Novel speciation method based on Diffusive Gradients in Thin Films for in situ measurement of uranium in the vicinity of the former uranium mining sites[☆]

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ABSTRACT

The Diffusive Gradients in Thin Films (DGT) technique using *PIWBA* resin (The Dow Chemical Company) was developed and validated for the measurement of uranium (U) concentration in natural and uranium mining influenced waters. The U uptake on the *PIWBA* resin gel was 97.3 $\pm$ 0.4% (batch method; V_{sol} = 5 mL; [U] = 20 μg L^{-1}; 0.01 M NaNO$_3$; pH = 7.0 $\pm$ 0.2). The optimal eluent was found to be HNO$_{3conc}$/70 °C with an elution efficiency of 88.9 $\pm$ 1.4%. The laboratory DGT investigation demonstrated that the *PIWBA* resin gel exhibits a very good performance across a wide range of pH (3—9) and ionic strength (0.001—0.7 M NaNO$_3$) at different time intervals. Neither effect of PO$_4^{3-}$ (up to 1.72 $\times$ 10^{-4} M), nor of HCO$_3^-$ (up to 8.20 $\times$ 10^{-3} M) on the quantitative measurement of uranium by DGT-*PIWBA* method were observed. Only at very high Ca^{2+} (2.66 $\times$ 10^{-4} M), and SO$_4^{2-}$ (5.55 $\times$ 10^{-4} M) concentration, the U uptake on DGT-*PIWBA* was appreciably lessened. *In-situ* DGT field evaluation was carried out in the vicinity of three former uranium mining sites in France (Loire-Atlantique and Herault departments), which employ different water treatment technologies and have different natural geochemical characteristics. There was a similar or inferior U uptake on DGT-Chelex®-100 in comparison with the U accumulation on a DGT-*PIWBA* sampler. Most likely, the performance of Chelex®-100 was negatively affected by a highly complex matrix of mining waters. The high concentration and identity of co-accumulating analytes, typical for the mining environment, did not have a substantial impact on the quantitative uptake of labile U species on DGT- *PIWBA*.

The use of the polyphenol impregnated anion exchange resin leads to a significant advancement in the application and development of the DGT technique for determination of U in the vicinity of the former uranium mining sites.

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1. Introduction

Uranium (U) is a naturally-occurring radioactive element, which is present in the aquatic systems at the wide range of concentration (0.002—20 μg L^{-1}) depending on the geological background, presence and type of anthropogenic activities (de Vos and Tarvainen, 2006; Vandenhove et al., 2010). The two dominant U aqueous redox states are U(IV) or U(VI), with the latter being mobile and stable under oxidizing conditions (Günther et al., 2002; Ragnarsdottir and Charlet, 2000; Vandenhove et al., 2010). In the (+VI) oxidation state, the U speciation is controlled by pH, redox potential and the occurrence of the complexing agents. The free uranyl ion (UO$_2^{2+}$) governs dissolved U(VI) speciation at low pH, while at higher pH, hydroxy and carbonate complexes dominate. Uranyl hydroxy complexes such as UO$_2$(OH)$^+$, play a significant role in uranyl aqueous speciation only under slightly acidic pH conditions. At near neutral and alkaline pH values, the dissolved U speciation is controlled by a series of a uranyl carbonates complexes (*i.e.* UO$_2$CO$_{3(aq)}^0$, UO$_2$(CO$_3$)$_2^{2-}$, UO$_2$(CO$_3$)$_3^{4-}$, (UO$_2$)$_2$(OH)$_3$CO$_3^-$) (Salbu et al., 2004; Wang et al., 2013).

The uranium biogeochemical cycling is a research field of a

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growing interest due to the fact that U is known of its dual toxicity. Uranium is often called a nephrotoxic element, as its toxic effects are more likely due to its chemical properties than its radioactivity. Total U concentration and the isotopic composition are responsible for the radiological toxicity, while the chemical toxicity of U depends on the speciation as only the dissolved and labile uranium fraction is chemically toxic (Chapman, 2008; Goulet et al., 2011; Sheppard et al., 2005). In this context, the Diffusive Gradients in Thin Films (DGT) technique is a promising *in-situ* speciation tool, because it provides time-averaged concentration of labile metal species in water (Davison and Zhang, 1994; Zhang and Davison, 1995), sediment (Gao et al., 2006; Hooda et al., 1999) and soil (Degryse et al., 2009; Duquène et al., 2010). The DGT technique is based on a simple device that accumulates solutes on a binding agent (*i.e.* resin/adsorbent immobilized in a thin layer of hydrogel) after a passage through a hydrogel. The key role of the hydrogel is a discrimination of metal species by their size, mobility and lability (so-called DGT labile metal species). Afterwards, the metal species are effectively immobilized and pre-concentrated on the binding phase gel. The DGT technique has been extensively applied for the range of the analytes over the wide pH and ionic strength ranges, however only few studies encompassed the DGT investigation under extreme field conditions, such as mining environments (Conesa et al., 2010; de Oliveira et al., 2013; Phrommavanh et al., 2013; Stockdale and Bryan, 2013). Mining environments are characterized by large variations in pH, ionic strength and high concentrations of competing and interfering ions, what might compromise the accuracy of the DGT measurement. Therefore, suitable resin for the DGT technique should be affected neither by the extreme pH and ionic strength values nor by high concentration of interferences such as Zn, Mn, Ca or SO_4^{2-}. Up to date, several binding phases such as Chelex®-100, Metsorb™, Whatman DE 81, Dowex 2 × 8–400 and Diphonix® have been proposed for the assessment of labile U species in aquatic environments (Table 1). In the current study we propose a novel DGT technique with polyphenol impregnated weak base anion exchange resin (for the purpose of this study called *PIWBA* resin) for determining aqueous U species in the vicinity of the former uranium mining sites. Polyphenols are secondary metabolites of plants and can be found in significant amounts in fruits, vegetables, cereals and beverages (Handique and Baruah, 2002). Those substances are known for their antioxidant, anti-cancer and anti-aging properties (Pandey and Rizvi; Scalbert et al., 2005), but it has also been found that they possess the capability to remove uranium from the environment (Alexandratos, 2009; Nakajima and Sakaguchi, 2007). Liu et al. (J. Liu et al., 2013a) and Nakajima et al. (Nakajima and Sakaguchi, 2007) hypothesized that the binding mechanism occurs via polyhydroxybenzene groups, polyphenolic or catechol-type polyphenolic ligands, however the exact mode of action of polyphenols is still unknown. The *PIWBA* resin has been developed and patented by Rohm and Haas Company (a wholly owned subsidiary of The Dow Chemical Company), however it is not yet commercially available (Rohm and Haas, 2014).

Novel DGT method using *PIWBA* resin was comprehensively investigated under laboratory conditions. The *PIWBA* resin gel preparation and the elution procedure protocols were developed. The linear relationships between the mass of U accumulated on DGT-PIWBA within the deployment time were demonstrated, thereby validating that the novel DGT method operated in accordance with the assumptions of the DGT equation. The influence of a wide range of pHs (3–9) and ionic strengths (0.001–0.7 M NaNO3) on the performance of the DGT technique was also investigated. Effects of ligands (Ca^{2+}, PO_4^{3-}, SO_4^{2-} and HCO_3^-) on the U uptake on DGT-*PIWBA* were tested. The effective diffusion coefficients of U over the pH range were determined as well.

Furthermore, the DGT field investigations in the vicinity of the former uranium mining sites were carried out. The DGT-*PIWBA* method was applied in natural and mining influenced waters and compared to the well-established DGT-Chelex®-100 method.

2. Materials and methods

2.1. General procedures

All chemicals were of analytical reagent grade or greater. Milli-Q (ultra-pure) water (>18.2 MΩ cm, Millipore, USA) was used for the preparation of the solutions, gels and cleaning glassware and containers. All plastic equipment were pre-cleaned in 10% (v/v) HNO_3 (pro analysis, Merck, Germany) for at least 24 h and rinsed thoroughly with Milli-Q water. Appropriate pH of all solutions was adjusted by using either 2% HNO_3 or 2% NaOH. Temperature and pH measurements were performed using pH probe (WTW GmbH, Germany) and monitored during the experiment. The deployment solutions were well-mixed using a mechanic stirring system, so the diffusive boundary layer (DBL) of DGT was considered negligible (Zhang and Davison, 1999).

2.2. DGT preparation and assembly

All experiments were carried out under laminar flow hood (class-100) in a clean room. All gels contained 15% (v/v) acrylamide solution (Merck, Germany) and 0.3% (v/v) patented agarose cross-linker (DGT Research Ltd., UK). N,N,N′,N′-tetramethylenediamine (TEMED) (Acros Organics, Belgium) was used as a catalyst and daily prepared solution of 10% ammonium persulphate (Merck, Germany) was used as an initiator for polymerization. The polyacrylamide (PAM) diffusive gel (Δg = 0.8 mm) was prepared according to the procedure described by Zhang and Davison (Zhang and Davison, 1995). The *PIWBA* resin gel (Δr = 0.4 mm) was prepared by modifying the Chelex®-100 resin gel preparation protocol (Zhang and Davison, 1995). The *PIWBA* resin was first ground (Fritsch Pulverisette, Type 02.102) and sieved manually to obtain the particle size of 250 μm. Furthermore, an amount of 1.5–2 g of the resin was added to 10 mL of gel stock solution, and then the

Table 1
Summary of the DGT binding phases used for determination of labile U species in aquatic systems.

Binding phase	Reference
Chelex®-100	(Drozdzak et al., 2016, 2015; Garmo et al., 2003; Hutchins et al., 2012; Li et al., 2005; Phrommavanh et al., 2013; Stockdale and Bryan, 2013; Turner et al., 2012)
Metsorb™	(Drozdzak et al., 2016, 2015; Hutchins et al., 2012; Turner et al., 2014, 2012)
Whatman DE 81	(Li et al., 2007, 2006)
Dowex 2 × 8-400	(Li et al., 2007)
Diphonix®	(Drozdzak et al., 2016, 2015; Turner et al., 2015)
Spheron Oxin®	(Gregusova and Docekal, 2011; Gregusova et al., 2008)