Evaluation and application of Diffusive Gradients in Thin Films (DGT) technique using Chelex®-100, Metsorb™ and Diphonix® binding phases in uranium mining environments

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Published in:
Anal Chim Acta

DOI:
10.1016/j.aca.2015.07.057

Publication date:
2015

Citation for published version (APA):
Evaluation and application of Diffusive Gradients in Thin Films (DGT) technique using Chelex\textsuperscript{R}-100, Metsorb\textsuperscript{TM} and Diphonix\textsuperscript{R} binding phases in uranium mining environments

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**Highlights**
- The DGT method to assess U concentration in mining impacted environments was evaluated.
- Diphonix\textsuperscript{R} resin displays extremely high binding capacity towards uranium.
- Neither pH nor ionic strength effect on U uptake on DGT-Diphonix\textsuperscript{R} resin observed.
- No correlation between U diffusion coefficients estimated by two different methods.
- Effective diffusion coefficients of U should be implemented into DGT calculations.

**Abstract**
A new resin- Diphonix\textsuperscript{R} in Diffusive Gradients in Thin Films (DGT) technique for the determination of uranium was investigated and compared with previously used binding phases for uranium, Chelex\textsuperscript{R}-100 and Metsorb\textsuperscript{TM}. The DGT gel preparation and the elution procedure were optimized for the new resin. The U uptake on Diphonix\textsuperscript{R} resin gel was 97.4 $\pm$ 1.5\% (batch method; [U] = 20 mg L\textsuperscript{-1}; 0.01 M NaNO\textsubscript{3}; pH = 7.0 $\pm$ 0.2). The optimal eluent was found to be 1 M 1-hydroxyethane-1, 1-diphosphonic acid (HEDPA) with an elution efficiency of 80 $\pm$ 4.2\%. Laboratory DGT study on U accumulation using a DGT samplers with Diphonix\textsuperscript{R} resin showed a very good performance across a wide range of pH (3–9) and ionic strength (0.001–0.7 M NaNO\textsubscript{3}). Diffusion coefficients of uranium at different pH were determined using both, a diffusion cell and the DGT time-series, demonstrating the necessity of the implementation of the effective diffusion coefficients into U-DGT calculations. Diphonix\textsuperscript{R} resin gel exhibits greater U capacity than Chelex\textsuperscript{R}-100 and Metsorb\textsuperscript{TM} binding phase gels (a Diphonix\textsuperscript{R} gel disc is not saturated, even with loading of 10.5 $\mu$mol U). Possible interferences with Ca\textsuperscript{2+} (up to 1.33 $\times$ 10\textsuperscript{-2} M), PO\textsubscript{4}\textsuperscript{3-} (up to 1.72 $\times$ 10\textsuperscript{-4} M), SO\textsubscript{4}\textsuperscript{2-} (up to 4.44 $\times$ 10\textsuperscript{-3} M) and HCO\textsubscript{3} (up to 8.20 $\times$ 10\textsuperscript{-3} M) on U-DGT uptake ([U] = 20 $\mu$g L\textsuperscript{-1}) were investigated. No effect or minor effect of Ca\textsuperscript{2+}, PO\textsubscript{4}\textsuperscript{3-}, SO\textsubscript{4}\textsuperscript{2-}, and HCO\textsubscript{3} on the
quantitative measurement of U by Diphonix\textsuperscript{®}-DGT was observed. The results of this study demonstrated the DGT technique with Diphonix\textsuperscript{®} resin is a reliable and robust method for the measurement of labile uranium species under laboratory conditions.

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1. Introduction

European Union legislation, and specifically Water Framework Directive 2000/60/EC (WFD), has compelled Member States to perform several duties and responsibilities concerning water protection and its management [1]. Each Member State, besides transposing the WFD into national legislation, can impose additional restrictions in order to achieve the objectives of the WFD. The Member State can, for instance, impose an additional list of the priority substances and their Environmental Quality Standards (EQS), if it is essential to reduce hazardous substances in water and obtain a good ecological status of water bodies. It is clear that the Member States face some difficulties in the implementation of the WFD. One of the exemplary drawbacks is correlated to the Article 19 of the WFD that highlights that the industries that are benefitting from the point sources are considered as main sources of pollutants, thus the main contributors to potential degradation of the environment. Therefore they should not only continually undertake risk assessments of their own discharges, but also make sure that the good ecological status of the receiving water bodies is accomplished and maintained.

Uranium is a trace element, naturally-occurring at low concentration in natural waters, however its abundance in terrestrial and aquatic ecosystems might be elevated by an anthropogenic activities. In accordance with the Article 16 of the WFD, EC has established the list of the EQS, but uranium is not considered as a priority substance due to its ubiquitous nature [1,2]. However, for the naturally occurring radionuclides, such as uranium, several additional restrictions and constraints of the environmental monitoring are enforced by the national environment agencies and inspectorates [3–6]. In this context, the technique of Diffusive Gradients in Thin Films (DGT) is a potential monitoring tool, as it provides in situ measurement of the time-averaged concentrations of labile metal species in solution [7]. The DGT technique is based on the accumulation of solutes on a binding gel (a resin immobilized in a thin layer of hydrogel) after passing through a diffusive hydrogel. Briefly, the diffusive gel may permit the solutes (the size of which should be smaller than 5 nm) to pass through and the role of the specific resin/adsorbent gel is efficiently binding with certain solutes. Hence, it is essential to evaluate the appropriate binding gel, taking into account not only the interest, but also the matrix, in which DGT will be deployed. The most common DGT device incorporates Chelex\textsuperscript{®}-100 resin with functional groups of iminodiacetate acid (IDA), which act as chelators for polynuclear metal ions, including uranium [8–11]. Chelex\textsuperscript{®}-100 (Bio–Rad, USA) is classed among the weak acid cation exchange resins, but it distinguishes from the other exchangers by its high selectivity for metal ions. The main disadvantage of Chelex\textsuperscript{®}–100 is its pH-dependence, what strongly influences its application in the mining impacted environments [12]. However, the replacement of Chelex\textsuperscript{®}–100 with alternative binding phase, for example, with Metsorb\textsuperscript{TM}, MnO\textsubscript{2} or with 3-mercaptoproply functionalized silica resin, can broaden the range of available analytes for DGT technique [13–16]. Metsorb\textsuperscript{TM} (Graver Technologies Ltd., USA) is a titanium dioxide (anatase) based adsorbent, that displays high uranium adsorption [17]. Titanium dioxide can adsorb both, anions and cations, on the positively and negatively charged surface, what indicates a wide operational pH range. Metsorb\textsuperscript{TM} is selective for As(V), PO\textsubscript{4}\textsuperscript{3–}, Se(IV) or V(IV), therefore its efficacy for the U determination might be mitigated, especially in the mining environments, where the concentrations of abovementioned elements can be elevated [14,18]. Diphonix\textsuperscript{®} (Eichrom Technologies, USA) is a strong cation-chelating resin with diphosphonic acid and sulfonic acid as functional groups (Fig. 1). Diphosphonic acid functional groups exhibit high affinity for tetra- and hexavalent actinides, while hydrophilic sulfonic acid groups facilitate the access to the selective diphosphonic acid groups and influence adsorption kinetics. It is not excluded though, that sulfonic acid groups might contribute to the metal uptake, as they can effectively bind metals to the negatively charged sites [19]. Diphonix\textsuperscript{®} resin was designed and used mainly for the preconcentration of actinides and the removal of uranium from radioactive wastewater [20–22].

The main objective of this study was to identify and evaluate a suitable binding phase for the determination of uranium species in mining impacted environments. Diphonix\textsuperscript{®} resin was investigated in detail and compared with previously used binding agents for uranium assessment [11,13,23–25]. Recently Turner et al. [25] reported a study about Diphonix\textsuperscript{®} resin in DGT technique. However, the present study sheds new light on the performance of Diphonix\textsuperscript{®} also under conditions characteristics for uranium mining impacted environments. The alternative gel preparation and the elution procedures for Diphonix\textsuperscript{®} resin gel, as opposed to Turner et al. [25], were determined.

This laboratory research provides the comparison of DGT technique using three different binding layers — Chelex\textsuperscript{®}–100, Metsorb\textsuperscript{TM} and Diphonix\textsuperscript{®} for the measurement of uranium species. The performance of the DGT technique using Chelex\textsuperscript{®}–100, Metsorb\textsuperscript{TM} and Diphonix\textsuperscript{®} binding phases was assessed across a wide range of pH and ionic strength. Diffusion coefficients of uranium species were determined by a diffusion cell and by controlled DGT time-series deployments over the pH range. The effective U capacities of each binding phase were examined. In order to mimic the real environmental conditions and to gauge the effect of interferences of Ca\textsuperscript{2+}, PO\textsubscript{4}\textsuperscript{3–}, SO\textsubscript{4}\textsuperscript{2–}, and HCO\textsubscript{3}– on performance of DGT
technique with Chelex®-100, Metsorb™ and Diphonix® binding phases, a set of experiments was undertaken as well.

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) HNO₃ (pro analyti, 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% HNO₃ 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 [26].

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’-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) diffuse gel (Δg = 0.8 mm) and Chelex®–100 resin gel (Δg = 0.4 mm) were prepared according to the procedure described by Zhang and Davison [7]. Metsorb™ adsorbent gel (Δg = 0.4 mm) was prepared based on the procedure of Bennett et al. [27]. In general, the protocol described by Zhang and Davison [7] for the preparation of Diphonix® resin gel (Δg = 0.8 mm) was followed, however a few modifications have been applied. An amount of 1.5–2 g of the resin was added to 10 mL of gel stock solution, and then the sample was sonicated for at least 5 min. Further, 120 μL of 10% ammonium persulphate solution and 28 μL of TEMED were added, the solution was well mixed on the stirrer and casted gently between two glass plates. The assembly was placed in an oven at 45 °C for 1 h, and then gels were removed from the glass plates and hydrated in Milli-Q water for at least 24 h. All binding phase gels were cut using a 2.5 cm diameter plastic cutter and stored in 0.01 M NaNO₃ at 4 °C prior to assembly. DGT samplers were supplied by DGT Research and assembled according to the protocol from Lancaster (www.dgtresearch.com). Concisely, the resin/adsorbent gel disc was placed on the bottom, with the resin/adsorbent side faced up, then a diffusive gel disc was overlying on it and the resin/adsorbent gel discs were transferred into new vials with the resin/adsorbent gel disc was placed. Assembled DGT samplers were stored at 4 °C for 1 h, and then gels were removed from the glass plates and hydrated in Milli-Q water for at least 24 h. All binding phase gels were cut using a 2.5 cm diameter plastic cutter and stored in 0.01 M NaNO₃ at 4 °C prior to assembly. DGT samplers were supplied by DGT Research and assembled according to the protocol from Lancaster (www.dgtresearch.com). Concisely, the resin/adsorbent gel disc was placed on the bottom, with the resin/adsorbent side faced up, then a diffusive gel disc was overlying on it and the resin/adsorbent gel discs were transferred into new vials with the resin/adsorbent gel disc was placed. Assembled DGT samplers were stored at 4 °C for 1 h, and then gels were removed from the glass plates and hydrated in Milli-Q water for at least 24 h.

2.3. Sample analysis

Sample analysis was performed using inductively coupled plasma sector field mass spectrometry (ICP-SF-MS, Element II, Thermo Fisher Scientific Bremen GmbH, Germany), equipped with ESI fast autosampler. Calibration was performed by external calibration, using Indium (2.5 μg L⁻¹ in 2% HNO₃) as internal standard and 2% HNO₃ as carrier solution. The internal standardization was applied (Indium added to all samples on each stage of analysis: calibration, measurement of blanks and samples) to compensate for instrumental drift. The use of 206Bi, 115In, 103Rh as internal standards has been investigated during the study. No difference in the analytical precision for U determination has been found when using 206Bi and 115In. The use of 103Rh as internal standard has been excluded due to some interactions with 1 hydroxyethane-1, 1-diphosphonic acid (HEDPA) used for the elution of Diphonix® resin gel discs. Indium as internal standard was selected as it has similar ionization energy to the one of U (558 kJ mol⁻¹ and 584 kJ mol⁻¹ respectively) and our experience with the use of Indium in multi-element analysis. Analytical standard solutions of U were prepared from a 1000 ng L⁻¹ in 2% HNO₃ stock solution (Johnson Matthey Materials Technology, UK). An average instrumental blank of 0.6 ng L⁻¹ was obtained, resulting in a detection limit of 1.3 ng L⁻¹ (determined as the average blank + 3 times standard deviation) and good repeatability.

2.4. Speciation modelling

The thermodynamic geochemical speciation software PhreeQC was used to predict the U speciation and to assist with the interpretation of the results due to the lack of up to date applicable techniques which are able to measure individual uranium chemical species in solution [28]. A consistent database was based on the LLNL database, modified to include the set of uranium thermodynamic data selected by NEA (Table S1 in S1) [29,30].

2.5. Binding phase gel blanks and DGT detection limits

It is necessary to verify the values of DGT blanks over the entire laboratory investigation, as they might vary according to the batch of binding phase gels, gel preparation, handling procedures or the batch of an eluent. The preparation of DGT blanks went through the whole procedure as for DGT samplers. All DGTs values in this study were corrected for the blank values of each binding phase and each eluent used. U concentrations measured by DGT samplers (C_DGT, μg L⁻¹) were calculated using Eq. (1) [7]:

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

where $M$ is accumulated mass of U on the binding layer (ng); $D$ is the temperature-corrected diffusion coefficient for U (cm² s⁻¹); $\Delta g$ is the thickness of the diffusion layer (cm); $t$ is the deployment time (s) and $A$ is the exposure area of DGT sampler (cm²).

2.6. Uptake and elution efficiency

The uptake and the elution efficiencies of each binding phase gel were evaluated by immersing a single gel disc in 5 mL of 20 μg U L⁻¹ solution (0.01 M NaNO₃ at pH 7.0 ± 0.2. After shaking for 48 h, each binding phase gel disc was transferred into new vials with the appropriate amounts of the eluents. The Chelex®-100 resin gel discs were eluted in 1 M HNO₃, U on Metsorb™ adsorbent gel discs were eluted with both 1 M HNO₃ and 1 M NaOH/H₂O₂ as those eluents were recommended by Hutchins et al. [13] and Turner et al. [24]. To elute U from Diphonix® resin gel discs several elution procedures were evaluated (1 M HNO₃; 1 M NaOH; HNO₃conc/70 °C; 1 M 1-hydroxyethane-1, 1-diphosphonic acid (HEDPA)). The tests of U uptake and elution efficiencies were conducted in 5 replicates. In order to estimate the presumptive adsorption of U to the walls of vials, a control experiment without binding phase gel disc was carried out as well. Afterwards, the eluted solutions were diluted 10-times with Milli-Q water, and filtered through a 0.45 μm syringe filter if necessary.
2.7. Binding of U into diffusive layer

A possibility of interactions between U and polyacrylamide (APA) diffusive gel was assessed by a batch method over the pH range of 3–9 and for a period of 2, 6, 10, 24 and 48 h. A diffusive gel disc was submerged in 5 mL of 20 μg U L⁻¹ solution (0.01 M NaNO₃) at pH 7.0 ± 0.2. After shaking for a period of 2, 6, 10, 24 and 48 h, a gel disc was transferred into new vials and U on diffusive gel disc was eluted in 0.1 M HNO₃. Likewise, the same procedure was applied over the pH range of 3–9 for the deployment time of 48 h.

2.8. The effect of pH on DGT uptake

In order to study the pH effect on DGT uptake, DGT samplers were deployed in 2 L well-mixed 20 μg U L⁻¹ U solution (0.01 M NaNO₃) over the pH range of 3–9 for a period of 2, 6, 10, 24 and 48 h, at room temperature. Before DGT deployment, the experiment solutions were stirred vigorously for at least 24 h in order to enable inorganic carbon in solution equilibrate with atmospheric CO₂. Additionally, for the deployment solution at pH 7.0 ± 0.2, after the vials were shaken for 48 h, binding layers were transferred into the new vials and the elution procedures for each binding phase described in Section 2.6 were followed. The capacity measurement of each binding phase was conducted in duplicate.

2.9. Diffusion coefficients of U species over the pH range

Diffusion coefficient (D, cm² s⁻¹) of U at each pH was calculated using the slope of the linear regression of the measured mass accumulation of U as a function of time (Fig. S5). Following equation was used Eq. (2):

\[ D = \frac{\alpha \Delta g}{A C} \]  

where \( \alpha \) is the slope of the linear regression of U accumulation on a binding phase gel disc over time; \( C \) is the U concentration in the solution; \( \Delta g \) is the thickness of the diffusion layer (cm) and A is the exposure area of DGT sampler (cm²). All diffusion coefficients were corrected for the temperature (T) using Stokes-Einstein equation [7].

2.9.1. The diffusion cell

The procedure for estimation of diffusion coefficients (Dcell) in polyacrylamide gels using a diffusion cell is described in detail elsewhere [26]. The diffusion cell comprised two 250 mL Plexiglas compartments, which are interconnected by a 1.5 cm diameter opening window. A 2.5 cm diameter polyacrylamide gel disc (\( \Delta g = 0.8 \) mm) and cellulose nitrate filter membrane (\( \Delta g = 0.17 \) mm) were placed between the opening windows of two compartments. Both, the source (1 mg L⁻¹ U; 0.01 M NaNO₃) and the receptor (0.01 M NaNO₃) solutions were stirred vigorously for at least 24 h prior the experiment and at pH 7.0 ± 0.2, a small quantity of NaHCO₃ was added into the carrier solutions in order to maintain stable pH. The diffusion cell compartments were stirred continuously with an overhead stirrer. Each compartment was filled in with 180 mL of appropriate carrier solutions; thereafter the subsamples of 0.5 mL were taken from each compartment every 15 min for up to 5 h.

2.10. The effect of ionic strength on DGT uptake

In order to test the effect of ionic strength on DGT uptake, U accumulation on binding phase gel disc was studied in solutions containing 20 μg U L⁻¹ U at pH 7.0 ± 0.2 with various concentrations of NaNO₃ (0.001, 0.01, 0.1, 0.4 and 0.7 M). The ionic strengths in the testing solution were within the range of those encountered in the environment. DGT samplers consisting of different binding phase gels were deployed in duplicate for 10, 24 and 48 h and after that period, they were removed and the elution procedures as per Section 2.6 were followed.

2.11. Uptake capacity of uranium on Chelex®-100, Metsorb™ and Diphonix® gels

The uptake capacity of U of each binding phase gel was assessed in this study. A single gel disc of each binding phase was immersed in 5 mL of solutions containing various concentrations of U (0.02–500 mg L⁻¹) at pH 5.0 ± 0.2. After the vials were shaken for 48 h, binding layers were transferred into the new vials and the elution procedures for each binding phase described in Section 2.6 were followed. The capacity measurement of each binding phase was conducted in duplicate.

2.12. Interferences effect on DGT uptake

The interference effects of calcium (Ca²⁺), phosphates (PO₄³⁻), sulphates (SO₄²⁻) and bicarbonates (HCO₃⁻) on DGT uptake were studied. Interference solution concentrations were selected for analytical and experimental convenience and to represent different water conditions, taking into account extreme mining impacted environments. DGT samplers consisting of each binding phase gel disc were deployed in triplicate in solutions containing 20 μg L⁻¹ U (0.01 M NaNO₃) and various concentrations of Ca²⁺, PO₄³⁻, HCO₃⁻ at pH 6.4 ± 0.1 and SO₄²⁻ at pH 4.0 ± 0.1 (Table S2 in SI). Piperazine-N, N’-bis (2-ethanesulfonic acid) (PIPES) with pKₐ 20 °C = 6.8 was used to make a buffer solution, which was added afterwards to the U solution to maintain the pH of 6.4 ± 0.1. PIPES is one of Good’s 3 non-complexing buffer and it has been chosen due to negligible metal binding abilities [31–34]. Each type of DGT sampler was removed every 12 h and followed the same elution procedures as described above.

3. Results and discussion

3.1. Binding phase gel blanks and DGT detection limits

Table 1 presents the average DGT blank values of Chelex®-100, Metsorb™ and Diphonix® binding phase gels and the method detection limits (MDL) based on 15 replicates measurement of each resin/adsorbent. A comparison with literature values is also included. The MDL obtained for Diphonix® resin gel is in line with the values of Chelex®-100 and Metsorb™ binding phase gels. Those results indicate that DGT containing Diphonix® resin gel discs is suitable for ultra-trace analysis of uranium as a conventional Chelex®-100 resin. Furthermore, the MDL values of Chelex®-100, Metsorb™ and Diphonix® binding phase gels obtained in this study are much lower than the levels encountered under the field conditions. Garmo et al. [9] used 21 DGT samplers packed with Chelex®-100 resin gel supplied by the DGT manufacturer, who has higher level of clean lab, therefore the average blank value and the MDL reported were much lower than the values in this study (0.04 ± 0.01 ng per gel disc and 0.003 μg U L⁻¹, respectively). Part of the difference, in our results and in the study of Garmo et al. [9], is also likely due to different diffusion coefficient of uranium used for the DGT calculations. Turner et al. [24,25] reported higher values for the average blank values and the MDL of Chelex®-100, Metsorb™ and Diphonix® binding phase gels than those stated here (Table 1). Most likely, higher MDL values are attributed to the fact that gel
preparation procedures were not handled under the class-100 clean bench conditions. In case of Diphonix® resin gel, the impact of this characteristic is even more profound as the resin is left to air dry for 2 h before gel preparation.

3.2. Uptake and elution efficiency

The U uptake on each binding phase was determined following the procedure described by Zhang and Davison[7] taking into account the U mass balance before and after resin/adsorbent gel discs immersion. The uptake of U on Chelex®-100 resin gel was 94.9 ± 1.3% and on Metsorb™ adsorbent gel was 96.3 ± 1.2%. The U accumulation on Diphonix® resin gel was 97.4 ± 1.5%. Control experiment showed no sorption of uranium into the walls of the vials.

Elution efficiency was calculated from the ratio of mass of uranium eluted from the resin/adsorbent gel disc and the mass of uranium accumulated on the binding phase gel disc. An elution efficiency of 83.2 ± 2.0% was obtained when using 1 M HNO3 for Chelex®-100 resin gel, what was either in concordance to previously reported results or slightly better [24,35]. For Metsorb™ adsorbent gel, an elution efficiency of 79.5 ± 4.3% was obtained when using 1 M HNO3 as eluent, while an improvement has been observed with the value of 98.4 ± 2.2% when using 1 M NaOH/H2O2. It has been reported by Hutchins et al.[13] that the addition of H2O2 enhances the elution efficiency due to re-oxidation of the peroxide. These results confirmed that the elution efficiency of Metsorb™ using NaOH/H2O2 is much better than the one previously reported [13,25]. However, since sodium is a suppressor of ICP-MS signal, 1 M HNO3 was designated as the eluent for Metsorb™ adsorbent gel for further experiments, even though a better elution efficiency can be obtained with NaOH/H2O2. Several elution procedures for Diphonix® resin gel were examined using 1 M HNO3, 1 M NaOH and HNO3/NaCl at 70 °C, yet it only resulted in the elution efficiencies below 30% when using all abovementioned eluents. The present results appear to be in disagreement with those reported by Turner et al.[25], who obtained an elution efficiency of 90% when using a mixture of 1 M NaOH/1 M H2O2. This difference may be due to the addition of H2O2 into the 1 M NaOH eluent solution and/or interferences caused by the mixing of the basic extracts with the acidic internal standard and carrier solution. In this study, the implementation of 1 M 1-hydroxyethane-1, 1-diphosphonic acid (HEDPA) as eluent gave the elution efficiency of 79.6 ± 4.2%. Consequently, this eluent was selected for U elution from Diphonix® resin gels for the following work. This confirms that uranium species are so strongly retained by the Diphonix® resin that the only effective eluent is the one, which contains the same ligand group as the resin. It also signposts very good performance of Diphonix® resin in very acidic conditions [20].

3.3. Binding of U into diffusive layer

It is essential to establish whether there is any binding of U on the APA diffusive layer as it could bias the measurement. Hutchins et al.[13], Li et al.[35] and Gregusova et al. suggested that there are some weak interactions between uranium and the traces of acrylic acid groups of the APA diffusive gel. Nevertheless, neither pH nor deployment time effect on U uptake on the APA diffusive layer was observed in this study, indicating that there is no significant interaction between U species and APA diffusion layer (Figs. S1 and S2 in SI).

3.4. The effect of pH on DGT uptake

The equilibration of the solution with atmospheric CO2 for 24 h and the addition of sodium bicarbonate were necessary to avoid U sorption on the containers walls and thus obtain consistent and reliable results (Figs. S3 and S4 in SI). A control experiment showed that at pH 6–8 about 25–30% of uranium is likely being absorbed to the walls of the plastic containers. In turn, when 24 h equilibration with atmospheric CO2 and the addition of NaHCO3 is introduced, no change of the U concentration in experiment solutions has been encountered [13,25,35]. These results illustrate that NaHCO3 has a function of stabilization of uranium in a solution through the formation of uranyl carbonates.

The mass of U accumulation on each binding phase gel disc showed a good correlation with the deployment time (R² > 0.99) over the pH range. This implies that each binding phase fulfills the criteria and assumptions of DGT equation over a wide pH range (3–9) in simple matrices (Eq. (1)). This is also the case of Diphonix® (Fig. S5 in SI), what is in concordance with Turner et al.[25], despite the different preparation and elution procedures implemented. The DGT measured concentrations of uranium (CdGT) were compared to the solution concentration of uranium (Csol), in order to study the pH effect on U uptake for each resin. The majority of the results obtained in this study falls within the ratio CdGT/Csol of 1.0 ± 0.1, indicating a quantitative measurement (Fig. 2). The accumulation of uranium species on the binding phase gels did not vary across the

<table>
<thead>
<tr>
<th>Binding phase</th>
<th>MDL (µg U L⁻¹)</th>
<th>Mean ± SD (ng U/gel disc)</th>
<th>References</th>
<th>MDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chelex®-100</td>
<td>0.003</td>
<td>0.04 ± 0.01</td>
<td>0.06 ± 0.003 ng U/gel disc [24]</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.0008 ± 0.0005 µg U L⁻¹ [9]</td>
<td></td>
</tr>
<tr>
<td>Metsorb™</td>
<td>0.003</td>
<td>0.03 ± 0.01</td>
<td>0.03 ± 0.02 ng U/gel disc [24]</td>
<td></td>
</tr>
<tr>
<td>Diphonix®</td>
<td>0.002</td>
<td>0.03 ± 0.01</td>
<td>0.79 ± 0.08 ng U/gel disc [25]</td>
<td></td>
</tr>
</tbody>
</table>
pH range of 3–9, except for Chelex®-100, which gave a value of 0.83 ± 0.03 for the ratio of $C_{DGT}/C_{sol}$ at pH 9. The U species and relative percentage distribution, which are present in the deployment solutions, are shown in Fig. 3.

It can be projected that some differences in the adsorption rate as a function of pH, both within and between the binding phases, might occur. This might be caused by the distribution of U species or/and by the functional properties of binding layers [9]. The structure of iminodiacetate (IDA) groups of Chelex®-100 resin changes over the pH range [7]. At pH range 2–4 the resin acts as an anion exchanger, therefore the U accumulation on the resin might decrease as Chelex®-100 is less reactive to the dominant U species in the solution (i.e. $UO_2^{2+}$), yet this was not found in this study [35]. At pH above 6, since the predominant U species are in anionic or neutral forms, a weaker and/or slower adsorption into the negatively charged carboxylic groups of Chelex®-100 might be observed. Therefore, it is most probable that at pH 9, a non-quantitative U uptake on Chelex®-100 (Fig. 2) was attributed to the prohibition of access of U species (i.e. $UO_2(CO_3)_2^{4-}$ and $UO_2(CO_3)_2^{2-}$) into the binding sites of resin. Metsorb™ contains titanium dioxide, with electroneutral hydroxyl groups on the surface, which interacts with uranyl species via surface complexion [17]. The point of zero charge of TiO2 occurs at pH 5.5–6.3, so under acidic conditions, the uptake of U species (i.e. $UO_2^{2+}$) might be impaired due to the electrostatic repulsion [36,37]. Likewise, a diminished U uptake might occur at alkaline pH, when negatively charged uranyl carboxylates species play a predominant role in a solution and hydroxyl groups of Metsorb™ resin are deprotonated [38]. The most remarkable feature of Diphonix® resin is its very high selectivity towards U species, especially under very acidic conditions [20]. The diphosphonic acid groups chelate positively charged uranyl species via either negatively charged ionized or through hydrogen bonding with neutral diphosphonic acid groups (i.e. via metal coordination to P=O groups) [39]. At circumeutral pH, the gem-diphosphonate groups can dissociate the uranyl species; hence the neutral U species should be still sorbed, although less efficiently than the positively charged complexes [40,41]. The uptake of negatively charged uranyl carboxylates species into the cationic exchange resin is likely to be significantly suppressed because of the Donnan potential [39,40].

This study demonstrates that there is no effect of pH on the U uptake either on Metsorb™ or on Diphonix®, indicating that those binding phases exhibit very high affinity towards U regardless the U species present in the solution. The U uptake is rapid and quantitative over the pH range irrespectively of the mechanism of the binding of a resin/adsorbent.

3.5. Diffusion coefficients of U species over the pH range

Table 2 presents the diffusion coefficients of U species at different pH by the diffusion cell experiment (Dcell) and based on the calculations of U mass accumulation on different types of DGTs containing Chelex®-100, Metsorb™ and Diphonix® gels (D=DGT). Along with the results obtained in this study, the U diffusion coefficients reported by other authors, the ones in aqueous solutions given in the literature (Dwa) and the U species distribution in the experiment solution are shown for the comparison.

The average of the effective diffusion coefficient obtained in this study at 25 °C was $4.40 ± 0.22 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$. No effect of pH, thus no effect of U species present in the solution, on the effective U diffusion coefficient can be observed. Within the pH range of 3–9 the $D_{DGT}$ estimated in this study are in general agreement with those reported before, however some minor discrepancies can be observed [9,13,35]. Those differences might be associated with a variation of the composition of the deployment solutions, a variation of pH, mass of U accumulated on DGT samplers consisting of different binding phase gels or the precision and accuracy of the method itself.

Hutchins et al. [13] reported increasing trend of the effective diffusion coefficients obtained by Metsorb™-DGT deployments at pH 3–5 (i.e. $2.67 ± 0.14 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ and $4.53 ± 0.27 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ at pH 3 and 5, respectively), but this was not observed in this study. At the range of pH 5–7, neutral and anionic U species (i.e. $UO_2CO_3$ and $UO_2(CO_3)_2^{2-}$) play a leading role and the averaged effective diffusion coefficients were $3.97 ± 0.16 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ and $4.54 ± 0.40 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ at pH 5 and pH 6 respectively. Similar findings were presented by Gregusova et al. [23], who stated an effective U diffusion coefficient of $4.39 ± 0.08 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ at pH 6.4. In contrast, Garmo et al. [9] reported the effective U diffusion coefficient of $4.7 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ and $3.4 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ at pH 5.0 and 5.9 respectively. Garmo et al. [9] indicated that DGT method provides rather an effective diffusion coefficients of solutes, as it includes not only diffusion of species through diffusive layer and membrane filter but also takes binding abilities of binding agent into account. Therefore, it can be expected that a variation of the effective U diffusion coefficients of U species over the pH range.
The diffusion coefficients ($D_{\text{DGT}}$) over pH range might appear, due to both, distribution of U species and to the properties of binding phases [9]. However, this was not observed in this study, as there is a very good agreement between $D_{\text{DGT}}$ values obtained by different types of DGTs, thus indicating that the ligand exchange between U and binding phase is very rapid regarding the binding mechanism of a resin/adsortent.

The diffusive coefficients of U species ($D_{\text{cell}}$) are in excellent agreement with the study of Li et al. [35]. Moreover, the $D_{\text{cell}}$ is very well correlated with $D_w$ for UO$_2^{2+}$ [42–47]. On the other hand, there is a significant discrepancy between the $D_{\text{cell}}$ and $D_w$ for UO$_2$CO$_3^{2-}$, however this $D_w$ value is established based only on molecular dynamics simulations [45]. Up to date, no other experimental values for other U species than UO$_2^{2+}$ are determined due to co-occurring of various U species under most of experimental conditions (Fig. 3) [30]. There is a clear trend of increasing $D_{\text{cell}}$ over the pH range due to the distribution of the uranium species. The relation of the diffusion coefficient with U species distribution can be explained by the Stokes Einstein equation, hence such a decreasing $D_{\text{cell}}$ trend with increasing radius of U species is anticipated [45,48].

It is assumed that the most accurate and precise results of diffusive coefficients in polyacrylamide (APA) gel can be obtained by using diffusion cell measurements [26]. However, the results depicted in Table 2 raise the question of the applicability of $D_{\text{cell}}$ into the U-DGT calculations, as the $D_{\text{DGT}}$ of U species do not correspond to $D_{\text{cell}}$ of U species over the pH range. It seems that in case of relatively large and strong U complexes, the differences between the processes occurring in the diffusion cell and in DGT experiment has significant impact of the diffusion coefficient of U species estimated by each method. The effective U diffusion coefficient ($D_{\text{DGT}}$) is significantly lower than $D_{\text{cell}}$ values at pH 3–4, when UO$_2^{2+}$ prevails. At higher pH values, the binding phase is inducing the dissociation of the neutral and negatively charged uranyl carbonate species present in the solution into UO$_2^{2-}$. Most likely, in diffusion cell experiment UO$_2^{2-}$ is bound to excess dissolved CO$_2$ and then diffuses through the diffusive layer without the dissociation, thus much slower that UO$_2^{2+}$ [49,50]. This can be particularly observed at pH 9 where UO$_2$(CO$_3$)$_2^{4-}$ ($\log K = -9.14$) dominates and the ratio $D_{\text{DGT}}$ to $D_{\text{cell}}$ is 2.23. Observed discrepancies between the D values obtained by a diffusion cell and the DGT time-series have been found also by other authors [14,49–51]. Therefore, it is recommended to apply $D_{\text{DGT}}$ into the U-DGT calculation rather than $D_{\text{cell}}$ as the effective U diffusion coefficient more accurately mirrors the mass transport and binding ability of the binding phase.

### 3.6. The effect of ionic strength on DGT uptake

The ratio of DGT measured U concentration ($C_{\text{DGT}}$) to U concentration in solution ($C_{\text{sol}}$) is plotted versus the ionic strength (Fig. S6 in SI). At all ionic strengths there was a good agreement between U concentration measured by DGT and the U concentration in the solutions. Only at NaNO$_3$ concentration of 0.7 M, the ratio of $C_{\text{DGT}}$/$C_{\text{sol}}$ decreased to 0.81 ± 0.04 for Chelex®–100 resin. This is still in an agreement or even higher than the results reported previously [35]. This is probably caused by the prevalent anionic U species under those conditions and/or by the competition of other ions (i.e. Na$^+$ and NO$_3^-$) for the binding sites of the resin [11]. There is no appreciable dependency of U accumulated on Metsorb$^\text{TM}$-DGT on the ionic strength of the deployment solution, what was reported by Turner et al. [24]. Alternatively, Hutchins et al. [13] reported the $C_{\text{DGT}}$/$C_{\text{sol}}$ ratio value of 0.82 and 0.76 for Metsorb$^\text{TM}$-DGT at ionic strengths of 0.1 M and 0.7 M NaNO$_3$ respectively. The uptake of U on Diphonix$^\text{®}$ resin gel was unaffected by increasing ionic strength. These results suggest the DGT technique using Diphonix$^\text{®}$ resin gel discs can be even used for the seawater deployments, but this needs to be confirmed in the field.

### 3.7. Uptake capacity of uranium on Chelex®–100, Metsorb$^\text{TM}$ and Diphonix$^\text{®}$ gels

The aim of the capacity test is to assess the maximum time of deployment or maximum amount of U that can be bound to a resin/adsortent gel [7]. If the capacity of the binding phase is reached during the DGT deployment, it might lead to the serious underestimation of the concentration measured by DGT. This is especially important in the mining impacted environments, where the concentrations of many metals are elevated, thus the threat of reaching the capacity of binding layer is real. Fig. 4 shows the mass of U accumulation on the binding phase gel disc as a function of the U spike. The most striking feature is the extremely high binding capacity towards uranium displayed by Diphonix$^\text{®}$ resin gel. Even though the U spike was 2500 μg, the saturation was not achieved on the Diphonix$^\text{®}$ gel disc (~0.0075 g resin cm$^{-2}$ of gel disc). This means that even with loading of 10.5 μmol U, a Diphonix$^\text{®}$ gel disc is still not saturated. Clearly, Diphonix$^\text{®}$ resin gel exhibits the highest capacity, thus has better potential to be used in highly
contaminated, mining-impacted environments for long term deployments. In this study, both Chelex®-100 resin and Metsorb™ binding agents exhibited maximum capacity of 1.05 µmol U per gel disc. Up to date, these results are the first data with regard to U capacity of Chelex®-100 and Metsorb™ gels. It has been described that the elution efficiencies might be dependent on the amount of metal bound on the binding phase gel disc [52]. Nevertheless, in this study the elution efficiencies were independent of the U bound on Chelex®-100, Metsorb™ and Diphonix™ gel discs, over experimental U mass range.

3.8. Interferences effect on DGT uptake

Uranium exhibits an extreme affinity to form uranyl carbonates at near neutral pH (OH\(^{-}\) > CO\(_3\)\(^{2-}\) > HPO\(_4\)\(^{2-}\) > H\(_2\)PO\(_4\) > F\(^{-}\) > SO\(_4\)\(^{2-}\) > Cl\(^{-}\)) [53]. Even small amount of bicarbonate buffer would significantly affect the speciation distribution, thus PIPES buffer was implemented in this set of experiments in order to stabilize the deployment solution [54].

It has been reported, among others, by Bernhard et al. [55] and Dong and Brooks [56] that calcium uranyl carbonates complexes play a prominent role in uranium impacted waters characterized by relevant contents of calcium and carbonates at near neutral pH. Therefore, it was of a great relevance for this study to investigate the performance of DGT technique in presence of Ca\(^{2+}\)-U complexes. Both Chelex®-100- and Metsorb™-DGT produced quantitative measurements at 0.27–2.66 × 10\(^{-5}\) M Ca\(^{2+}\) (log 2 and log 3 respectively shown in Fig. 5). The U uptake on Chelex®-100- and Metsorb™-DGT decreased at very high Ca\(^{2+}\) concentration (log 5.7) to 67.1 ± 2.8% and 71.1 ± 4.5%, respectively. This is assumedly associated with the competition for the binding sites between uranium and calcium ions. Under those conditions, approximately 100% of the U in deployment solution occurs as Ca\(_2\)UO\(_2\)(CO\(_3\))\(_2\)\(^{2-}\) and 97% of the Ca is expected to be present as the free metal ion Ca\(^{2+}\). The increasing Ca\(^{2+}\) concentration did not affect U uptake on Diphonix-DGT over a wide Ca\(^{2+}\) concentration range, which is in agreement with Turner et al. [25]. It seems that the competition effects of Ca\(^{2+}\) even at very high Ca\(^{2+}\) concentration are negligible, probably due to the extreme affinity of Diphonix™ functional groups towards uranium species and superior ability to extract uranium species from a high-salt concentrations [57,58].

At pH range 6–9 in aqueous environment, U(VI) phosphate complexes will dominate, only if the total concentration ratio of [PO\(_4\)\(^{3-}\)/CO\(_3\)\(^{2-}\)] is greater than 10\(^{-1}\), thus in some uranium milling and mining environments and in areas of phosphate industry [59]. Fig. 57 showed a quantitative adsorption of uranium species on Chelex®-100- and Metsorb™-DGT at PO\(_4\)\(^{3-}\) concentration of 0.34–5.16 × 10\(^{-5}\) M (log 2 and log 3.2 respectively). In the presence of very high PO\(_4\)\(^{3-}\) concentration (i.e. 1.72 × 10\(^{-4}\) M; log 3.7), the U uptake on Chelex®-100- and Metsorb™-DGT was appreciably lessened (75.3 ± 1.4% and 60.9 ± 4.1%, respectively). Under those conditions, the dominant U species were uranyl phosphate complexes UO\(_2\)PO\(_4\)\(^{2-}\) and UO\(_2\)HPO\(_4\)\(^{3-}\), as the ratio of [PO\(_4\)\(^{3-}\)]\(_T\)/[CO\(_3\)\(^{2-}\)]\(_T\) was 0.3. This U uptake diminution in the presence of a greater PO\(_4\)\(^{3-}\) concentration is presumably a consequence of the direct competition for the binding sites between uranium phosphate complexes and dihydrogen phosphate ion [19,58]. The greater impact of increasing PO\(_4\)\(^{3-}\) concentration on the performance of Metsorb™-DGT is most likely due to the fact that Metsorb™ adsorbent was successfully used beforehand for the measurement of the dissolved reactive phosphorus in an aqueous solution [14,60]. The U uptake on the Diphonix™-DGT was quantitative over experimental PO\(_4\)\(^{3-}\) concentration range.

It is also noteworthy that small, but significant decrease in U concentration at high PO\(_4\)\(^{3-}\) concentrations has been observed, which is most likely attributed to the precipitation of U. Uranyl phosphate complexes are extremely insoluble under circumneutral pH conditions (e.g. the calculated saturation index of (UO\(_2\))(PO\(_4\))\(_2\)·4H\(_2\)O was 0.22 at 5.16 × 10\(^{-5}\) M PO\(_4\)\(^{3-}\)) [61].

Only at low pH in sulphates-containing environments, the uranyl sulphates complex comprises a dominant species. Above pH 6, UO\(_2\)SO\(_4\) is considered negligible, as uranium has a higher propensity to form carbonates complexes with dissolved CO\(_2\). Therefore operational pH of 4 and very high SO\(_4\)\(^{2-}\) concentrations have been chosen for this set of experiment to ensure that UO\(_2\)SO\(_4\) prevails in the deployment solution. Another aim was to mimic, to some extent, the acid sulphates-rich mine drainage waters and to evaluate the performance of DGT technique in a simple lab matrix before a field deployment. Quantitative U uptake was obtained for Chelex®-100- and Metsorb™-DGT at SO\(_4\)\(^{2-}\) concentration of 0.11–5.55 × 10\(^{-5}\) M (log 3-log 4.7), while at 4.44 × 10\(^{-3}\) M of SO\(_4\)\(^{2-}\), it dropped to 54.0 ± 0.7% and 70.4 ± 3.4%, respectively (Fig. 6). It is likely that this diminished uptake value for both, Chelex®-100- and Metsorb™-DGT, is related to the decrease in UO\(_2\)OH\(^{+}\) species and concurrent increase in UO\(_2\)SO\(_4\). It seems that the performance of Chelex®-100- and Metsorb™-DGT was not disturbed by low pH. Diphonix™-DGT quantitatively accumulated U species, over experimental SO\(_4\)\(^{2-}\) concentration range.

The speciation distribution and the mobility of U(VI) in aquatic environment are mostly controlled by the formation of uranyl carbonate complexes under neutral and alkaline conditions. It was vital to assess whether increasing HCO\(_3\)\(^{-}\) concentration has any interference effect on the performance of DGT technique. Only at the lowest HCO\(_3\)\(^{-}\) concentration, a quantitative U uptake was observed for Chelex®-100- and Metsorb™-DGT, while it dropped to approximately 75% for both Chelex®-100- and Metsorb™-DGT at 0.82–8.20 × 10\(^{-3}\) M HCO\(_3\)\(^{-}\) concentration (log 4.7-log 5.7). Similar diminution of U uptake on Chelex®-100- and Metsorb™-DGT with increasing HCO\(_3\)\(^{-}\) concentration has been observed by Gregusova et al. [23] and Turner et al. [24]. Increasing HCO\(_3\)\(^{-}\) concentration influences the U species distribution in a deployment solution, as at carbonates concentration above 30 mg L\(^{-1}\), UO\(_2\)(CO\(_3\))\(^{2-}\) starts to predominate and UO\(_2\)(OH)\(^{+}\) and UO\(_2\)(OH)\(_2\) become inferior (Fig. 58). Likewise, the U species distribution and the possible competition with NaCO\(_3\) and HCO\(_3\)\(^{-}\) for the binding sites, may account for the significant mitigation of the performance of Chelex®-100- and Metsorb™-DGT [62]. No effect of increasing HCO\(_3\)\(^{-}\) concentration on U uptake on Diphonix™-DGT was found over experimental concentration range studied, which is in accordance with the observation of Turner et al. [25]. It seems that the Diphonix™ resin affinity towards U is strong enough to suppress the influence of elevated levels of calcium, phosphates, sulphates and bicarbonates.
4. Conclusions and perspectives

This comprehensive study provides an insight on the feasibility of the DGT technique for the estimation of dissolved U concentration in mining impacted environments. The application of Chelex®-100, Metsorb™ and Diphonix® binding agents allows assessing the U concentration even in the environments with elevated U levels, like those impacted by uranium mining. Laboratory investigation has demonstrated that all three binding phases produced quantitative U measurements across the environmentally relevant range of pH and ionic strength. The performance of DGT-Chelex®-100 has been hampered at alkaline pH and at high ionic strength (0.7 M NaNO₃). A diminished U uptake on DGT-Chelex®-100 and DGT-Metsorb™ was observed at high and at very high concentrations of Ca²⁺, PO₄³⁻, SO₄²⁻, HCO₃⁻, most likely as a result of a competition for the binding sites and/or U species distribution. Neither pH nor ionic strength nor even high concentrations of Ca²⁺, PO₄³⁻, SO₄²⁻, HCO₃⁻ effects on the U uptake have been observed. Moreover, Diphonix® resin gel displays an extremely high U binding capacity. Clearly, the DGT-Diphonix® technique described in this study has considerable advantages over DGT-Chelex®-100 and DGT-Metsorb™. The use of Diphonix® resin leads to a significant advance in the application and development of DGT technique for determination of U in uranium mining impacted environments.

For the first time an extensive investigation on the diffusion coefficients of uranium species over the pH range using both, a diffusion cell and the DGT time-series, has been conducted. No good correlation between two methods has been found, suggesting that different processes occur in a diffusion cell and in a DGT device. The effective diffusion coefficients of U species are neither pH- nor binding phase-dependent, suggesting that U uptake on each binding layer is rapid and quantitative regardless the functional groups of each binding phase and U species present in a solution. We recommend the implementation of the effective diffusion coefficient into DGT calculations to ameliorate the accuracy and reliability of DGT measurement.

Future work is required to investigate the performance of the Chelex®-100, Metsorb™ and Diphonix® resins in DGT technique under the field conditions, both in uranium impacted and natural environments. Taken that Diphonix® is known to be selective not only for uranium, but also for a range of elements such as Sr, Ra, Al or Fe, future research should gauge the suitability of DGT technique with Diphonix® resin for a wide range of analytes. This would lead to more comprehensive understanding of competitive uptake of co-adsorbing analytes and their influence on the performance of Diphonix® resin.

Fig. 5. (A) The effect of Ca²⁺ on U uptake on Chelex®-100 (■), Metsorb™ (■■) and Diphonix® (▲-▲) DGTs. The solid and dotted horizontal lines represent target values 1 ± 0.1. (B) Speciation of U(VI) in the deployment solution modelled with Phreeqc program. Only major U species displayed: [U] = 20 μg L⁻¹; [Ca²⁺] = 2.66 × 10⁻⁶–1.33 × 10⁻³ M; [NaNO₃] = 0.01 M; [PIPES] = 0.03 M; pH = 6.4 ± 0.1; deployment time = 48 h; D_DGT = 4.40 ± 0.22 × 10⁻⁷ cm² s⁻¹ (25 °C); mean ± standard deviation; n = 3.
Acknowledgements

We acknowledge AREVA Mines France for funding this project. We thank the Hercules Foundation for financing the ICP-SF-MS instrument (UABR/11/010). Furthermore the authors thank Graver Technologies (www.gravertech.com) for providing the Metsorb™ adsorbent. Professor W. Baeyens is gratefully acknowledged for helpful comments and assistance.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.aca.2015.07.057.

Fig. 6. (A) The effect of SO4\(^{2-}\) on U uptake on Chelex\(^{®}\)-100 ( ), Metsorb™ (■) and Diphonix\(^{®}\) (-●-) DGTs. The solid and dotted horizontal lines represent target values 1 ± 0.1. (B) Speciation of U(VI) in the deployment solution modelled with PhreeQC program. Only major U species displayed. [U] = 20 µg L\(^{-1}\), [SO4\(^{2-}\)] = 1.11 × 10\(^{-4}\)–4.44 × 10\(^{-5}\) M; [NaNO\(_3\)] = 0.01 M; pH = 4.0 ± 0.1; deployment time = 48 h; DDGT = 4.40 ± 0.22 × 10\(^{-6}\) cm\(^2\) s\(^{-1}\) (25 °C); mean ± standard deviation; n = 3.

References
