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Evaluation of DGT techniques for measuring inorganic uranium species in natural waters: Interferences, deployment time and speciation

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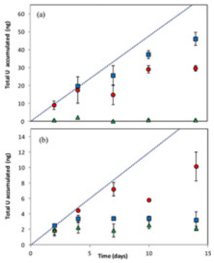
HIGHLIGHTS

- ▶ The adsorbents Chelex-100, Metsorb and MnO_2 were investigated for use with DGT.
- ▶ All three adsorbents performed well in low ionic strength solutions.
- ▶ MnO_2 resin was found to be the most suitable for marine deployments.
- ▶ DGT is able to measure isotopic ratios of U down to concentrations of 0.1 $\mu g\,L^{-1}$.
- ▶ DGT underestimated U concentrations by at least 50% if the DBL was not taken into account.

GRAPHICAL ABSTRACT

In situ field deployment of DGT devices – manganese dioxide (🟦) best suited for sea water monitoring (a) up to 7 days and Metsorb (●) best suited for fresh water monitoring (b) of inorganic uranium species up to 7 days.



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ABSTRACT

Three adsorbents (Chelex-100, manganese dioxide [MnO_2] and Metsorb), used as binding layers with the diffusive gradient in thin film (DGT) technique, were evaluated for the measurement of inorganic uranium species in synthetic and natural waters. Uranium (U) was found to be quantitatively accumulated in solution (10–100 $\mu g\,L^{-1}$) by all three adsorbents (uptake efficiencies of 80–99%) with elution efficiencies of 80% (Chelex-100), 84% (MnO_2) and 83% (Metsorb). Consistent uptake occurred over pH (5–9), with only MnO_2 affected by pH < 5, and ionic strength (0.001–1 mol L^{-1} $NaNO_3$) ranges typical of natural waters, including seawater. DGT validation experiments (5 days) gave linear mass uptake over time ($R^2 \geq 0.97$) for all three adsorbents in low ionic strength solution (0.01 M $NaNO_3$). Validation experiments in artificial sea water gave linear mass uptake for Metsorb ($R^2 \geq 0.9954$) up to 12 h and MnO_2 ($R^2 \geq 0.9259$) up to 24 h. Chelex-100 demonstrated no linear mass uptake in artificial sea water after 8 h. Possible interferences were investigated with $SO_4{}^{2-}$ (0.02–200 $mg\,L^{-1}$) having little affect on any of the three DGT binding layers. $PO_4{}^{3-}$ additions (5 $\mu g\,L^{-1}$–5 $mg\,L^{-1}$) interfered by forming anionic uranyl phosphate complexes that Chelex-100 was unable to accumulate, or by directly competing with the uranyl species for binding sites, as with MnO_2 and the Metsorb. $HCO_3{}^{-}$ (0.1–500 $mg\,L^{-1}$) additions formed anionic species which interfered with the performance of the Chelex-100 and the MnO_2, and the Ca^{2+} (0.1–500 $mg\,L^{-1}$) had the affect of forming labile calcium uranyl species which aided uptake of U by all three resins. DGT field deployments in sea water (Southampton Water, UK) gave a linear mass uptake of U over time with Metsorb and MnO_2 (4 days). Field deployments in fresh water (River Lambourn, UK) gave linear uptake

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for up to 7 and 4 days for Metsorb and MnO_2 respectively. Field deployment of the Metsorb-DGT samplers with various diffusive layer thicknesses (0.015–0.175 cm) allowed accurate measurements of the diffusive boundary layer (DBL) and allowed DBL corrected concentrations to be determined. This DBL-corrected U concentration was half that determined when the effect of the DBL was not considered. The ability of the DGT devices to measure U isotopic ratios with no isotopic fractionation was shown by all three resins, thereby proving the usefulness of the technique for environmental monitoring purposes.

1. Introduction

Uranium (U) is a primordial radioactive element, originating from the three naturally occurring decay chains (^{235}U, ^{238}U and ^{230}Th), with three important isotopes: ^{238}U (99.276%), ^{235}U (0.718%) and ^{234}U (0.0056%) [1]. It is released in the environment *via* anthropogenic nuclear processes, such as nuclear power generation, nuclear weapons testing and accidental releases, or *via* natural processes such as weathering or erosion of rocks and sediments containing U. It is highly toxic and important to monitor due to its chemical and radiological properties [2].

U is predominantly found in the 6+ state as the uranyl ion (UO_2^{2+}) at pH < 4–5, and at pH > 7 occurs as the stable uranyl carbonates $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$ or its complexes, although U(IV) is also found under reducing conditions [3]. Partitioning between the solid and the solution phases, which is mediated by chemical characteristics such as pH, redox potential, ionic strength, presence of complexing ligands ($OH^- > CO_3^{2-} > HPO_4^{2-} > H_2PO_4^- > F^- > SO_4^{2-} > Cl^-$), surfactants or flocculating agents, is important in natural waters [4]. These all act to influence the oxidation states of the radionuclide and will affect reactions with other dissolved components and sediment–solution interactions.

Table 1 shows the concentration of U in a range of natural environments; typical marine concentrations are 3 $\mu g\,L^{-1}$, while estuarine concentrations can be as low as 0.3 $\mu g\,L^{-1}$, with typical fresh water values of 0.1–0.3 $\mu g\,L^{-1}$. The higher dissolved sea water concentrations are due to the formation of stable soluble uranyl carbonate complexes. The largest global sink for U is oceanic sediments, with oceanic carbonates solubilising fluvial and ground water inputs of U. The low environmental concentrations of U can be challenging to detect using conventional analytical techniques such as mass spectroscopy, particularly in complex matrices such as marine or estuarine waters. Isotopic ratios of $^{235}U/^{238}U$ are of interest as a tool to identify pollution sources. ^{235}U occurs in very low concentrations, even when enriched, and is normally below limits of detection without any form of pre-concentration; by precipitation, ion-exchange, solvent extraction or extraction chromatography [5]. Pre-concentration and radiochemical separation require large volume (up to 5 L) [6] grab samples of water. These approaches that use considerable sample processing can also introduce contamination and chemical transformations each time the sample is handled or during storage [7].

Alternative measurement approaches include bio-monitoring [8,9], technologies based on the redox reactions between analyte and a chelate [10] and fibre optical methods [11]. As many of these techniques have poor limits of detection they can be used only to indicate the presence of U or, during a pollution event where environmental concentrations are elevated. Passive sampling is another approach [12]. This method avoids many of the sources of error associated with grab sampling by pre-concentrating the analyte *in situ*. Furthermore, passive samplers can be used to measure time-weighted averaged (TWA) concentrations over the deployment period, which can be beneficial in investigations where concentrations fluctuate highly [12,13].

Diffusive gradients in thin films (DGT) are passive samplers that measure the labile, dissolved fraction of analytes *in situ* [14]. The device consists of three layers: (i) a binding agent, which contains a resin or functional groups selective to the target ions, held in a thin layer of hydrogel (binding gel); (ii) a layer of hydrogel of known thickness, which serves as the diffusive layer; and (iii) a protective outer membrane with a known pore size. A diffusive boundary layer (DBL) that forms on the exposed face of the device must also be accounted for and added to the diffusive layer. After deployment, the metal ions accumulated in the resin layer are eluted (*e.g.* in nitric acid) and the extract analysed by sensitive instrumental techniques, *e.g.* ICP-MS.

U has been measured in artificial and natural waters using DGT in five reported studies [15–19]. Li et al. [15,16] measured U uptake in artificial alkaline waters using a device that comprised a Whatman DE 81 membrane and Chelex-100 resin (BioRad; www3.bio-rad.com). In a later study they investigated the use of a Dowex 2 × 8-400 resin as the receiving phase [16]. Gregusova et al. [20] assessed a chelating ion-exchange resin, Spheron-Oxin® as a candidate binding phase, examining the effects of carbonate concentrations in artificial waters on the uptake of U. Vandenhove et al. [17] and Mihalik et al. [19] used a DGT containing Chelex-100 as a proxy for phyto-availability but did not undertake any further validation work. A recent study by Hutchins et al. [18] measured U in natural waters using a TiO_2-based resin, Metsorb (Graver Technologies; http://www.gravertech.com).

In this study we compared the uptake of U using a DGT device containing either Chelex-100 resin, Metsorb resin, or manganese dioxide (MnO_2), as described by Burnett et al. [21]. MnO_2 is a natural scavenger of metals and radionuclides from waters and is stable in the presence of high radiation levels. It has applications in the remediation of nuclear aquatic waste and pre-concentration of radionuclides in sea water [22]. An MnO_2 precipitate has been used previously in passive samplers to study sediment redox profiles through remobilisation of the MnO_2 within the gels [23] and with DGT to measure ^{226}radium [24,25]. The performance of each resin in the presence of complexing agents such as HCO_3^-, PO_4^{3-} and SO_4^{2-} and common ionic interference Ca^{2+} were evaluated [26]. Experiments to assess the accumulation of U over time for artificial sea water and low ionic strength water were undertaken. Two 14-day field deployments in carbonate rich river water and in a marine harbour were used to validate laboratory results.

2. Experimental

Chemicals were of analytical grade or better and supplied by Fisher Scientific (Loughborough, U.K.), unless otherwise specified. Milli-Q (ultra-pure) water (>18.2 MΩ cm, Millipore, Watford, U.K.) was used as the laboratory water. All U ICP-MS standards and experimental working solutions were prepared in low density polyethylene (LDPE) or polystyrene (PS) containers with polypropylene lids (PP) from a 1000 mg L^{-1} in 2% HNO_3 (Spex Certiprep, Fisher Scientific) U stock solution unless otherwise stated. The ICP-MS internal standard was prepared from a 1000 mg L^{-1} in 2% HNO_3 (Spex Certiprep) bismuth stock solution. These solutions were adjusted to a given pH by addition of either 1 M HNO_3 or 1 M NaOH, and to a given ionic strength by addition of $NaNO_3$, with the pH monitored throughout experiments. Solutions were equilibrated with atmospheric CO_2 for 24 h before use unless otherwise