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Selective sampling and measurement of Cr (VI) in water with polyquaternary ammonium salt as a binding agent in diffusive gradients in thin-films technique

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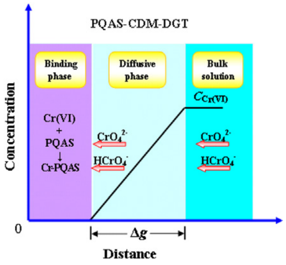
HIGHLIGHTS

- We develop a new DGT device for in situ sampling Cr (VI) in water.
- Polyquaternary ammonium salt (PQAS) was used as binding agent of DGT device.
- Cr (VI) can be accumulated in the PQAS binding phase whereas Cr (III) cannot.
- The DGT performance was independent of pH 3–12 and ionic strength 1×10^{-3}–1 mol L^{-1}.

GRAPHICAL ABSTRACT



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ABSTRACT

A diffusive gradients in thin films (DGT) device with polyquaternary ammonium salt (PQAS) as a novel binding agent (PQAS DGT) combined with graphite furnace atomic absorption spectrometry (GFAAS) was developed for the selective sampling and measurement of Cr (VI) in water. The performance of PQAS DGT was independent of pH 3–12 and ionic strength from 1×10^{-3} to 1 mol L^{-1}. DGT validation experiments showed that Cr (VI) was measured accurately as well as selectively by PQAS DGT, whereas Cr (III) was not determined quantitatively. Compared with diphenylcarbazide spectrophotometric method (DPC), the measurement of Cr (VI) with PQAS DGT was agreement with that of DPC method in the industrial wastewater. PQAS-DGT device had been successfully deployed in local freshwater. The concentrations of Cr (VI) determined by PQAS DGT coupled with GFAAS in Nuer River, Ling River and North Lake were 0.73 ± 0.09 μg L^{-1}, 0.50 ± 0.07 μg L^{-1} and 0.61 ± 0.07 μg L^{-1}, respectively. The results indicate that PQAS DGT device can be used for the selective sampling and measurement Cr (VI) in water and its detection limit is lower than that of DPC method.

1. Introduction

The toxicity and bioavailability of chromium are strongly affected by its chemical speciation. With several oxidation states possible for chromium, the two most common states present in an ambient environment are Cr (VI) and Cr (III). Cr (III) exists as

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Cr^{3+} and Cr $(OH)^{2+}$ cationic species or neutral Cr $(OH)_3$ whereas Cr (VI) exists as various hydrophilic anionic species such as $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} in a water environment. Cr (III) is considered to be an essential trace element species, whereas Cr (VI) compounds are known to be toxic and can cause cancer in humans [1]. Moreover, Cr (VI) has been reported to be 100–1000 times more toxic than Cr (III) and the World Health Organization (WHO) has thus recommended a provisional upper limiting value of 0.05 mg L^{-1} in groundwater [2,3]. Therefore, quantitative discrimination between Cr (VI) and Cr (III) is desirable. A considerable number of Cr speciation methods have been developed [4–8]. Considering the different toxicities of Cr (III) and Cr (VI), rather than the total concentration of Cr, the development of a simple and robust method specific to Cr (VI) in environmental samples could be powerfully employed to accurately assess pollution levels and help prevent further environmental contamination [3]. Unfortunately, sampling and handling of chromium can introduce changes in the distribution of species prior to measurement. The problems associated with ex situ speciation measurements can be overcome by utilizing in situ sampling techniques [9].

Diffusive gradients in thin films (DGT) has been developed [10,11] and become one of the most promising in situ sampling and measuring techniques of trace metals in natural waters, soils and sediments [12–20]. 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 sample trace metal species present in natural water. The metals measured by DGT are referred to as DGT-labile metals and include free metal ions and labile metal complexes. The DGT technique also avoids the problematic behavior of metal species in collected water samples as metals that are bound to the binding phase are unaffected by changing physical parameters [16,18]. For most of DGT devices, the polyacrylamide hydrogel is used as the diffusive phase [14,15,17]. However, polyacrylamide hydrogel has some disadvantages such as poor mechanical resistance and poorly defined gel structure. Li et al. [21,22] reported a new DGT device with dialysis membrane as the diffusive phase and poly (4-styrenesulfonate) solution as the binding phase with some advantages, such as an excellent contact between the binding phase and the diffusive phase, a theoretically ideal mass transport and accumulation, a well-defined reproducible diffusive phase, and no need for elution procedures. Several liquid binding phases such as sodium polyacrylate solution [23,24], polyvinyl alcohol solution [25], thiol-poly (vinyl alcohol solution) [26], poly (aspartic acid) [27,28] and polymer-bound Schiff base [29] have been developed.

DGT has been developed as a useful approach for speciation analysis [30–32]. DGT should be an ideal candidate for modification to allow in situ speciation analysis of dissolved inorganic chromium. However, there was few research on it, and the research only focused on the sampling and measurement of Cr (III) in water and soil using DGT technique with chelex resin as binding phase [33–36]. Therefore, the selective sampling and measurement of Cr (VI) using DGT technique needs to be developed. Polyquaternary ammonium salt (PQAS) is a water-soluble cationic polymer and interacts with anionic high- and low-molecular-weight substances present in aqueous solutions [37]. In this paper, A DGT technique with the dialysis membrane as the diffusive phase and PQAS as the binding phase (PQAS-DGT) was evaluated for the measurement of dissolved Cr (VI) in water. The influences of solution pH and ionic strength on the performance of PQAS DGT were investigated. PQAS-DGT performance for the measurement of dissolved Cr (VI) was evaluated under laboratory conditions and then deployed in the local industrial wastewater and natural water.

Table 1
Furnace operating conditions.

Parameters	
Lamp current (mA)	4.0
Wavelength (nm)	357.9
Slit (nm)	0.4
Ar flow rate (mL min^{-1})	200 (stopped during atomizing)
Sample volume (μL)	20
Temperature program	
Drying	150 (Ramp 10 s, Hold 30 s)
Ashing	1000 (Ramp 15 s, Hold 30 s)
Atomizing	2400 (Ramp 0 s, Hold 4 s)
Cleaning	2500 (Ramp 1 s, Hold 3 s)

2. Experimental

2.1. Material

Cellulose acetate dialysis membrane (CDM, ~14 000 or greater retain) was purchased from Shanghai Yuanju Bio-Tech Co., Ltd., Shanghai, China. Cellulose nitrate membrane (0.45 μm) was purchased from Dikma (Tianjin, China). Poly (quaternary Ammonium salt) (PQAS, *Mw* 1×10^4) was obtained from Henan Titaning Chemical Technology Co., Ltd., Zhengzhou, China. Cr (VI) and Cr (III) standard solutions were purchased from National Standard Samples Website, Beijing, China. Diphenylcarbazide (DPC), $NaNO_3$, NaOH, HCl, KCl, $MgCl_2$, $CaCl_2$ were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China.

2.2. Apparatus

A TAS-990 atomic absorption spectrometer (Beijing Puxi Instrument Factory, Beijing, China) was used, equipped with deuterium lamp background correction and a transversally heated graphite atomizer. Pyrolytic graphite coated tubes (Beijing Puxi Instrument Factory, Beijing, China) were used throughout. A chromium hollow cathode lamp was employed as radiation source at 357.9 nm with a slit width of 0.4 nm. The integrated absorbance mode was used throughout. The limit of detection for Cr was 0.3 μg L^{-1}. The optimum operating parameters for graphite furnace atomic absorption spectrometry (GFAAS) are given in Table 1. UV-1600 Spectrophotometer (Beijing Rayleigh Analytical Instrument Corporation, Beijing, China) was used for the measurement of Cr (VI) in the industrial wastewater to test robustness of PQAS DGT. A PB-10 digital pH-meter (Sartorius, German) equipped with a combined glass electrode was used for the measurements of pH.

2.3. Pretreatment of the dialysis membrane and the binding agent

Cellulose acetate dialysis membrane can be used as the diffusive phase of DGT technique [21,22]. Cellulose acetate dialysis membrane was pretreated following the procedures recommended by Li et al. [21] 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 120 h with the water frequently replenished [21]. This process effectively removed all of the low molecular weight PQAS that passed through the dialysis membrane. The dialyzed PQAS was then filtered with a 0.45-μm pore size cellulose nitrate filter membrane to remove any undissolved particles.

2.4. Optimization of concentration of PQAS

To assess the optimal concentration of PQAS solution and its capacity for the DGT technique, the DGT devices with various concentrations of PQAS solutions (0.010, 0.020, 0.030, 0.040, 0.050,