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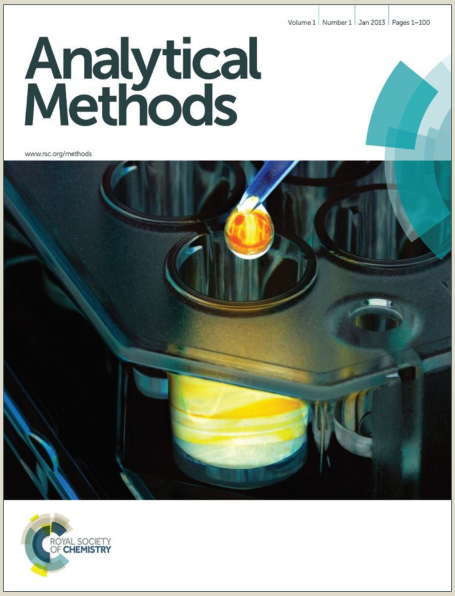

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Determination of Mo (VI) in water with poly (quaternary ammonium salt) as a binding phase of diffusive gradients in thin-films

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Abstract

A technique of diffusive gradients in thin films (DGT) for the measurement of Mo (VI) in water was developed using poly (quaternary ammonium salt) (PQAS) solution as the binding phase in the liquid-type DGT device (PQAS DGT). The Mo (VI) uptake by PQAS DGT increased linearly with time ($r^2 = 0.9989$) with a recovery of 98.8% in synthetic solution. The DGT performance was independent of solution pH over the pH range of 4-10 and ionic strength range from 0.0001 to 0.1 mol L^{-1} $NaNO_3$. The concentration of Mo (VI) in river water determined by PQAS DGT was 3.21μg L^{-1}, and the recoveries of the spiked Mo (VI) were 97.3-101.5%. The results show that PQAS can be used as a binding phase in the liquid-type DGT device for the measurement of Mo (VI) in water.

Keywords: Diffusive gradients in thin-films; Liquid binding phase; Mo (VI); Water

1. Introduction

Molybdenum (Mo) is an essential trace element for both plants and animals, including humans. In animals, it is a component of xanthine oxidase and other redox enzymes. In plants, it is necessary for the fixation of atmospheric nitrogen by bacteria at the start of protein synthesis[1]. Nevertheless, it is harmful at high concentrations. It appears to be toxic when its concentration in plants is higher than 5μg g^{-1}, whereas potential toxicity for ruminants occurs at 10μg g^{-1}[2]. Therefore, its determination in environmental samples is increasingly important. Spectrometric techniques such as ultra-violet visible spectrophotometry, flame (FAAS) and elctrothermal atomic absorption spectromrtry (ETAAS), inductively coupled plasma combined optical emission spectromrtry (ICP-OES) or mass spectrometry (ICP-MS) have been mostly applied for a variety of samples in the analysis of Mo[1].

Speciation strongly influences the reactivity, mobility, bioavailability and toxicity of Mo in natural waters. Environmental fractions of Mo include water soluble Mo, exchangeable Mo, mineral Mo, and organic Mo. Water soluble Mo(VI) species (MoO_4^{2-} and $HMoO_4^-$) are the most bioavailable forms, readily taken up by plant and animals. Therefore, accurate measurement of Mo (VI) in the water environment is required. Measurement of Mo speciation in natural water are challenging: methods must be both very sensitive for low concentrations and specific for distinction between chemical species.

Diffusive gradients in thin films (DGT) technique has been developed and become one of the most promising in situ sampling and measuring techniques of trace metals in natural waters[3-5], soils[6,7] and sediments[8,9]. The DGT technique combines the processes of mass transport through a diffusive phase and accumulation within a binding phase during a deployment[10]. DGT technique can selectively measure trace metal species present in natural water. Only labile species that are able to pass through the diffusive phase and that are accumulated in the binding phase are measured. DGT technique can lower effective detection limits for trace species due to its pre-concentration effect.

Various DGT samplers, including solid binding phases (e.g. Chelex resin[11], precipitated ferrihydrite[12], poly (acrylamidoglycolic acid-coacrylamide) [13], Thiol-Speron resin[14], copper ferrocyanide[15]) and liquid binding phases (e.g. poly (4-styrenesulfonate) (PSS) solution[16], polyvinyl alcohol (PVA) solution[17], sodium polyacrylate (PAAS) solution[18], poly (ethyleneimine) (PEI) solution[19], polymer-bound Schiff base (Py-PEI) solution[20], sodium of polyaspartic acid (PASP) solution[21,22], polyquaternary ammonium salt

(PQAS)[23]), have been developed for the measurement of labile soluble metal species. The homogeneous mobile liquid binding phase provides better contact between the binding agent and the diffusive layer with good reproducibility and no need for elution corrections[16]. solid-type DGT have been developed for the measurement of labile soluble Mo[24,25]. However, the measurement of Mo speciation using liquid-type DGT has never been reported up to now.

In this study, a new approach for the selective determination of Mo (VI) was developed using liquid-type DGT with poly (quaternary ammonium salt) (PQAS) solution as the liquid binding phase. The influences of solution pH and ionic strength on the performance of PQAS DGT were investigated. PQAS DGT performance was evaluated in synthetic solution and Mo (VI) in the river water was sampled and determined by PQAS DGT combined with eletrothermal atomic absorption spectrometry (ETAAS).

2. Experimental

2.1 Chemicals and materials

All reagents used were analytical reagent grade unless otherwise stated and deionised water was used throughout the experiments. Cellulose acetate dialysis membrane (CDM, ~ 14 000 or greater retain) was purchased from Shanghai Yuanju Bio-Tech Co., Ltd. Shanghai, China. Cellulose nitrate membrane (0.45μm) was purchased from Dikma (Tianjin, China). Poly (quaternary ammonium salt) (PQAS) was obtained from Henan Titaning Chemical Technology Co., Ltd, Zhengzhou, China. Mo (VI) standard solutions were purchased from National Standard Samples Website, Beijing, China. HNO_3, $NaNO_3$, NaOH and HCl were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.2 Instrumentation and Analysis

A TAS-990 atomic absorption spectrometer (Beijing Puxi Instrument Factory, Beijing, China), equipped with deuterium lamp background correction and a transversally heated graphite atomizer, was used for the determination of Mo (VI). A PB-10 digital pH-meter (Sartorius, German) equipped with a combined glass electrode was used for the measurements of pH.

2.3 DGT procedures

2.3.1 Pretreatment of the diffusive and binding phases

Cellulose acetate dialysis membrane can be used as the diffusive phase of DGT technique [16-23]. It was pretreated following the procedures recommended by Li et al.[16] The treated membranes were stored in deionized water.

A 50.0 g portion of PQAS solution was transferred into a dialysis membrane bag, prepared as described above, which was placed in deionized water for 96 h with the water replenished every 24h [16]. This process effectively removed all of the low molecular weight PQAS that passed through the dialysis membrane. After purification, a PQAS stock solution of 0.050 molL^{-1} was prepared.

2.3.2 DGT deployment

DGT devices were assembled as previously reported.[23] The DGT devices were constructed by clamping a 3.0-cm-diameter dialysis membrane on a polypropylene tube with a 2.0-cm-diameter opening and containing 2.0 mL of purified 0.050 mol L^{-1} PQAS deionized water solution. The opening of the tube was covered smoothly and sealed tightly with a pretreated dialysis membrane of 85 μm thickness. The devices were deployed with membrane side facing down to ensure the contact of membrane and PQAS solution. DGT samplers were deployed in plastic containers in 20-30 L of well-mixed solution.

2.3.3 Calculation of the DGT concentration

The DGT-measured concentration was calculated using the DGT eq 1.

$$C_{\mathrm{DGT}} = M\ \Delta g / DtA \qquad (1)$$

Where M is the mass of analyte in the binding phase, Δg is the diffusion phase thickness, D is the diffusion coefficient of the analyte, t is the deployment time and A is the area of the sampler exposed to the solution.

2.4 DGT method evaluation

2.4.1 Diffusion coefficient measurement

Diffusion coefficient of Mo (VI) in the dialysis membrane was measured using a diffusion cell similar to that described by Li et al. [16] The cell consisted of two perspex compartments connected by a 2.0 cm diameter opening. A 3.0 cm diameter and 85 μm thickness disc of freshly pretreated dialysis membrane was placed on the opening between the compartments, ensuring that the membrane was the only mass transport medium. 50 mL of carrier solution containing Mo (VI) was introduced into the source solution compartment, and 50 mL of the same carrier solution with an experimentally optimized concentration of PQAS solution was introduced into the receptor solution compartment. Both compartments were stirred continuously during the experiment using magnetic stirrers. Samples were taken from both compartments at 0.5 h intervals up to 3 h and measured by ETAAS.

Diffusion coefficient, D ($cm^2\ s^{-1}$), was calculated from the slope of a linear plot of measured mass of Mo (VI) diffused through the dialysis membrane vs. time, using eq 2[16], where A is the exposed area of the dialysis membrane, Δg is the thickness of diffusive layer, and C is the concentration of Mo (VI) initially present in the source compartment of the diffusion cell.

$$D = \frac{\text{slope}\ \Delta g}{CA} \qquad (2)$$

Using the Stokes-Einstein equation below (eq 3), the diffusion coefficient of Mo (VI) at different temperature can be established.

$$\frac{D_1\eta_1}{T_1} = \frac{D_2\eta_2}{T_2} \qquad (3)$$

where D_1 and D_2 are the diffusion coefficients at temperatures T_1 and T_2 and η_1 and η_2 are the viscosities of water at those temperatures [26].

2.4.2 Validation of DGT performance

A validation test for the binding phase of DGT was undertaken according to the procedures described previously. The DGT devices were deployed in 30 L of 0.010 $\mathrm{molL^{-1}}$ $NaNO_3$ spiked with 50μg$\mathrm{L^{-1}}$ Mo (VI) at 20 ºC; triplicate devices were removed at 24, 48, 72, 96, and 120 h. The PQAS binding phases were taken at each time point and analyzed by ETAAS.

The concentration gradient that is established within the diffusive phase allows the amount of analyte, *M*, that is accumulated in the binding phase from a solution, after passing through a diffusive layer of area (*A*) and thickness (Δg) with diffusive coefficient (*D*), over a deployment time (*t*), to be related directly to the concentration of analyte in the bulk solution measured by DGT (C_{DGT}) [16].

$$M = \frac{D \cdot A \cdot C_{DGT} \cdot t}{\Delta g} \tag{4}$$

PQAS DGT devices are validated by testing the relationship between the mass of Mo (VI) accumulated in the binding phase (*M*) and the deployment time (*t*) with a solution of known concentration. The performance of PQAS DGT to take up Mo (VI) is also assessed by measuring the recovery (*R* %), defined by the following equation [20]:

$$R\% = \frac{C_{DGT}}{C_{bulk}} \times 100\% \tag{5}$$

where C_{bulk} is the total concentration of Mo (VI) in the bulk solution directly measured by ETAAS.

2.4.3 Effect of solution pH and ionic strength on DGT performance

To estimate the effects of varying pH (3, 4, 5, 6, 7, 8, 9, 10, 11, 12) and electrolyte concentration (0.0001, 0.001, 0.01, 0.1 and 1.0 $\mathrm{molL^{-1}}$ as $NaNO_3$) on PQAS DGT response, the devices were immersed in solutions containing 50 μg$\mathrm{L^{-1}}$ of Mo (VI) at a series of pH values and ionic strengths for the deployment time from 24 to 120 h with a 24-hour interval. The pH values of the bulk solutions were adjusted using 2% HCl or NaOH. The ionic strengths of the solutions were adjusted with appropriate addition of $NaNO_3$ at pH ~7.

2.5 Measurement of Mo (VI) in river water

PQAS DGT devices were deployed in triplicate in Nver river water and Mo (VI) spiked river water (Jinzhou, China), triplicate devices were removed at 24, 48, 72, 96, and 120 h. The PQAS binding phases were taken at each time point and analyzed by ETAAS.

3. Results and discussions

3.1. Diffusion coefficient of Mo (VI)

The diffusion coefficient of Mo (VI) through the dialysis membrane was determined using a specially designed diffusion cell,[16] the measured diffusion coefficient of Mo (VI) was 5.86×10^{-7} cm^2s^{-1} in synthetic river water. The lower value of *D* for commercial dialysis membrane compared with the synthetic plolyacrylamide hydrogel (6.28×10^{-6} cm^2s^{-1})[25] was due to the restrictions in mobility by the structure of dialysis membrane, a lower porosity, and lower water content of the dialysis membrane.

3.2. Validation of DGT performance

The performance of DGT is assessed in two ways. First, a linear relationship is expected between mass accumulated in the binding phase, *M*, and deployment time, *t*. Second, the recovery should be in the range of 90-110%.[13] The uptake of Mo (VI) by PQAS in the synthetic solution containing 50 μg L^{-1} Mo (VI) increased linearly with time up to 120 h ($r^2 = 0.9989$, recovery: 98.8%) (Figure 1), which indicated that Mo (VI) could be measured quantitatively by PQAS DGT.

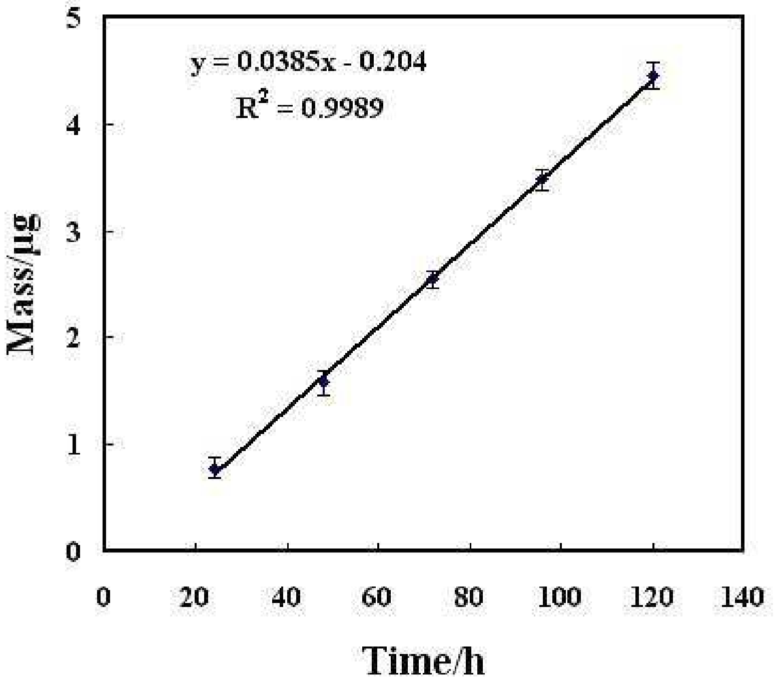

Figure 1. The uptake of Mo (VI) by PQAS DGT as a function of time. 50 μg·L^{-1} Mo (VI) spiked synthetic solution, Δg = 85 μm, A= 3.14 cm^2, temperature: 20 °C.

3.3. Effect of pH

The DGT measurement was independent of solution pH over the pH range of 4-10, which covers most of the pH conditions in natural water (Figure 2), probably as a result of no significant difference between the bindings of PQAS with MoO_4^{2-} and PQAS with $HMoO_4^-$. This result was consistent with the earlier findings that DGT measurements of anions were not dependent upon pH[12]. The recovery of Mo (VI) decreased rapidly at pH values below 3, probably as a result of the speciation change of Mo (VI) from MoO_4^{2-} and $HMoO_4^-$ to H_2MoO_4. The recovery of Mo (VI) decreased at pH values above 11, probably because the competitive diffusion between OH^- and MoO_4^{2-} in the dialysis membrane was enhanced with the increase of solution pH. As the DGT measurement was independent of solution pH in the range of 4-10, PQAS DGT is suitable for the measurement of Mo (VI) in natural waters.

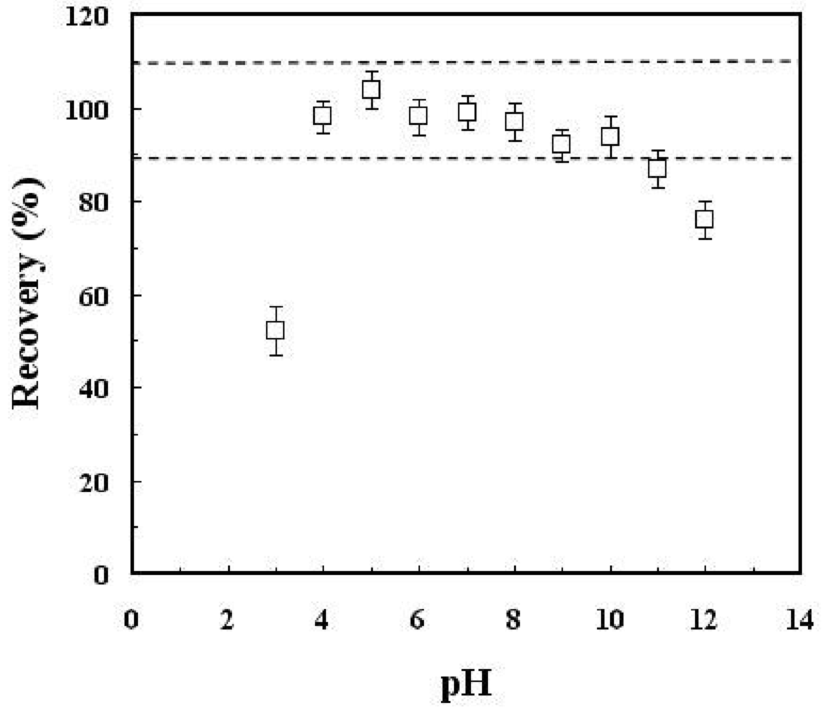

Figure 2. Effect of pH on the performance of PQAS DGT by ploting recovery of Mo (VI) versus the pH. Concentration of Mo (VI) , 50μg L^{-1}; ionic strength, 0.01M $NaNO_3$; deployment time, from 24 to 120 h; and temperature: 20 °C.

3.4. Effect of ionic strength

The binding behavior of PQAS DGT for Mo (VI) was investigated in Na_2MoO_4 aqueous solutions containing various ionic strength (0.0001, 0.001, 0.01, 0.1, and 1.0 mol L^{-1} as $NaNO_3$; Figure 3). The recovery of Mo (VI) decreased with the increase of the ionic strength range from 0.0001 to 1 mol L^{-1} $NaNO_3$, probably because the competitive diffusion between NO_3^- and Mo (VI) in the dialysis membrane was enhanced with the increase of the concentration of $NaNO_3$. The result was not consistent with the experimental results reported by Lucas etc.[27] Lucas and co-workers found that the diffusion coefficients of Au (III) through a diffusive gel increased with the increase of ionic strength.[27] However, accumulation was quantitative and consistent across the ionic strength range 0.001-0.1 mol L^{-1}, with recoveries between 90% and 110%. These results suggest that this technique can be accurately used in the majority of natural fresh and marine waters, although further testing in seawater is necessary to ensure that competing anions other than nitrate do not interfere with the measurement of Mo (VI) by PQAS DGT.

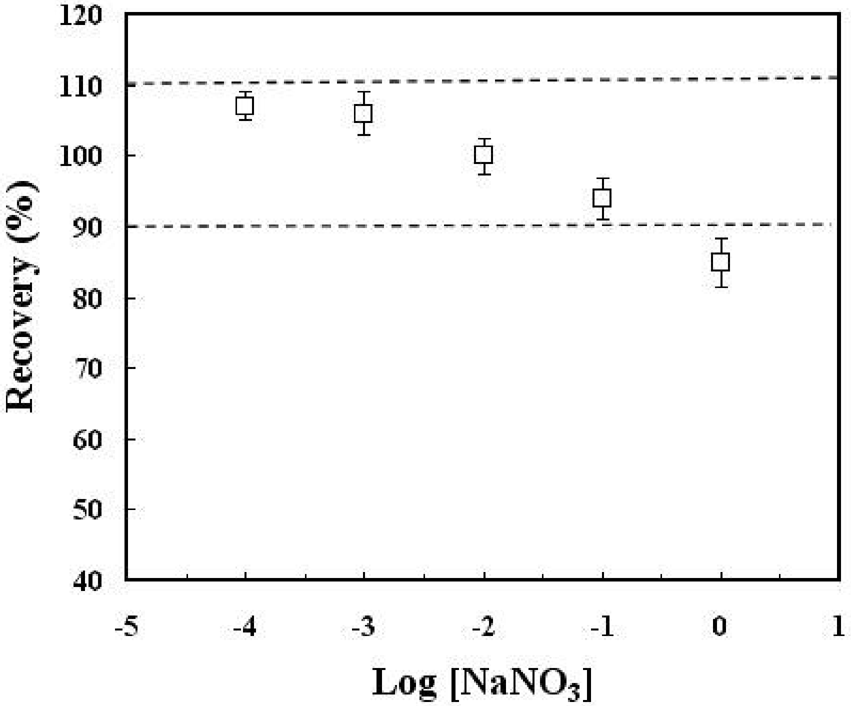

Figure 3. Influence of the ionic strength on the performance of PQAS DGT by plotting the recovery of Mo (VI) versus the NaNO$_3$ concentration (presented as logarithmic concentration of NaNO$_3$). Concentration of Mo (VI), 50μg L^{-1}; pH, 7; deployment time, from 24 to 120 h; and temperature: 20 °C.

3.5. Measurement of Mo (VI) in river water

The concentration of Mo (VI) in Nver river water determined by PQAS DGT was 3.21μg L^{-1}, and the recoveries of the spiked Mo (VI) were 97.3%-101.5% (Table 1). All the accumulated mass by PQAS-DGT increased linearly with deployment time over all deployment time, although not all the linear corrections are very ideal (r^2=0.8861-0.9975). The results suggest that PQAS can be used as DGT binding phase for the sampling and measuring Mo (VI) in waters.

Table1. The measurement of Mo (VI) by PQAS DGT in Nver river water (n=3)

Original /μg L^{-1}	Added /μg L^{-1}	Found /μg L^{-1}	Recovery /%	RSD /%
3.21	2.0	5.07	97.3	5.1
	4.0	7.32	101.5	3.8
	6.0	9.10	98.8	2.3

4. Conclusions

It has been demonstrated in this study that PQAS can be used as a binding agent in DGT applications for the measurement of Mo (VI) in waters with varying matrixes. The performance of PQAS-DGT was independence of pH in the range of 4-10 and ionic strength in the range from 0.0001 to 0.1 molL^{-1} $NaNO_3$. Mo (VI) in waters can be sampled and determined by PQAS DGT combined with ETAAS.

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A DGT device with poly (quaternary ammonium salt) as a binding agent was developed for the sampling and measurement of Mo (VI) in waters.