the metal-EDTA complex. The results revealed that the concentrations of labile metals measured by PEI-DGT were in agreement with the theoretical concentrations of free ions and followed the same trend with the molar ratios of metals/EDTA varied. The complexes of EDTA with Cu^{2+}, Cd^{2+} and Pb^{2+} were inert for PEI-DGT.

3.7.2. *Labile metals in the presence of humic acid*

Humic acids (HA) which are the one of main components of natural organic matter in the environment are insoluble in water at acid condition and water-soluble at alkaline pH [38]. The concentration of metals was fixed at 0.50 mg L^{-1} and the mass of humic acid was changed from 4.0 to 7.5 to 15.0 mg L^{-1} in synthetic solution with 0.01 mol L^{-1} $NaNO_3$ in order to investigate the effect of HA on the measurement of labile metals. The percentages of labile metals were measured with PEI-DGT as a function of the different concentrations of HA at a fixed metals concentration (as shown in Table 2). For copper, the percentages of the DGT-labile Cu^{2+} dramatically dropped from 24.64 ± 4.24% to 14.69 ± 3.56% to 5.14 ± 2.11%. For cadmium, the percentages of the DGT-labile Cd^{2+} decreased from 32.88 ± 3.24% to 21.05 ± 3.12% to 10.18 ± 2.58%. For lead, the percentages of the DGT-labile Pb^{2+} decreased from 12.81 ± 2.12% to 8.51 ± 1.52% to 1.84 ± 1.12%. The results showed that the percentages of the labile metals decreased with increasing the concentration of humic acid due to the effect of the complexation of HA with metal ions. The speciation of metals plays a decisive role in the uptake of labile metals. The same results were reported by Dočekal et.al. [39]. The percentages of the labile Cd^{2+} were found to be higher for the Cd^{2+}–HA system than for the Pb^{2+}–HA and Cu^{2+}–HA systems due to the relatively weak binding strengths of Cd^{2+} with humic acid [40,41]. The conditional binding constant are in the order $Cu^{2+} > Pb^{2+} > Cd^{2+}$, and the conditional binding constant of Cd^{2+} is about one order of magnitude smaller than those of Pb^{2+} and Cu^{2+} [40,41]. The same trends have been described in the similar investigations [42]. Cu^{2+}–HA was found to be somewhat more labile than Pb^{2+}–HA due to the stronger complex ability of PEI with Cu^{2+} [43,44].

Table 2
The uptake percentages of labile metals by PEI-DGT in solutions containing EDTA and HA at different ratios.

Metal ions	C_M:C_{EDTA} (molar ratio)			C_M:C_{HA} (mass ratio)		
	2:1 (%)	1:1	1:2	1:8 (%)	1:15 (%)	1:30 (%)
Cu^{2+}	49.50 ± 2.84[a]	N.D.	N.D.	24.64 ± 4.24	14.69 ± 3.56	5.14 ± 2.11
Cd^{2+}	53.92 ± 4.12	N.D.	N.D.	32.88 ± 3.24	21.05 ± 3.12	10.18 ± 2.58
Pb^{2+}	52.45 ± 3.86	N.D.	N.D.	12.81 ± 2.12	8.51 ± 1.52	1.84 ± 1.12

[a] The uptake percentages of labile metals is defined as the DGT-labile metal concentration (C_{DGT}) divided by the total metal ion concentration (C_{FAAS}). Data presented here are the mean values of three replicates.

Table 3
The uptake percentages of labile metals by PEI-DGT, PA-DGT and PSS-DGT in spiked waters.

Samples	Percentages of labile metals by PEI-DGT (%)			Percentages of labile metals by PA-DGT (%)			Percentages of labile metals by PSS-DGT (%)		
	Cu^{2+}	Cd^{2+}	Pb^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}
Spiked river water	11.51 ± 1.21	24.98 ± 2.56	12.65 ± 1.42	7.24 ± 0.88	9.96 ± 1.02	–[a]	2.75 ± 0.58	8.32 ± 1.02	2.62 ± 0.56
Spiked lake water	8.69 ± 1.12	14.03 ± 1.58	9.23 ± 1.07	5.27 ± 0.56	7.35 ± 0.94	–	1.68 ± 0.42	3.94 ± 0.67	1.04 ± 0.45
Spiked treated wastewater	5.24 ± 1.81	7.99 ± 2.52	4.89 ± 2.01	3.58 ± 0.63	3.12 ± 0.68	–	0.63 ± 0.48	2.53 ± 0.89	0.22 ± 0.14

[a] PA-DGT cannot determine accurately the concentration of Pb^{2+} as the previous research reported [48]. Data presented here are the mean values of three replicates.

3.8. *Comparison of DGT devices with different binding agents for the measurement of labile metals*

In order to investigate the performance of DGT devices with the different liquid binding agents comprising various functional groups (amino groups for PEI, carboxyl groups for PA and sulfonic acid group for PSS) for the measurement of labile Cu^{2+}, Cd^{2+} and Pb^{2+}, each of the three DGT devices was deployed in various water samples to measure the concentrations of labile metals. Except for PA-DGT device which can not bind Pb^{2+} as previously reported [45], Table 3 shows the concentrations of labile metals measured by PEI-DGT, PA-DGT and PSS-DGT over the concentrations of total metals in different water samples at varying time intervals.

For copper, the percentages of labile Cu^{2+} by PEI-DGT, PA-DGT and PSS-DGT in the spiked river water were 11.51 ± 1.21%, 7.24 ± 0.88% and 2.75 ± 0.58%, respectively. The percentages of labile Cu^{2+} by three DGT devices in the spiked lake water were 8.69 ± 1.12%, 5.27 ± 0.56% and 1.68 ± 0.42%, respectively. The percentages of labile Cu^{2+} by the above DGT devices in the spiked treated wastewater were 5.24 ± 1.81%, 3.58 ± 0.63% and 0.63 ± 0.48%, respectively. For cadmium, the percentages of labile Cd^{2+} by the above DGT devices in the spiked river water were 24.98 ± 2.56%, 9.96 ± 1.02% and 8.32 ± 1.02%, respectively. The percentages of labile Cd^{2+} by three DGT devices in the spiked lake water were 14.03 ± 1.58%, 7.35 ± 0.94% and 3.94 ± 0.67%, respectively. The percentages of labile Cd^{2+} by the above DGT devices in the spiked treated wastewater were 7.99 ± 2.52%, 3.12 ± 0.68% and 2.53 ± 0.89%, respectively. For lead, the percentages of labile Pb^{2+} by PEI-DGT and PSS-DGT in the spiked river water were 12.65 ± 1.42%, and 2.62 ± 0.56%, respectively. The percentages of labile Pb^{2+} by two DGT devices in the spiked lake water were 9.23 ± 1.07% and 1.04 ± 0.45%, respectively. The percentages of labile Pb^{2+} by both DGT devices in the spiked treated wastewater were 4.89 ± 2.01% and 0.22 ± 0.14%, respectively. For all the metals investigated, the DGT results in the three kinds of spiked water showed the same trend. The results indicated that the concentrations of labile Pb^{2+}, Cu^{2+} and Cd^{2+} by the above DGT devices had a direct relationship with DOC in different spiked waters and decreased with the increase of the DOC concentration due to the complexation between DOC and the heavy metals [46,47]. Comparing the concentrations of labile Pb^{2+}, Cu^{2+} and Cd^{2+}, the results showed that the higher concentrations of labile Cd^{2+} were observed with respect to Pb^{2+} and Cu^{2+} in three water samples because the DOC-complexed species were generally more significant for Cu^{2+} and Pb^{2+} than for Cd^{2+} [48].

Table 4
The uptake percentages of labile metals by PEI-DGT, PA-DGT and PSS-DGT in mine waters.

DGT devices	Percentages of metal ions		
	Cu^{2+} (%)	Cd^{2+} (%)	Pb^{2+} (%)
PEI-DGT	8.99 ± 1.01	16.33 ± 2.02	51.62 ± 2.34
PA-DGT	6.12 ± 0.79	10.23 ± 0.84	–[a]
PSS-DGT	4.42 ± 0.42	6.54 ± 0.64	20.34 ± 2.16

[a] PA-DGT cannot determine accurately the concentration of Pb^{2+} as the previous research reported [48]. Data presented here are the mean values of three replicates.

3.9. *Application*

The DGT devices with different binding agents were used to measure the concentrations of labile Cu^{2+}, Cd^{2+} and Pb^{2+} in the untreated mine wastewater. As shown in Table 4, the DGT-labile fractions for Cu^{2+} (8.99 ± 1.01%, 6.12 ± 0.79% and 4.42 ± 0.42% of labile Cu^{2+} percentages for PEI-DGT, PA-DGT and PSS-DGT respectively), Cd^{2+} (16.33 ± 2.02%, 10.23 ± 0.84% and 6.54 ± 0.64% of labile Cd^{2+} percentages for PEI-DGT, PA-DGT and PSS-DGT respectively) and Pb^{2+} (51.62 ± 2.34% and 20.34 ± 2.16% of labile Pb^{2+} percentages for PEI-DGT and PSS-DGT respectively) by DGT devices with different binding agents were obtained in the untreated mine wastewater. The results indicated that the percentages of labile Cu^{2+}, Cd^{2+} and Pb^{2+} by PEI-DGT was higher in untreated mine wastewater in comparison with that by PA-DGT and PSS-DGT. The comparison showed that the binding agents were a key factor for the measurement of labile heavy metals. The difference of the concentrations measured by the DGT devices with different binding agents was commonly interpreted as the result of different reactivities of the free analyte ions and their complexes. The same results were also obtained by previous studies [49–51]. It is postulated that the combination deployments of different DGT devices in waters may provide useful information on the speciation and bioavailability of the analyte under various conditions, reflecting somewhat the interactions between metals species and biomolecular in biological environment with varying mechanisms [49–51].

4. Conclusions

The PEI solution had been successfully used as a binding agent for DGT application. This was confirmed by the linear response with the uptake mass vs. deployment time and 95–104% of the total concentrations of metals with uptake experiment of DGT technique. The binding capacities of PEI-DGT for Cu^{2+}, Cd^{2+} and Pb^{2+} were 11.8, 10.2 and 10.6 μmol mL^{-1}, respectively. PEI-DGT performance had been shown to be independent of pH (4–8), ionic strength in the range of $NaNO_3$ or NaCl concentration from 1×10^{-4} to 0.1 mol L^{-1}, and the concentrations of Ca^{2+} or Mg^{2+} in range of 1×10^{-4}–5×10^{-2} mol L^{-1}. The agreements between the concentration of labile metals measured by PEI-DGT and the values of theoretical calculations showed that PEI-DGT measured only the concentrations free metal ion in the EDTA solutions and the complexes of metals-EDTA were inert for PEI-DGT. The concentrations of labile metals by PEI-DGT were markedly affected by the presence of HA and decreased with the increase of HA concentrations. Lower concentrations of labile metals were measured with the higher level of DOC in the tested waters due to the complexation of natural organic matter with metals. In different waters, the concentrations of labile metals measured by DGT devices with various binding agents were different. The PEI-DGT had higher concentrations of labile metals compared with PA-DGT and PSS-DGT. These different concentrations of labile metals were determined by the binding strengths of the binding agents with metals. The results indicated the dependence of DGT measurements for labile metals on the binding agents used. However, DGT devices with various binding agents that had the different capture efficiencies remained for applying in other water sites, and finding out what these different labile metals fractions represented in terms of environmental significances. The DGT technique will be an effective tool for the environmental research and analysis.

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References

[1] J.A.B. Neto, B.J. Smith, J.J. McAllister, Environ. Pollut. 109 (2000) 1–9.
[2] S.V. Dimitrova, Water Res. 36 (2002) 4001–4008.
[3] Z.-C. Li, H.-T. Fan, Y. Zhang, M.-X. Chen, Z.-Y. Yu, X.-Q. Cao, T. Sun, Chem. Eng. J. 171 (2011) 703–710.
[4] M.M. Matlock, B.S. Howerton, D.A. Atwood, Ind. Eng. Chem. Res. 41 (2002) 1579–1582.
[5] M. Filella, D. Klockow, A.M. Mota, Fresenius J. Anal. Chem. 370 (2001) 793–794.
[6] S. Inaba, C. Takenaka, Environ. Int. 31 (2005) 603–608.
[7] V. Sarathy, H.E. Allen, Ecotoxicol. Environ. Safe 61 (2005) 337–344.
[8] M. Pesavento, G. Alberti, R. Biesuz, Anal. Chim. Acta 631 (2009) 129–141.
[9] Ph. Quevauviller, TrAC-Trend Anal. Chem. 23 (2004) 171–177.
[10] J. Liu, X. Feng, G. Qiu, C.W.N. Anderson, H. Yao, Environ. Sci. Technol. 46 (2012) 11013–11020.
[11] N. Glæsner, E. Donner, J. Magid, G.H. Rubæk, H. Zhang, E. Lombi, Environ. Sci. Technol. 46 (2012) 10564–10571.
[12] Y.S. Hong, E. Rifkin, E.J. Bouwer, Environ. Sci. Technol. 45 (2011) 6429–6436.
[13] H. Zhang, W. Davison, Anal. Chem. 67 (1995) 3391–3400.
[14] W. Li, P.R. Teasdale, S. Zhang, R. John, H. Zhao, Anal. Chem. 75 (2003) 2578–2583.
[15] W. Li, H. Zhao, P.R. Teasdale, F. Wang, Talanta 67 (2005) 571–578.
[16] H. Fan, T. Sun, W. Li, D. Sui, S. Jin, X. Lian, Talanta 79 (2009) 1228–1232.
[17] H. Fan, Y. Bian, D. Sui, G. Tong, T. Sun, Anal. Sci. 25 (2009) 1345–1349.
[18] H.-T. Fan, T. Sun, M.-Z. Xue, G.-F. Tong, D.-P. Sui, Chin. J. Anal. Chem. 37 (2009) 1379–1381.
[19] W. Li, H. Zhao, P.R. Teasdale, R. John, F. Wang, Anal. Chim. Acta 533 (2005) 193–202.
[20] P. Diviš, M. Leermakers, H. Dočekalová, Y. Gao, Anal. Bioanal. Chem. 382 (2005) 1715–1719.
[21] W. Li, J. Zhao, C. Li, S. Kiser, R.J. Cornett, Anal. Chim. Acta 575 (2006) 274–280.
[22] V.N. Kislenko, L.P. Oliynyk, J. Polym. Sci. Part A: Polym. Chem. 40 (2002) 914–922.
[23] M. Sun, B. Ding, J. Yu, RSC Adv. 2 (2012) 1373–1378.
[24] C.Y. Yin, M.K. Aroua, W.M.A.W. Daud, Chem. Eng. J. 148 (2009) 8–14.
[25] B. Gao, F. An, K. Liu, Appl. Surf. Sci. 253 (2006) 1946–1952.
[26] M. Amara, H. Kerdjoudj, Talanta 60 (2003) 991–1001.
[27] K. Ueda, A. Hirao, S. Nakahama, Macromolecules 23 (1990) 939–945.
[28] R.P. Quirk, P.L. Cheng, Macromolecules 19 (1986) 1291–1294.
[29] H. Zhang, W. Davison, Anal. Chim. Acta 398 (1999) 329–340.
[30] S. Scally, W. Davison, H. Zhang, Anal. Chim. Acta 558 (2006) 222–229.
[31] L. Giusti, S. Barakat, Water Air Soil Pollut. 161 (2005) 313–334.
[32] L.-Y. Chang, W. Davison, H. Zhang, M. Kelly, Anal. Chim. Acta 368 (1998) 243–253.
[33] B.J. Larner, A.J. Seen, Anal. Chim. Acta 539 (2005) 349–355.
[34] Ø. Garmo, O. Røyse, E. Steinnes, T.P. Flaten, Anal. Chem. 75 (2003) 3573–3580.
[35] H.-T. Fan, J.-B. Wu, X.-L. Fan, D.-S. Zhang, Z.-J. Su, F. Yan, T. Sun, Chem. Eng. J. 198–199 (2012) 355–363.
[36] W. Li, H. Zhao, P.R. Teasdale, R. John, Polymer 43 (2002) 4803–4809.
[37] J. Hur, M.A. Schlautman, S. Yim, J. Environ. Monit. 6 (2004) 89–94.
[38] M.S. Diallo, C.J. Glinka, W.A. Goddard III, J.H. Johnson Jr., J. Nanopart. Res. 7 (2005) 435–448.
[39] B. Dočekal, V. Řezačova-Smetkova, H. Dočekalova, Chem. Pap. 59 (2005) 298–303.
[40] F.J. Ochoa-Loza, J.F. Artiola, R.M. Maier, J. Environ. Qual. 30 (2001) 479–485.
[41] Y. Cao, M. Conklin, E. Betterton, Environ. Health Perspect. 103 (1995) 29–32.
[42] I. Gaabass, J.D. Murimboh, N.M. Hassan, Water Air Soil Pollut. 202 (2009) 131–140.
[43] M. Amara, H. Kerdjoudj, Desalination 168 (2004) 195–200.
[44] S. Deng, Y.-P. Ting, Water Res. 39 (2005) 2167–2177.
[45] H.-T. Fan, T. Sun, D.-P. Sui, H. Chen, S. Jin, B. Liu, Environ. Chem. 28 (2009) 247–250.
[46] A.W. Glynn, Arch. Toxicol. 70 (1995) 28–33.
[47] J. Voets, L. Bervoets, R. Blust, Environ. Sci. Technol. 38 (2004) 1003–1008.
[48] L. Weng, E.J.M. Temminghoff, S. Lofts, E. Tipping, W.H. Van Riemsdijk, Environ. Sci. Technol. 36 (2002) 4804–4810.
[49] M. Gregusova, B. Docekal, Anal. Chim. Acta 684 (2011) 142–146.
[50] H. Dočekalová, P. Diviš, Talanta 65 (2005) 1174–1178.
[51] W. Li, C. Li, J. Zhao, R.J. Cornett, Anal. Chim. Acta 592 (2007) 106–113.