

Development of a novel DGT binding layer for simultaneous measurements of anions and cations



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1. Zusammenfassung

DGT (Diffusionsgradienten in Dünnschichten) ist eine relativ neue Technik, die 1994 von Davison und Zhang eingeführt (entwickelt) wurde und wegen ihrer Einfachheit und vielfältigen Anwendungsmöglichkeiten weit verbreitet ist. Sie basiert auf der quantitativen Diffusion gelöster Stoffe durch eine dünne Schicht eines Hydrogels. Ionen, die durch diese dünne Schicht diffundieren, werden rasch an ein Ionentauscherharz adsorbiert. Das Harz wird mit einer Diffusionsgelschicht bedeckt und durch einen Membranfilter vom Außenmedium getrennt. Das am häufigsten verwendete Gel zur Kationenbindung ist Chelex-100.

Ziel dieser Arbeit war, ein DGT-Gel zu entwickeln, das sowohl Kationen als auch Anionen binden kann. Dazu wurden anionenadsorbierende Mineralien (Pulver von Anatas, Rutil und Lanthanhydroxid) mit Chelex-100 gemischt und die Anionensorptionseigenschaften sowohl der reinen Zusatzstoffe als auch der Mischungen untersucht.

Alle reinen Mineralien hatten sehr gute Anionensorptionseigenschaften, bei Lanthan-Chelex-Komplexen und Rutil-Chelex-Mischungen nahm die Anionensorption deutlich ab. Nur Anatas und Lanthanhydroxid zeigten auch in der Mischung mit Chelex-100 sehr gute Anionenadsorption.

2. Abstract

Diffusive Gradients in Thin films (DGT) is a relatively recent technique that was introduced by Davison and Zhang in 1994. The DGT technique is widely used because of its simplicity and wide applicability. It is based on the quantitative diffusive transport of solutes through a thin layer of hydrogel. Ions that pass through the diffusive layer are rapidly immobilised on an ion resin. A layer of resin gel is covered by a layer of diffusive gel separated from the outer medium by a membrane filter. Chelex-100 is the most used as ion exchange resin in DGT for cation binding whereas iron oxides have been employed for anionic species such as phosphate or arsenate.

The objective of this work was to develop a DGT resin-gel that is able to bind cations and anions in a single assay. The first strategy was to develop a novel DGT gel by modifying Chelex-100 resin. Anion-sorbing mineral powders (anatase, rutile and lanthanumhydroxide) were also tested. DGT gels with these minerals were made and investigated for their anion sorption characteristics.

All resins used in our experiments showed high affinity to adsorb anionic analytes when used as pure resins. Incorporation of La-loaded chelex as well as of rutile in DGT gels reduced their resins' sorption capability for anions. Anatase and lanthanumhydroxide, however, showed high affinities for anion sorption as both, pure powders as well as after incorporation in DGT gels.

3. Introduction

3.1. What is DGT?

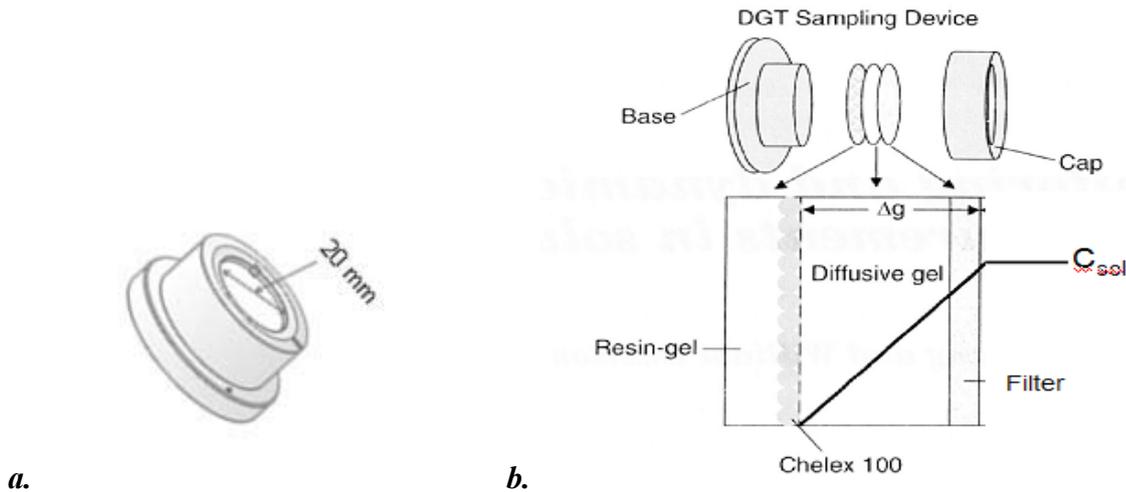
Diffusive Gradients in Thin films (DGT) is a relatively recent technique that was introduced by Davison and Zhang (Davison & Zhang, 1994) in 1994. Since then it has been used to measure analyte concentrations in waters, sediments and soils, as a tool to determine analyte speciation and the bioavailability of solutes. The DGT technique is widely used because of its simplicity and wide applicability. It is based on the quantitative diffusive transport of solutes through a thin layer of hydrogel. In DGT a diffusive hydrogel prepared from an acrylamide monomer that is cross-linked with a patented agarose derivative (Zhang, 2003) serves as a diffusive layer. They can be fabricated with a range of properties, including almost unimpeded diffusion due to the gel having water content as high as 95% (Zhang and Davison, 1999). This layer is usually 0.8 mm thick. Chemical species with molecular sizes smaller than the pore sizes of this hydrogel diffuse freely through the hydrogel. Several studies by Zhang et al. (Zhang and Davison, 2000; Zhang and Davison, 2001; Zhang, 2004) used hydrogels with different pore sizes.

The second important part of a DGT sampler is a hydrogel containing an ion resin that is able to bind (adsorb) analytes. Cations that pass through the diffusive layer are rapidly immobilised on the resin. Chelex-100* (which is selective for polyvalent transition metals) has been utilized as an cation exchange resin in DGT. In the early stages of DGT development the technique was characterized for the cationic metals Ni, Zn, Mn, Fe, Cu and Cd measurements (Zhang and Davison, 1995). By replacing Chelex-100 with alternative ion resins such as ferrihydrite, thiol-modified silica, Speron-Thiol and silver iodide, the range of analytes for DGT has been broadened (*see part 3.2. for detailed information*).

These gels are often used in the standard DGT sampling devices (supplied by DGT Research Ltd, Lancaster University, UK) which consist of a plastic base and top that can be welded together (*Picture 3.1.1*). A layer of resin gel is covered by a layer of diffusive gel separated from the outer medium by a membrane filter. This membrane filter contacts the outer medium through a 20 mm-diameter-window on the plastic top of the DGT device.

The space between a base and a top is ~1.34 mm (suitable for a 0.4 mm resin gel layer, a 0.8 mm diffusive gel layer and a 0.135 mm filter) in a DGT device (*Picture 1.a*). During deployment of the device in a solution, the analytes diffuse from the bulk solution through the diffusion layer and are adsorbed onto the binding layer. Thereby a concentration gradient develops in the diffusion layer (*Figure 1.b*).

* Chelex 100 is a chelating material from Bio-Rad used to purify other compounds via ion exchange. It is a styrene-divinylbenzene co-polymer containing iminodiacetic acid groups.



Picture 3.1.1. DGT-plastic sampling device: a. device is assembled, b. device is not assembled (Warnken et al., 2007)

The concentration at the medium-gel interface is close to the concentration in the sampled medium. The concentration in the binding layer is effectively zero. The concentration gradient is maintained as long as the binding layer is not saturated with analyte. The flux, J , through the diffusive layer can be described by Fick's first law of diffusion (Eq 1):

$$J = D \frac{dC}{dx} \quad \text{Eq. 1}$$

where D is the diffusion coefficient, C is the concentration and x the distance (and dC/dx the concentration gradient). DGT is a kinetic technique, which means that it actually directly measures a flux (e.g. $\mu\text{g cm}^{-2} \text{s}^{-1}$) of analytes into a DGT sampler. DGT requires various parameters in the DGT equation to be known accurately (Ryan et al., 2003). Diffusion coefficients* of each element can be taken from the manual of DGT Research Ltd (Zhang, 2003). Diffusional characteristics of hydrogels used in DGT technique were investigated by Zhang and Davison (Zhang and Davison, 1999) and the diffusive properties of hydrogels such as polyacrylamide gel are dependent on the concentration of the original monomer, the concentration and composition of the cross-linker, the amounts of initiator and catalyst used (Chramback, 1985).

Since diffusion is temperature dependent, D must be corrected to the actual deployment temperature, T (Zhang and Davison 1995):

$$\text{Log}D = \frac{1.37023(T - 25) + 8.36 * 10^{-4} (T - 25)^2}{109 + T} + \text{Log} \frac{D_{25}(273 + T)}{298} \quad \text{Eq. 2}$$

* It is determined experimentally and differs between analytes. In DGT research this coefficients are prepared by DGT Research Ltd mainly.

where D and D_{25} are the diffusion coefficients at the deployment temperature and at 25°C, respectively.

If Δg (Picture 1.b) is the thickness of the diffusive layer, the flux is given by the following:

$$J = D \frac{C}{\Delta g} \quad \text{Eq. 3}$$

After retrieval the analytes are eluted from the binding layer* and their masses of metal accumulated in the binding layer (M) are calculated using equation 4. :

$$M = C_e \frac{V_g + V_e}{f_e} \quad \text{Eq. 4}$$

C_e (Eq 4) is the measured concentration of the analyte in the eluate; V_g is the volume of the binding layer gel and V_e the volume of the eluent. f_e is the elution factor for each analyte, typically 0.8 for trace metals (Zhang, 2003). Knowing the accumulated mass (M) determined by a suitable analytical technique†, it is possible to calculate the average flux through the diffusion layer during the exposure time (t):

$$J = \frac{M}{A \times t} \quad \text{Eq. 5}$$

where A = exposure area.

Combining Equations 3 and 5 and rearranging gives the average concentration at the sampler-solution interface, C_{DGT} (Zhang, 2003):

$$C_{DGT} = \frac{M \Delta g}{D t A} \quad \text{Eq. 6}$$

Diffusion coefficient (D) of the analyte, as well as the deployment time (t) and temperature (T) are needed for the calculation of J and C_{DGT} .

An essential prerequisite of the DGT procedure is that there is no reaction between the gel used as diffusive layer and the measured solute(s). If this condition holds, when a simple diffusive gel is immersed in a solution, the concentration of the solute in the gel should, at equilibrium, be the same as the solute concentration in the solution (Chang et al. 1998).

* synonyms are: binding phase, resin-gel, resin-hydrogel

† e.g. colorimetry, ICP-MS, AAS etc.

Until today the technique has been applied on almost every continent by researchers from all over the world (e.g Antarctica: Larner et al. 2006; Asia: Aung et al. 2008; Australia: Warnken et al. 2004; Europe: Forsberg et al. 2006; North America: Balistrieri et al. 2007; South America: Wallner-Kersanach et al. 2009). *Figure 3.1.1* summarizes the DGT development of DGT technique (Oesterlund, 2010).

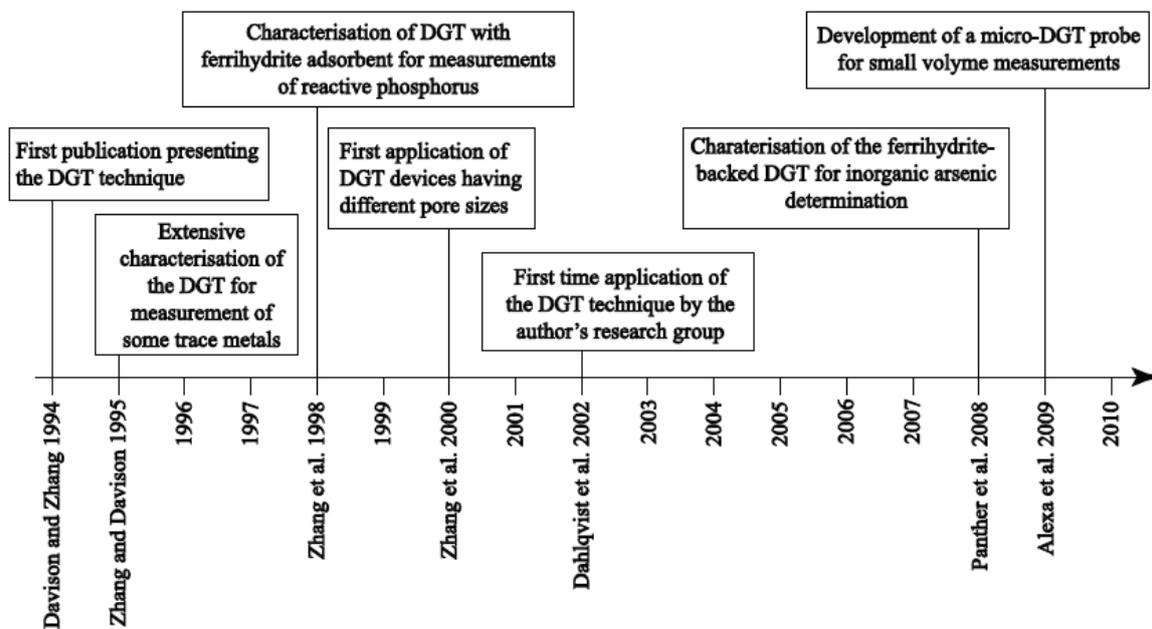


Figure 3.1.1. The development of DGT technique summarized by Oesterlund (2010)

3.2. Binding layers

As mentioned earlier, the solute diffuses through the diffusion layer prior to accumulation on a selective binding agent, which is chosen according to the solute that is to be measured. Most frequently, Chelex-100, a resin containing iminodiacetate functional groups, is used in DGT. It has been applied to measure a large number of divalent and trivalent metal ions. Garmo et al. (2003) investigated the applicability of Chelex 100 containing gels for 55 elements. Diffusion coefficients for these elements were determined by these authors using DGT. Applicability of Chelex 100 in DGT measurements was shown for the elements Pb, Zn, Co, Ni, Cu, Cd, Al, Mn, Ga, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Tb, Lu, and Y. An additional eight elements (Fe, Cr, Ba, Sr, U, V, Mo, and Ti) were, to some extent, also taken up by Chelex 100. *Table 3.2.1* summarizes the research on various binding layers of DGT.

Table 3.2.1 Some binding layers tested in DGT research

Analytes and purpose	Resin	Authors
Co, Ni, Cu, Zn, Cd, Pb, Al, Mn, Ga (Pb and Zn) La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Tb, Yb, Lu, Y Li, Na, K, Rb, Mg, Ca, B, Tl, P, S, As, Bi, Se, Si, Sn, Sb, Te, Zr, Nb, Hf, Ta, W, Th, and Ag	Chelex-100	Garmo et al., 2003
Cs, Sr	AG50W-X	Chang et al., 1998
S	Silver iodide	Teasdale et al., 1999
P	Ferrihydrite	Zhang et al., 1998
Radionuclides Cs	Ammoniummolybdophosphate (AMP)	Murdock et al., 2001
Tc	TEVA	French et al., 2005
MeHg	3-mercaptopropyl functionalized silica gel resin	Clarisse & Hintelmann, 2006
Heavy metals	Thiol-modified silica resin gel	Feng et al., 1997
Hg	Spheron - Thiol	Docekalova et al. (2005)
As	Ferrihydrite	Fitz et al., 2003
Se (soil)	Ferrihydrite	Sogn et al., 2008
Cu, Cd	a Poly(4-styrenesulfonate) Liquid binding layer (PSS)	Li et al., 2003
Cd, Cu, Mn, Zn and P	Mixed binding layer (Chelex+ferrihydrite)	Mason et al., 2005
Co Ni, Cu, Cd and Pb (natural waters)	SPR-IDA (suspended particulate reagent-iminodiacetate) (smaller bead size than the coarser chelex-100	Warnken et al., 2004

Before the year of 2000, different resins have been tested depending on the species of interest. A general cation exchange resin (AG50W-X8) was tested (Chang et al., 1998). It may be appropriate

for measuring a range of cations, including Ca, Mg, and K, especially Cs and Sr, when present at low concentration. The use of this resin is however limited. A DGT technique for the measurement of dissolved sulphide has been developed by Teasdale et al (1999). They used a silver iodide containing resin gel to measure sulphide. Sulphide reacts with the pale yellow AgI. The reaction product, Ag₂S is black. The accumulated sulphide was measured with a conventional purge-and-trap method followed by colorimetry measurement (methylene blue). They demonstrated that sulphide can be measured in a quantitative manner with AgI-DGT. AgI was chosen as the binding agent because it is very insoluble in water, it readily forms Ag₂S which is even more insoluble, and its rapid reaction with sulphide is accompanied by a colour change from pale yellow to black.

In natural waters, for example, phosphorus exists in several chemical forms, not all of which are biologically active. Thus DGT resins were developed also for anionic analytes. A ferrihydrite containing binding layer was prepared by Zhang et al. (1998) adding 2 g of ferrihydrite slurry into 10 ml of gel solution. This work demonstrated that DGT can be used to measure phosphorus species *in situ* in natural waters. Ammoniummolybdophosphate (AMP) was used as the binding agent by Murdock et al. (2001). AMP has been widely used as adsorbent for the analysis of caesium in surface waters as adsorbant. Their experiments, using known added concentrations of ¹³⁴Cs, showed that DGT measurements using AMP gels closely reproduced the immersion solution concentration, with a good degree of accuracy and precision for sampling periods up to 1d. The overall implication of this work is that, for natural waters, the DGT technique can provide an accurate estimation of the average caesium concentration over periods of up to a month. This DGT technique was proven to be simple as analysis involves very little sample preparation and as it has several advantages over traditional sampling methods for monitoring radionuclides in the solution phase.

French et al. (2005) published reports on the development of a method for measuring ⁹⁹Tc using the DGT with trialkyl methylammonium nitrate (TEVA) as a binding agent. The active component of the TEVA resin is an aliphatic quaternary amine. As such it has properties similar to those of typical strong base anion exchange resins (<http://www.eichrom.com>, Sep.2010). They performed systematic testing and validation for the measurement of ⁹⁹Tc in seawater. The laboratory investigations demonstrated the validity of DGT using TEVA. It has been shown that uptake of ⁹⁹Tc by DGT is independent of ionic strength and pH for seawater conditions, and uptake is proportional to solution activity and deployment time. Thus, the potential of the technique for the *in situ* monitoring of ⁹⁹Tc is shown by this investigation.

Mercury is well known as one of the most toxic metals in nature. The considerable interest in this element is due to the well-known toxicity of its major organic form, methylmercury (MeHg), the accumulation of MeHg in biota and its up-concentration in the aquatic food chain. Therefore

Docekalova et al. (2005) tested two different binding resins (Chelex-100 with iminodiacetic and Spheron-Thiol with thiol groups) for the determination of mercury. Two different diffusive gels including polyacrylamide and agarose gels were tested because they assumed that the mercury ions were covalently bound to amide groups of polyacrylamide diffusive gel. Agarose diffusive gels of three thicknesses were used for this experiment. The mass of mercury measured by DGT with Spheron-Thiol resin layer was three times higher than that measured by Chelex-100. This can be explained by the higher affinity of thiol groups to Hg(II) bound in non-labile complexes.

Moreover, Clarisse & Hintelmann (2006) developed a DGT technique for in situ sampling of dissolved MeHg in natural waters. Instead of Chelex 100, a 3-mercaptopropyl functionalized silica gel resin, which is specific for mercury ions, was used. The new resin was characterized, optimized and calibrated to be used in a quantitative time-integrating monitoring device. Also the thiol-modified silica gel resin exhibited selective complexation affinity for mercury and silver (Vieira et al., 1997; Nooney et al., 2001) while other metal ions (Cd^{2+} , Pb^{2+} , Zn^{2+} , Co^{3+} , Cr^{3+} , Fe^{3+} , Cu^{2+} and Ni^{2+}) bound little or not at all onto this adsorbent (Brown et al., 1999; Liu et al., 2000). Therefore, it was concluded that the other metal ions do not compete with mercury ions for binding sites on that resin.

Until recently, only few studies have reported arsenic and selenium determinations by DGT, with only one attempt to speciate inorganic arsenic in natural waters. Ferrihydrite was used to determine total dissolved inorganic arsenic in freshwater by Panther et al. (2007), in freshwater sediments by Stockdale et al. (2008) and to estimate arsenic fluxes in soils by Fitz et al (2003). Sogn et al. (2008) investigated ferrihydrite as adsorbent for selenium in soil solutions; however, speciation was not considered and a comprehensive method evaluation was not performed.

The Chelex-100 resin also binds Ca^{2+} and Mg^{2+} , although with lower selectivity than most polyvalent trace metal ions (Dahlqvist et al., 2002). It is, therefore, possible to measure these ions simultaneously with trace metals in one DGT device. When sampling natural water it can only be used for Ca^{2+} and Mg^{2+} if Chelex 100 is not saturated with Ca^{2+} and Mg^{2+} . After saturation has been reached Ca^{2+} and Mg^{2+} will gradually be replaced by ions which are more strongly bound to the Chelex-100, e.g. Cu^{2+} and Fe^{2+} . A maximum deployment time should be estimated from the resin capacity before sampling *in situ*. This study showed that DGT using Chelex-100 as a binding agent accurately measures Ca^{2+} and Mg^{2+} concentrations in synthetic solutions, where no trace metals are present.

Recently a DGT method was developed to allow for simultaneous measurement of both, anions and cations. Mason et al. (2005) developed a mixed binding layer (MBL) containing ferrihydrite as the sorbent for phosphate and Chelex 100 as the sorbent for metal cations.

Warnken et al. (2004) tested suspended particulate reagent-iminodiacetate (SPR-IDA)* instead of Chelex-100 as an alternative binding agent for cations. Deployment of DGT in solutions with increasing concentrations of trace metals yielded linear results, suggesting that quantitative analysis using laser ablation techniques should be possible using this newly characterized SPR-IDA resin gel.

In several experiments of Zhang et al. (Zhang and Davison, 2000; Zhang and Davison, 2001; Zhang, 2004) diffusive layers made from different materials with different pore sizes were used to discriminate between complexed metal species and free metal ions. Three types of gels (*i.* 1.5% pure agarose, *ii.* an acrylamide monomer cross-linked with a patented agarose derivative, and *(iii)* an acrylamide monomer cross-linked with bis-acrylamide) with various pore sizes were used in their investigation in 2001. Inorganic metal species diffused freely through all diffusive gels, whereas larger complexes with fulvic and humic acids diffuse less freely through more restricted gels (gels with smaller pore size). This approach relies on the assumptions that (i) most labile metal-organic complexes in freshwaters are fairly large molecules and (ii) small (i.e. fast diffusing), labile metal-organic complexes have negligible concentrations compared to the total inorganic metal species. It is applicable to any organic or inorganic diffusing species.

* This chelating resin has a much smaller bead size and is, therefore, more homogeneously distributed within the resin-gel layer than the coarser Chelex 100. Similar to Chelex 100 it consists of a polystyrene divinylbenzene substrate, this has been chemically derivitized with iminodiacetate functionality.

3.3. Uses of DGT

The use of the DGT technique is increasing for many different purposes, including (1) *in situ* measurements, (2) speciation measurements, and (3) monitoring of contaminant levels. It can be also used as a (4) kinetic tool and (5) for measuring the metal dynamics (fluxes of elements) in soils (Zhang, 2003). It plays also important role in (6) bioavailability studies. DGT has been applied for most of these purposes in waters such as rivers, lakes, estuaries, the deep sea sediments and soils.

1. *In situ* measurements: The DGT technique was developed for *in situ* measurements of labile trace metal species in aquatic environments and has been applied to waters (e.g. Zhang and Davison, 1995), soils (e.g. Zhang et al. 2001) and sediments (e.g. Zhang et al 1995, Widerlund and Davison 2007). As DGT samples are simple, small devices, their deployment *in situ* is uncomplicated.

Numerous papers (Gimpel et al., 2003; Cleven et al., 2005) state that *in situ* measurements avoid problems of to contamination during sampling, transport and storage prior to measurement through processes of aggregation, transformation to volatile species, precipitation, and metal adsorption to container walls. Fe and Mn concentrations measured by DGT (Gimpel et al., 2003) in lake water samples that were transported to the laboratory were much lower than *in situ* concentrations, illustrating the need for *in situ* measurements. Laxen and Chandler (1982) found metal concentrations in filtered river water samples changed within a 2 h delay between sampling and filtration. Benes and Steinnes (1974) measured a 35% drop in Mn concentrations after 1 day of storage of lake water samples collected by dialysis.

DGT has been deployed *in situ* in a wide range of natural waters, including fresh waters, such as soft Canadian shield lakes, several rivers, coastal sea-water (Twis and Moffett, 2002) and open ocean sea-water. Odzak et al. (2002) evaluated the application of DGT as a tool to determine Cu, Zn, Ni, Cd, Pb and Mn concentrations and speciation in a hardwater eutrophic lake and it provided a convenient way of measuring *in situ* average concentrations of labile species over several days in the water column of a lake.

DGT with measurements by computer-imaging densitometry (CID) was used by Widerlund & Davison (2007) to study the *in situ*, two-dimensional distribution of sulphide producing microniches in sediments from a eutrophic lake (Esthwaite Water, UK).

(2) Speciation measurements: Although methods to determine metal speciation in natural freshwater exist, these are generally laboratory methods which imply heavy handling of the samples and might consequently induce inaccuracy and contamination. Furthermore, they are often

either time consuming or not accurate at low metal concentration (Meylan et al., 2004). However, very low free and labile metal concentrations can be measured by DGT provided that the device is deployed during a sufficiently long period of time. The use of DGT probes to determine metal concentrations is sometimes intricate: For elements such as Mn, which in the dissolved form is essentially 100% Mn^{2+} , it is straightforward to determine total concentrations from DGT accumulation data (Twiss and Moffett, 2002). However, for elements such as Cu, where speciation is dominated by organic complexes spanning a range of stabilities and sizes, it is much more difficult. Recently, Zhang and Davison (2002) showed that Cu complexes (*coastal water*) with humic and fulvic acids do accumulate in DGT. According to their research Cu was most strongly complexed in noncontaminated locations and less strongly complexed in contaminated waters because, in the latter, most of the strongest chelators were completely saturated.

Several techniques (DGT, GIME-VIP^{*}, SCP[†], FTPLM & HFPLM[‡], DMT[§], and CLE-SV^{**}) for speciation analysis of Cu, Zn, Cd, Pb, and Ni in *freshwater* systems were compared with respect to their performance and to the metal species detected (Sigg et al., 2006). All methods could be used under both, *hardwater* and *softwater* conditions, although in some cases problems with detection limits were encountered at low metal concentrations. The detection of Cu, Cd, and Pb concentrations in waters were highest when they used DGT devices.

In two Australian *river systems* DGT assemblies were deployed for the investigation of Cu, Cd and Mn speciation (Denney, 1999) and this work has demonstrated the effectiveness of using DGT to measure labile metal concentrations in *river waters*. One of the major conclusions from this practical use of DGT is that it is simple to use and provides reliable, reproducible results. The technique provided an *in situ* speciation measurement integrated over 72 h in this study, which is potentially useful for monitoring in streams of highly variable water quality, or for long-term ecotoxicity studies.

(3) Monitoring of contaminant levels:

Field and experimental data from Munksgaard and Parry (2003) showed that DGT devices provided adequate detection limits, accuracy and precision for monitoring of near-pristine levels of labile Mn, Co, Cu, Cd and Pb in north Australian *coastal seawater* when deployed for periods of 3 days. Ryan et al. (2003) evaluated the use of DGT as a monitoring tool for Ni, Cu, Pb, and Zn concentrations at various locations in the Gold Coast Broadwater, a subtropical, *coastal lagoon estuary* in southeast Queensland, Australia. DGT measurements were compared with measurements

* Gel integrated microelectrodes combined to voltammetric *in situ* profiling system

† Stripping chronopotentiometry

‡ Flow-through and hollow fiber permeation liquid membranes

§ Donnan membrane technique

** Competitive ligandexchange/ stripping voltammetry

made on conventional sampling system. Commonly the conventional sampling approach to characterise the trace metal concentrations in estuarine waters is time-consuming and logistically expensive, requiring hourly sampling across tidal and diurnal cycles at least one occasion in each major season (Kramer et al., 1994). Here DGT has shown a great potential as a monitoring tool, particularly for dynamic *estuarine waters*, because of its ability to continually accumulate analytes and to provide a genuine, time-integrated average measurement.

The potential of DGT as a monitoring tool and its performance characteristics for monitoring studies have been studied also by Cleven et al. (2005) in laboratory experiments and *in situ* application under several operational conditions in *river water*. They applied DGT in the Dutch parts of the rivers Meuse and Rhine to assess the development of the DGT-labile solute fraction over a long period of time: during nine months in 2003 for the river Meuse, and during four months in 2003 for the river Rhine. The ratio of the non-labile and labile fractions of the Ni, Cu, and Pb appeared to decrease with increasing content of dissolved organic carbon in this study. Comparison between total dissolved concentration and bioavailable metal concentration estimated by DGT highlights the potential for an estimation of the ecotoxicological risk associated with metal pollution.

(4) Kinetics:

A further application of DGT is the determination of stability constants of complexes and their dissociation kinetics. As DGT can be readily deployed *in situ* in natural waters, soils, and sediments, it offers the possibility of obtaining kinetic information directly in natural systems and advancing our understanding of metal availability to biota (Sally et al., 2003).

(5) Metal dynamics in soils:

Contamination of soils with heavy metals and metalloids is a widespread problem all over the world. Low cost, non-invasive, *in situ* technologies are required for remediation processes. The evaluation of labile metal pools in soil is a fundamental issue in soil pollution level determination, risk estimation and remediation design (Fava and Sani, 2000; Bonomo, 2005). There are several sequential extraction procedures (SEP) available in the literature (Sahuquillo et al., 2002) but they may not reflect the real processes in soils (Honeyman et al., 1988; McKinley and Jenne, 1991; Benoit and Rozan, 1999). SEP procedures are not only difficult but also labour-intensive. In this context, the need for new techniques to study solute solubility and mobility in soils and interstitial

pore water has arisen. In a recent study of Ruello et al. (2008) the labile pool of several metals (Cu, Fe, Mn, Ni) in a polluted site was evaluated both with SEP and DGT techniques. The aim was to investigate the suitability of the DGT technique in soil risk assessment. DGT was used by Ernstberger et al. (2005) for measuring the distribution and rates of exchange of Zn, Cd, and Ni between solid phase and solution in five different soils. An accurate and reliable soil test would reduce the cost associated with unnecessary fertilizer application and also reduce the risks of environmental pollution as a result of excessive fertilizer application. DGT could become a very important tool for defining nutrient deficient soils and, therefore, fertilizer requirements. Lombi et al. (2002) measured the flux of Zn, Cd, Cu and Ni from the soil solid phase to solution by DGT. The comparison of the results indicated that soil amendments significantly reduce not only the solubility of metals in soil pore water, but also the flux of metals from solid phases to a sink such as DGT.

DGT has been developed also to measure elements at concentrations more representative of uncontaminated agricultural soils. The study of Mason et al. (2005) focused on measurement of Cu, Mn, Mo, P, and Zn because they are important plant nutrients and they evaluated the performance of DGT devices containing a new binding layer (mixture of ferrihydrite and Chelex). The DGT technique only measures labile species and therefore will exclude kinetically inert organic species, large colloids and strong organic-metal complexes (Davison and Zhang 1994, Zhang et al. 1995, Harper et al. 1998). When applied to soil, the DGT device is continuously supplied with the elements that are transported by a diffusive flux from the pore water. This process leads to a depletion of pore water concentrations near the DGT device. This depletion effect is counteracted by a resupply from the element fraction bound to the solid phase and decreases with distance from the device (Harper et al. 1998).

(6) Bioavailability studies:

Soil nutrient availability has proven difficult to assess although partial chemical extraction methods are still the most common procedures used for assessing nutrient availability in soils. Phosphorus is a prime example of an important macronutrient for which traditional extraction methods routinely fail to provide an accurate assessment of its availability to crops. It has been hypothesized that this is due to the numerous forms of P present in soils (Mason et al., 2005). DGT measurements have been shown to be a good predictor of the concentration of metal in plants (*Zhang, 2001*). The good correlations indicate that the DGT-soil system effectively mimics the major processes involved in plant uptake of elements in the soil. It might not clearly mimic mass flow and root interception processes in the rhizosphere but DGT has been suggested by Degryse et al. (2003) to sample an

available fraction of metals in soil. The resin acts as a sink, thus causing a depletion of trace metals in the pore water and a resupply from the labile metal pool on the solid phase, a process that is similar to plant uptake. The metal uptake by DGT to mimic processes in soils that affect uptake of metals by plants was examined also by Lehto et al. (2006). This work expands on and helps to explain the existing evidence that under some conditions DGT performs better than other measuring techniques in assessing bioavailability to plants.

Zhang et al. (2001) introduced the new concept of effective concentration, CE, which includes both the soil solution concentration and an additional term, expressed as a concentration, which represents metal supplied from the solid phase of the soil. Highly significant correlations have been obtained between the concentration of trace metals including Cu in plants and the DGT measurements. Later Fischerova et al. (2005) demonstrated also that DGT locally decreases the metal concentration of the soil solution and thereby triggers a resupply by diffusion from the bulk solution and desorption from solid phase. Thus DGT allows the estimation of the bioavailable metal concentration that can interact with living organisms (Garofalo et al., 2004). Simon et al. (2009) tested the possibility of using DGT to assess Mn availability in soils under different conditions relevant to agricultural crops. Experiments with different soil deployment time showed that DGT was able to register differences in plant availability caused by redox changes. The result of this work suggested that the DGT technique represents an efficient and reliable way of getting information on the plant availability of Mn in agricultural soils.

3.4. Mechanisms of binding

Although a few elements occur uncombined in nature, the great majority exist in compounds.

1. Ionic compounds form when a metal transfers electrons to a nonmetal, and the resulting positive and negative ions attract each other to form a three dimensional array. In many cases, metal atoms lose and nonmetal atoms gain enough electrons to attain the same number of electrons as in atoms of the nearest noble gas. Ionic bonding can be named also as electrostatic bonding.

In context of DGT works, the Chelex-100 was the most commonly used resin in the binding layer (Li et al., 2003) which is acting by ionic bonding of analytes. Chelation is the formation or presence of two or more separate bonds between a polydentate ligand and a single central atom. Usually these ligands are organic compounds, and are called chelants, chelators, chelating agents, or sequestering agents. The ligand forms a chelate complex with the substrate. *Figure 3.4.1.a* depicts the structure of Chelex-100. The use of Chelex-100 in conjunction with a metal ion for the removal of anions from wastewater was investigated by Wu et al. (2007) using of La for sorption of phosphate (*Fig.3.4.1.b.c*).

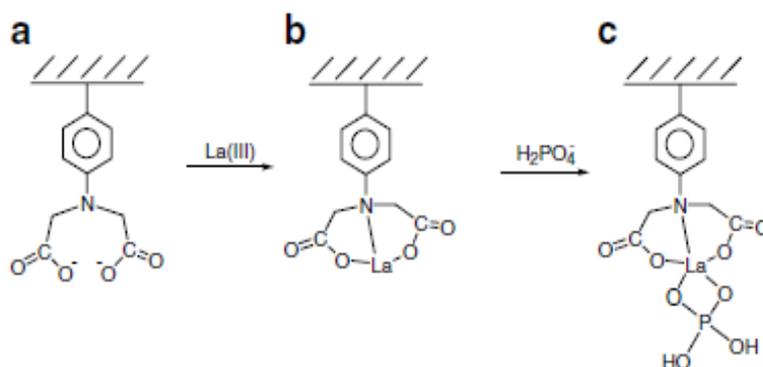


Figure 3.4.1. (a) Structure of chelex-100, (b) Chelex-100 compound with La after impregnation with La, (c) La-chelex-phosphate after deployment in phosphate solution. (After Wu et al., 2007)

Cotton et al. (1995) mentioned that La has a high affinity for oxyanions such as phosphate because of its hard Lewis acidic* property, and it has been used successfully by Kanamoto et al. (1988) for removal of fluoride ions from water.

2. Covalent compounds form when elements, usually nonmetals, share electrons. Each covalent bond is an electron pair mutually attracted by two atomic nuclei. Monatomic ions are derived from one atom. Polyatomic ions consist of two or more covalently bonded atoms that have a net positive or negative charge due to a deficit or excess of electrons. The process of concentrating materials at

* Lewis acid-base reactions are electron pair transfers

the interface is called adsorption. The term *specific adsorption* has been defined as a type of *covalent bonding* of solutes by the sorbents.

Two different titanium dioxides: (i) anatase and (ii) rutile (*Figure 3.4.2*) were tested within this work. Binding layer gels with anatase, rutile and lanthanumhydroxide were made and investigated. The binding mechanism of these mineral powders with anionic analytes represents covalent bonding.

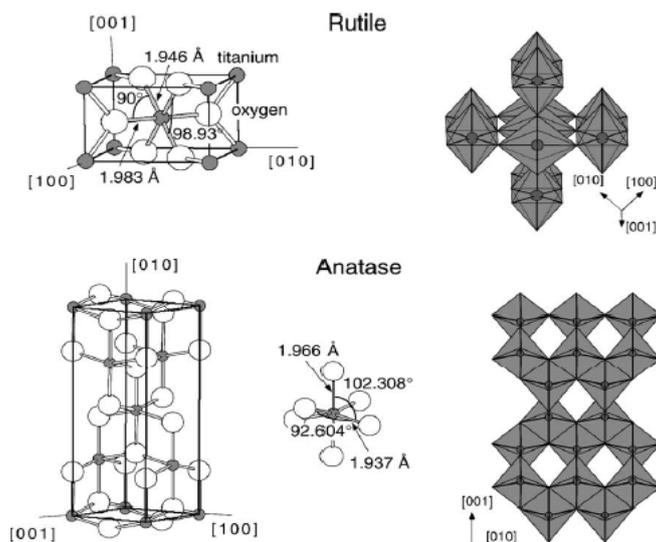


Figure 3.4.2. Bulk structures of rutile and anatase.

Titanium has four valence electrons $3d^24s^2$. The most stable and common oxidation state is Ti^{IV} compounds in lower oxidation states. The energy for removal of four electrons is high, so that Ti^{4+} ion may not exist and Ti^{IV} compounds are generally covalent. In rutile, the commonest, the Ti is octahedral. Although rutile has been assumed to be the most stable form because of its common occurrence, anatase is 8 to 12kJ mol^{-1} more stable than rutile.

3.5. Research objective

The objective of this work was to produce a DGT resin-gel that is able to bind cations and anions in a single assay and that is, in contrast to the ferrihydrite and Chelex 100 containing gel developed by Mason et al. (2005), capable of measuring Fe.

(i). The first strategy was to develop a novel DGT gel modifying Chelex-100 for adsorption of anions and cations.

(a). Chelex 100 resin impregnated with La

(b). Chelex 100 resin gel impregnated with La

were tested for anion adsorption and use in DGT.

(ii). Anion sorbing powder minerals (anatase, rutile and lanthanumhydroxide) were tested. DGT gels with these minerals were made and investigated for their properties of anion adsorption.

4. Material and methods

4.1. Resin and gel preparation

Chelex 100 loaded with lanthanum (Wu et al. 2007), and the mineral powders – anatase, rutile, and lanthanumhydroxide were the binding resins in our investigation (*Table 4.1.1*).

About 100 mL of Milli-Q water were added to 15 g of Chelex-100 in a 100 mL-vial. After hydration, the water was poured off. This moist Chelex-100 resin was used for further experiments. Chelex-100 was loaded with La in order to obtain a resin capable of binding anions and cations as described by Wu et al (2007). Eight g wet Chelex-100 were soaked in 150 mL of a 0.1 mol L⁻¹ La solution prepared from LaCl₃ x 7H₂O for 2h. Afterward the resin was rinsed twice to wash off the excess La solution. This resin is termed ‘La-Chelex 1’ throughout this work.

Table 4.1.1.: Resins and gels prepared thereof used in this work

	Resin / gel name	Amount of resin g	Gel solution ml	APS μ l	TEMED μ l
1	La-Chelex 1	1	2,5	20	6,25
	La-Chelex 2	Chelex gel (purchased) immersed in La solution. This formulation was only used in gel form, no powdery resin existed. For details see text.			
3	Anatase	0,5	2,5	15	4,8
4	Rutile	0,5	2,5	15	4,8
5	La(OH) ₃	0,5	2,5	15	4,8

4.2. Preparation of resin gels

Resin gels (La-Chelex 1 resin gel, anatase resin gel, rutile resin gel and lanthanumhydroxide resin gel) were prepared according to the procedure of Zhang and Davison (1995) by mixing (*Picture 4.2.1.a*) appropriate amounts of tested resin (La, anatase, rutile, and lanthanumhydroxide), gel solution, freshly prepared ammonium persulphate (APS) solution and N,N,N',N'-tetramethylethylenediamine (TEMED). The gel solution consists of acrylamide and cross linker (15% by volume acrylamide and 0.3% by volume agarose cross-linker) and can be obtained from DGT Research Ltd. (Lancaster, UK). Table 1 shows the formulations that were used for preparing the different resin gels.

The ‘La-Chelex 2’ resin gels were prepared using the Chelex-100 resin gels. The Chelex-100 resin gels are generally prepared at DGT Research Ltd in Lanchaster, UK. The gels were purchased and impregnated in the La solution ($\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ was used) to embed La into the Chelex-100 resin gels for making La-Chelex 2 resin gel.

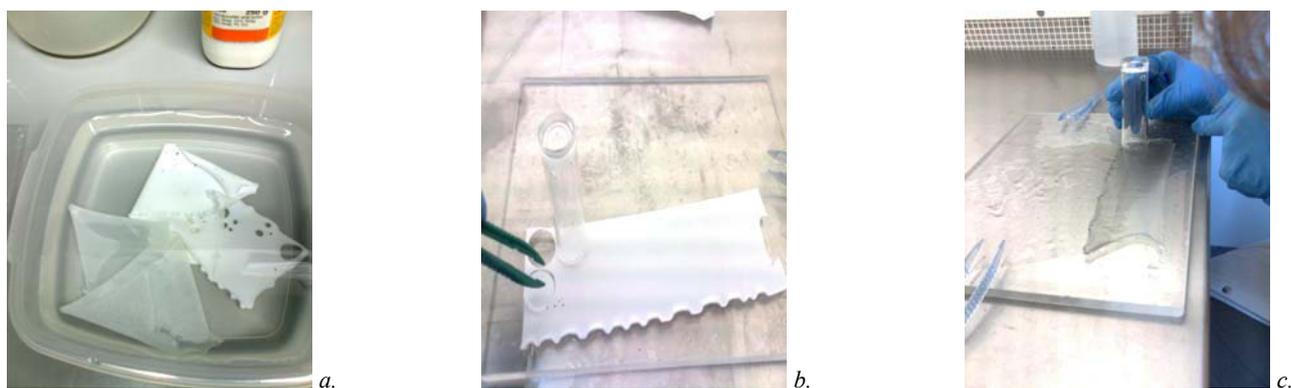
Anatase resin gels, rutile resin gels and lanthanumhydroxide resin gels were prepared without Chelex-100 resin.

An ultrasonic bath (*Picture 4.2.1.b*) was used for mixing the dry, powdery mineral resins homogeneously into the viscous gel solution. After mixing the components, the suspension was immediately cast between two glass plates (*Picture 4.2.1.c*) separated by plastic spacer of appropriate thickness and allowed to set at about $42 \pm 2^\circ\text{C}$.



Pictures 4.2.1.: a. A pipette was used for mixing the La-Chelex resin with the viscous gel solution; b. An ultrasonic bath was used for mixing the powdery mineral resins with the viscous gel solution; c. Glass plates were used to prepare DGT resin gels.

The gel setting time was about 2 h. The gels were removed from the plates and hydrated in deionised water (*Picture 4.2.2.a*) for at least 24 h before use with at least 3-4 changes of water. The minimum time between changes of water was 3 h. During hydration the gels expanded to their stable dimension while impurities within the gel were able to diffuse out. The resin gels were stored in $0.03 \text{ mol L}^{-1} \text{ NaCl}$ solution. Disks of 2.5 cm diameter were cut from these gel sheets (*Picture 4.2.2.b and 4.2.2.c*). The 0.8-mm diffusive gels used in this study were purchased from DGT Research Ltd.



Picture 4.2.2.: a. DGT gel discs including anatase gels with and without the use of an ultrasonic bath: the bright, white colored gel was treated with ultrasonic bath whereas the transparent colored gel was not; b. DGT gel discs with TiO_2 discs; c. DGT gel disc with La-chelex 1.

4.3. Preparation of test solution

Ninety mL stock solutions of Cu, Cd, P, Zn, Mo, Mn, Ni, Co, As, Se, Pb, Cr and W were prepared separately using following chemicals:

- $\text{Na}_2\text{O}_4\text{W}\cdot 2\text{H}_2\text{O}$ ($\geq 99\%$, purchased from Sigma-Aldrich Ltd. Austria)
- K_2CrO_4 (min 99.5 %, Sigma-Aldrich Ltd. Austria)
- $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (99,999 % Merck Ltd. Austria)
- CdCl_2 (99.99 %, Merck Ltd. Austria)
- KH_2PO_4 (99%, Merck Ltd. Austria)
- ZnCl_2 (99.99 %, Merck Ltd. Austria)
- $\text{MnO}_4\text{S}\cdot \text{H}_2\text{O}$ (99 %, Sigma-Aldrich Ltd. Austria)
- $\text{MoNa}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ (99 %, Sigma-Aldrich Ltd. Austria)
- $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (min 98 %, Merck Ltd. Austria)
- $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (min 99 %, Merck Ltd. Austria)
- $\text{Na}_2\text{HAsO}_4\cdot 7\text{H}_2\text{O}$ (99.995 %, Merck Ltd. Austria)
- $\text{Na}_2\text{SeO}_4\cdot 10\text{H}_2\text{O}$ (99,999 %, Sigma-Aldrich Ltd. Austria)
- PbSO_4 (99,995 %, Sigma-Aldrich Ltd. Austria)

The concentration of each element in stock solution was 1000 mg L^{-1} . Test solutions containing several chemical elements were prepared from stock solutions during each experiment. Test solutions were stirred to avoid precipitation after adding each element from the stock solutions.

4.4. Analyte uptake of resin powders

The pure resin powders were immersed into the test solutions. The resins were removed from the test solution after deployment. Deployment times were various depending on each experiment's purpose (5h to 24h). The resins were rinsed afterward with Milli-Q water twice and placed in acid (HCl was mainly used) for elution for at least 24 h. The masses of analytes in the eluate and the remaining analytes in the test solutions were measured by inductively coupled plasma mass spectrometry (ICP-MS).

4.5. Analyte uptake of resin gel disks & elution coefficient determination

For testing uptake and elution efficiencies of resin gels, gel discs were immersed in 10 mL of solutions containing anionic and cationic analytes (As, Cd, Co, Cr, Cu, Ni, Mn, Mo, P, Pb, Se, W, Zn). After immersing resin-gel discs into experimental solutions (deployment times are mentioned in each experimental part), the gel discs were put into acid (mentioned at each experiment) for elution for at least 24 h. Elemental concentrations of the immersion solutions before and after immersion of resin gel discs, as well as eluate concentrations were measured by ICP-MS. The results were evaluated for uptake and elution efficiencies.

The capability of the resin to take up elements was assessed by measuring the percentage of uptake (U), defined by equation 7:

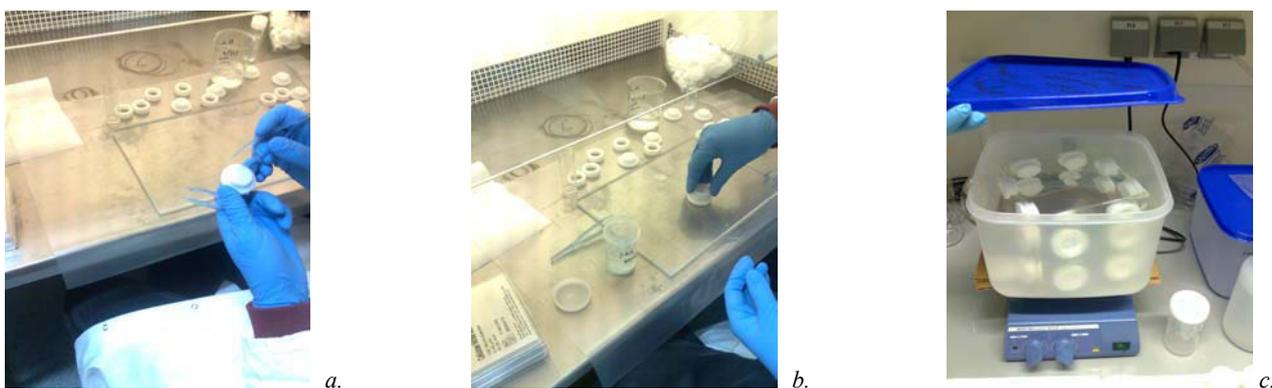
$$U = \frac{(M_i - M_r)}{M_i} * 100 \quad (\text{Eq. 7})$$

M_i is the mass initially present in the solution and M_r is the mass remaining after exposure to a resin-gel for chosen deployment times.

Quantitative analysis by DGT requires reproducible elution of analytes from the resin gel. The elution efficiency (f_e) was defined (Eq. 8) as the mass of ions eluted from the resin-gel (M_{resin}) expressed as a percentage of the initial mass loaded on the resin gel (M_{in}):

$$f_e = \frac{M_{\text{resin}}}{M_{\text{in}}} * 100 \quad (\text{Eq. 8})$$

DGT sampler mouldings were obtained from DGT Research Ltd. A resin gel disc was placed on the base of the sampler piston (*Picture 4.5.1.a*). As granular resins (in this work Chelex 100) settle on one side of the resin gel, care was taken to orienting the disk surface containing the Chelex 100 beads towards the sampler window. The diffusive gel was put on the top of the resin gel. A filter membrane was covered by the diffusive gel and the front cap (top) was pressed down afterward (*Picture 4.5.1.b*). The assembled DGT devices were stored in plastic zip lock bags until use to avoid dehydration of the gels. Deionised water (1-2 mL) in the bags maintained a humid environment.



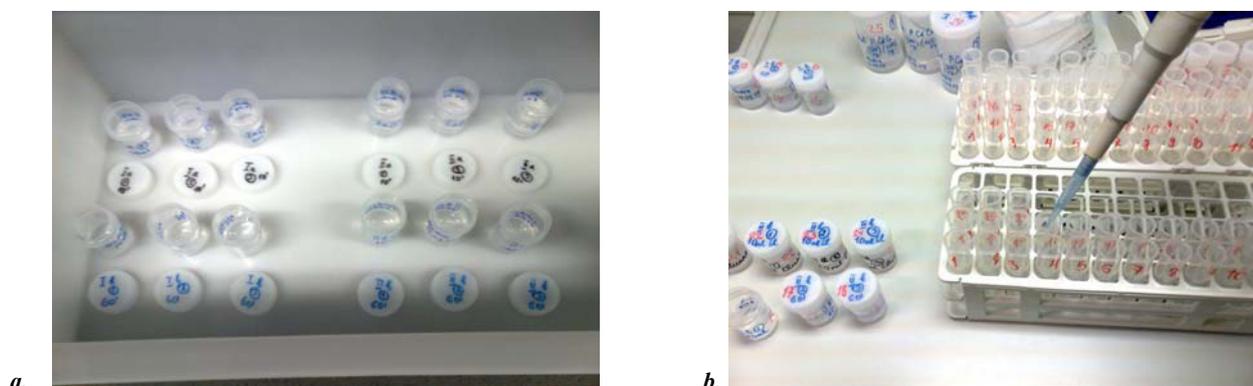
Picture 4.5.1.: a. The base of DGT device; b. The base and top are assembled together after placing binding and diffusive layers; c. DGT devices are in application

The water used in this study was reagent grade water type I (18.2 MΩ cm water from a Milli-Q water purification system, Millipore, Watford, UK). All plastic and glass (gel casting plates) labware was acid washed in 10% HCl followed by thorough rinsing with reagent grade water.

All experiments were carried out in 4 replicates.

4.6. ICP-MS measurement – Standard preparation and sample dilution

For ICP-MS (ELAN DRcE from Perkin Elmer) analysis, calibration standards were prepared in the range of 1 μg L⁻¹ to 500 μg L⁻¹. The samples were diluted and acidified prior to analysis if necessary (Picture 4.6.1.b).



a.

b.



c.

Picture 4.6.1.: a. 20 mL vials as used for the experiments; b. Sample dilution for ICP-MS analysis; c. Inductively coupled plasma mass spectrometry (ICP-MS)

4.7. Experiments

4.7.1. Comparison of ion binding efficiency of pure La-Chelex resin powder with a mixture of La-Chelex and Chelex resin

The purpose of this experiment was to compare the uptake of anionic and cationic analytes of pure La-chelex powder with a 1:1 mixture of La Chelex and Chelex-100. One g of the resin was exposed to 20 mL of a test solution for 10 and 60 min. The concentrations of Cu, Cd and P in the test solution were 29.5, 19.5 and 89.7 $\mu\text{g L}^{-1}$ respectively.

The resin suspensions were shaken during deployment on a horizontal shaker (*Figure 4.7.1.a*). A 10 mL sample of the immersion solution were taken and analyzed for the remaining analyte concentration after uptake by resin beads. The resin beads were rinsed twice with reagent grade water and eluted in 20 mL of 1 mol L^{-1} HCl for 24 h. Eluates were syringe filtered to remove all resin beads (*Figure 4.7.1.b and c*) and analyzed. Uptake and elution efficiencies were calculated after analysis.



Picture 4.7.1.: a. The DGT resins gel discs were shaken during deployment; b. and c. Syringe filters were used to filter the immersion solution

4.7.2. Kinetics of ion binding to La chelex 1 resin gel

Test solution contained various cations (Cd, Co, Cu, Mn, Ni, and Zn) and anions (As Cr, Mo, P, Se) in this experiment. *Table 4.7.2.1* shows the concentrations of each analyte in the test solution.

Table. 4.7.2.1. Concentrations of analytes in test solution for the La-Chelex 1 kinetics experiment

Analytes	Cd	Co	Cu	Mn	Ni	Zn	As	Cr	Mo	P	Se
Concentration, $\mu\text{g L}^{-1}$	65.8	44.9	42.5	42.8	45.8	46.9	33.1	38.2	50.1	160.1	49.5

La-Chelex 1 gel discs were immersed in the test solutions for eight different periods of time. The exposure times were 1, 3, 6, 10, 30, 60, 120 and 300 min. The gel containing solutions were shaken

at room temperature. After retrieval, the disc gels were eluted in 10 mL of 1 mol L⁻¹ HCl. The eluates and the immersion solution were analysed for elemental concentrations using ICP-MS.

4.7.3. Comparison of different deployment times - La-Chelex 2 resin gel

Sorption of anions and cations onto La-Chelex 2 gel discs was investigated by immersing La-Chelex 2 gel discs in 10 mL of solutions containing the elements shown in table 4.7.3.1. Deployment times were 5 h and 24 h. The gels were then eluted in 10 mL of 1 mol L⁻¹ HCl. Eluates and immersion solution samples were analysed using ICP-MS.

Table. 4.7.3.1. Analytes concentrations in test solution in the La-Chelex 2 deployment time experiment

Analytes	Cd	Co	Cu	Mn	Ni	Zn	As	Cr	Mo	P	Se
Concentration, $\mu\text{g L}^{-1}$	34	43	17	41	48	34	53	40	47	147	51

4.7.4. La concentrations effect to produce La-Chelex 2 resin gel & elution efficiencies with different concentrations of HCl

La-Chelex 2 gels were produced by placing Chelex 100 gels in LaCl₃ solutions at La concentrations of 0.001, 0.01 and 0.1 mol L⁻¹. After gel rinsing, sorption of anions and cations onto these gels was tested. The experimental solutions contained the analytes shown in Table 4.7.4.1.

The 2 mol L⁻¹ and 5 mol L⁻¹ HCl were tested to increase the low elution efficiency observed in the previous experiment. Eluates and immersion solution samples were analysed using ICP-MS.

Table. 4.7.4.1. Analytes concentrations in test solution in the experiment with La-Chelex 2 resin gels affected by different La concentrations

Analytes	Cd	Co	Cu	Mn	Ni	Zn	As	Cr	Mo	P	Se
Concentration, $\mu\text{g L}^{-1}$	53	59	36	58	66	56	52	64	64	180	65

4.7.5. DGT experiment with La-Chelex 2 resin gel

Sixteen DGT assemblies were deployed (Picture 4.5.1.c) in 4 L of a solution containing Cd and Mo and retrieved after 3, 7 or 24 hours after the start of the experiment. The plastic box (Picture 4.5.1.c) used in DGT experiment was prepared well to avoid adsorbing the analytes onto the inner

wall of the box. The plastic box was filled with test solution and stored for 48 h before the experiment started.

The initial concentrations of Cd and Mo in test solution were $182.9 \mu\text{g L}^{-1}$ and $280.8 \mu\text{g L}^{-1}$ respectively. After elution the samples were analysed. The measured concentrations in the extracts were corrected for blank values of unexposed La-Chelex 2 gels. C_{DGT} values were calculated according to equation 6.

4.7.6. Sorption test of anatase, rutile and lanthanumhydroxide resins

0.5 g of anatase, rutile or lanthanumhydroxide was added to 10 mL of test solution. The concentrations of As, Mo and P in test solutions were $227.3 \mu\text{g L}^{-1}$, $201.5 \mu\text{g L}^{-1}$ and $181.0 \mu\text{g L}^{-1}$ respectively in the beginning of the experiment. After shaking the samples with an overhead-shaker overnight the samples were centrifuged with the relative centrifugal force of 5473 (speed - 7000 rpm; $r=10$ cm) twice for 25 min. As particle sedimentation was not complete, the centrifugation was done again with the relative centrifugal force of 16087 (speed- 12000 rpm; $r=10$ cm) for 25 min. Six mL of the supernatant were used for ICP-MS analysis.

4.7.7. Sorption and elution test with anatase, rutile and lanthanumhydroxide resin gels

Sorption and elution of gels containing anatase, rutile and lanthanumhydroxide were studied in this experiment. The 0.25 mol L^{-1} , 0.5 mol L^{-1} and 1 mol L^{-1} of ammonium bicarbonate (NH_4HCO_3) were tested as eluent for anatase and rutile. Lanthanumhydroxide containing gels were eluted with the $0.25 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$.

The initial concentration of the experimental solution was $243 \mu\text{g L}^{-1}$ for As, $221 \mu\text{g L}^{-1}$ for Mo and $204 \mu\text{g L}^{-1}$ for P.

4.7.8. Elution of anatase and lanthanumhydroxide resin gels with 1 mol L^{-1} , 3 mol L^{-1} and 5 mol L^{-1} of HCl and H_2SO_4

Adsorption of analytes onto anatase and lanthanum hydroxide gel discs was studied. The gel discs were immersed in solutions containing different anions. Elution efficiencies of the anatase gel with 1 mol L^{-1} , 2 mol L^{-1} and 5 mol L^{-1} of HCl and 1 mol L^{-1} , 2 mol L^{-1} and 5 mol L^{-1} of H_2SO_4 were investigated. Same acids (HCl and H_2SO_4) with three different concentrations (1 mol L^{-1} , 2 mol L^{-1} and 5 mol L^{-1}) were used also for the lanthanumhydroxide gel elution. The initial concentration of the test solution in this experiment was $207.9 \mu\text{g L}^{-1}$ for As, $204.8 \mu\text{g L}^{-1}$ for Mo and $154.1 \mu\text{g L}^{-1}$ for P.

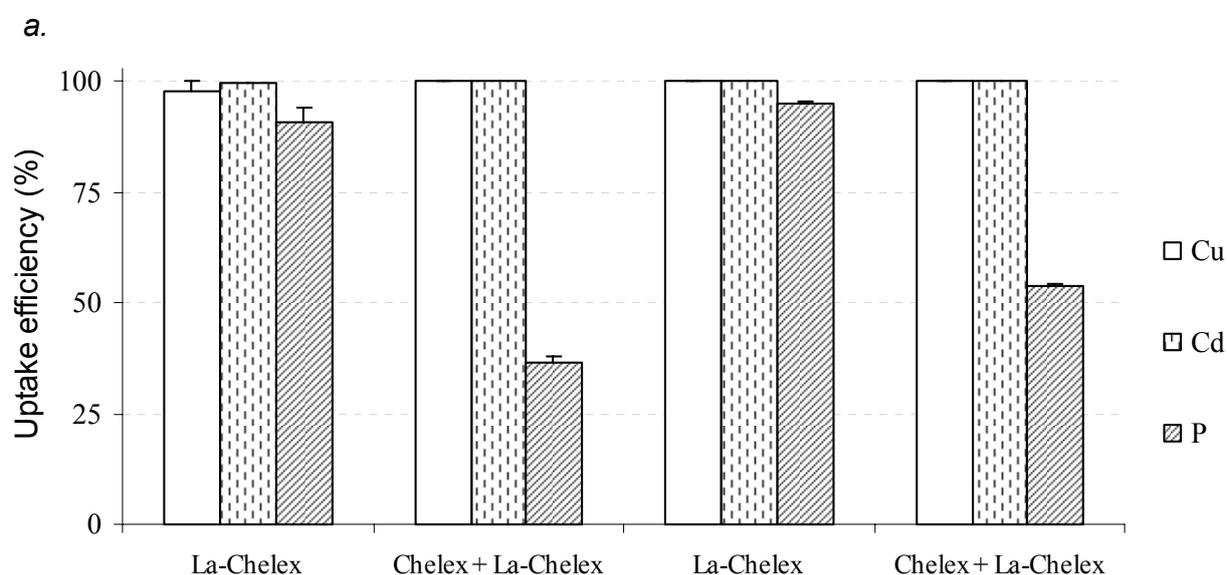
5. Results

5.1. Comparison of ion binding efficiency of pure La-Chelex resin powder with a mixture of La-Chelex and Chelex resin

All elements tested (Cd, Cu, and P) were successfully bound to the La-Chelex resin. The uptake efficiency was 98% for Cu, 100% for Cd and 91% for P after both deployment times of 10 min and 60 min (*Figure 5.1.1.a*). The P uptake efficiency of La-Chelex resin after 60 min deployment time was 4% higher than 10 min deployment time of this resin.

A mixture of La-Chelex and Chelex resins showed 100% uptake efficiency for cationic analytes after both deployment times. Although the uptake efficiency of the mixed resins was higher for cationic analytes, P uptake of this gel was only 36 % after 10 min exposure time. After 60 min, the uptake was still only 54%. The masses of cationic and anionic analytes that were bound onto each tested resin and mixture of resin are presented in *Figure 5.1.2* in *Appendix*.

The elution efficiencies of the resins are shown in *Figure 5.1.1.b*. Elution efficiencies higher than 90% were obtained for Cu. The P elution by 1 mol L⁻¹ HCl was 96% from the resin of La-Chelex which was deployed in analytical solution for 10 min, and 95% for 60 min respectively. Generally the elution efficiency of P from mixed resins showed lower values than La-Chelex resins.



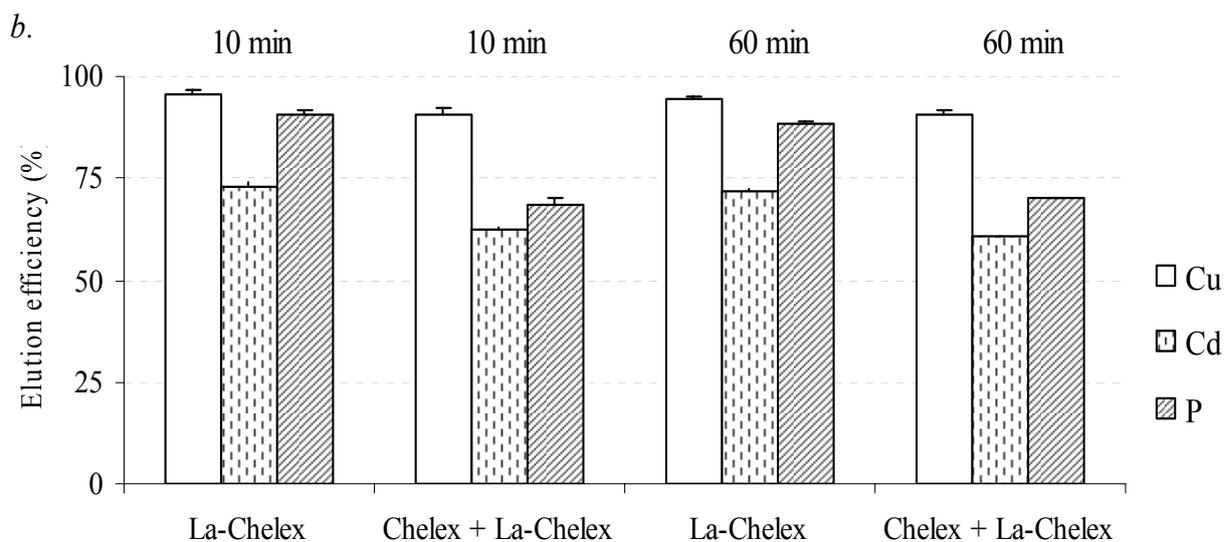


Figure 5.1.1. (a) Uptake and (b) elution efficiencies of La-Chelex and Chelex + La-Chelex (mixtu re) resins after deployment in the test solution containing cationic and anionic analytes. Deployment times were 10 min and 60 min. Error bars represent the standard errors.

5.2. Kinetics of ion binding to La chelex 1 resin gel

The objective of this experiment was to investigate the uptake kinetics of various analytes to the La-chelex 1 resin gel. Analysis of resin-gel samples and the immersion solutions allowed the calculation of a mass balance. The elution efficiency in 1 mol L⁻¹ HCl was investigated for Cd, Co, Cu, Mn, Ni, Zn, Cr, Se and Mo after determination of the uptake kinetics. The uptake of the investigated elements had increased with increasing deployment time (*Figure 5.2.1.a*). Cadmium uptake efficiency of La-Chelex 1 resin gel after 1 min immersion time was 11%, 10 min 59%, 120 min 92% and 300 min 100% respectively. The results of 3 min, 6 min, 30 min and 60 min exposures are not presented. These values for the analytes of Co, Cu, Ni and Zn show slightly higher values than the values of Cd for each time of deployment. In contrast, Mn showed lower uptake efficiencies. The accumulation of the anionic analytes on La-chelex 1 was ~5 times lower than cationic analytes after 300 min deployment time. It varied from 13% for Cr, 13% for Se and 37% for Mo.

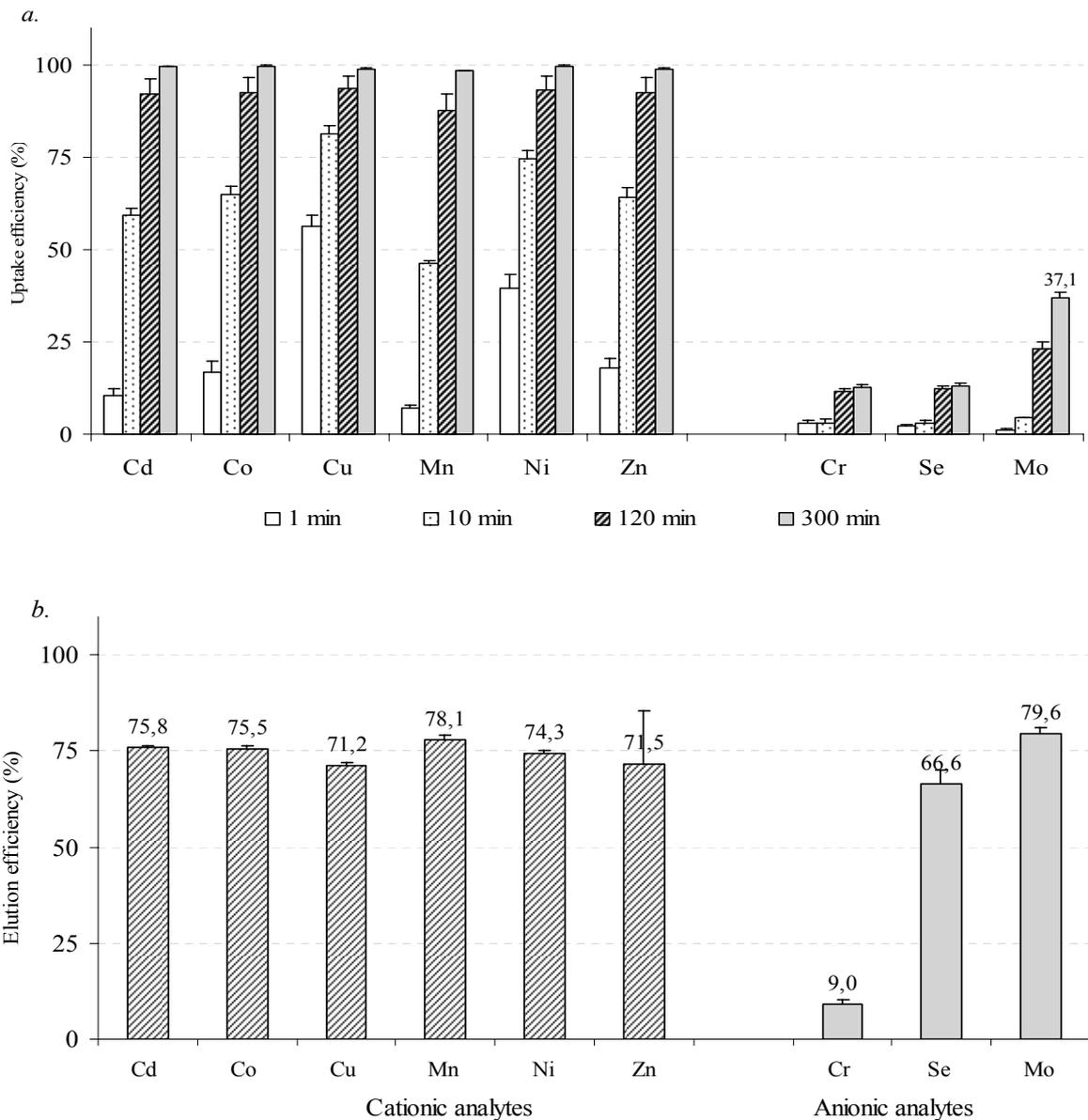


Figure 5.2.1. (a) Uptake and (b) elution efficiency of La-Chelex 1 resin gel after deployment in the experimental solution containing cationic and anionic analytes. Deployment times were 1 min, 10 min, 120 min and 300 min. Error bars represent the standard errors.

The uptake kinetics is shown for two representative elements in *Figure 5.2.2*: Cd and Mo. The masses of each of these metals accumulated by La-Chelex 1 resin gels were found to be increased with deployment time. (The results of other elements are not given here).

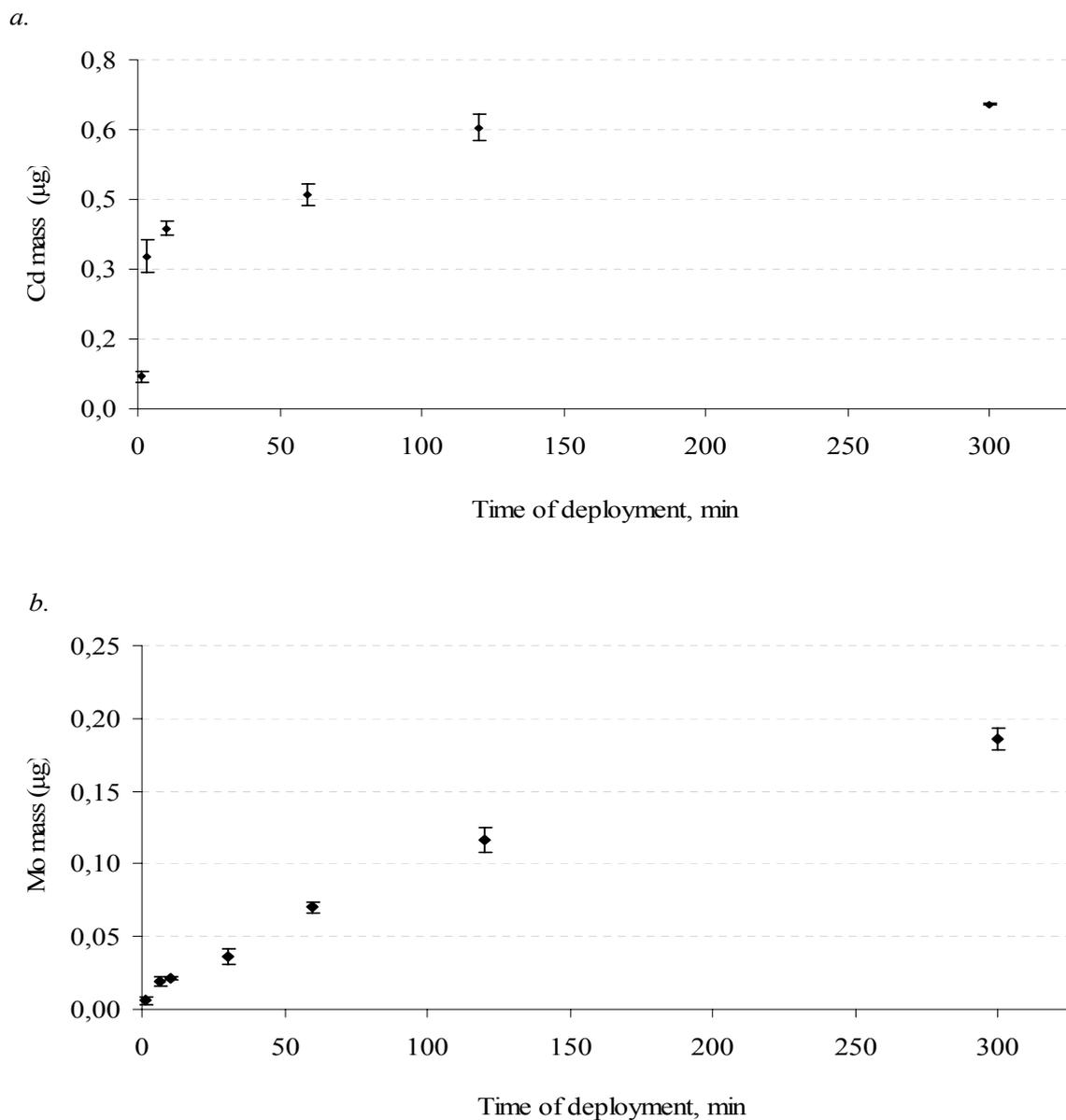


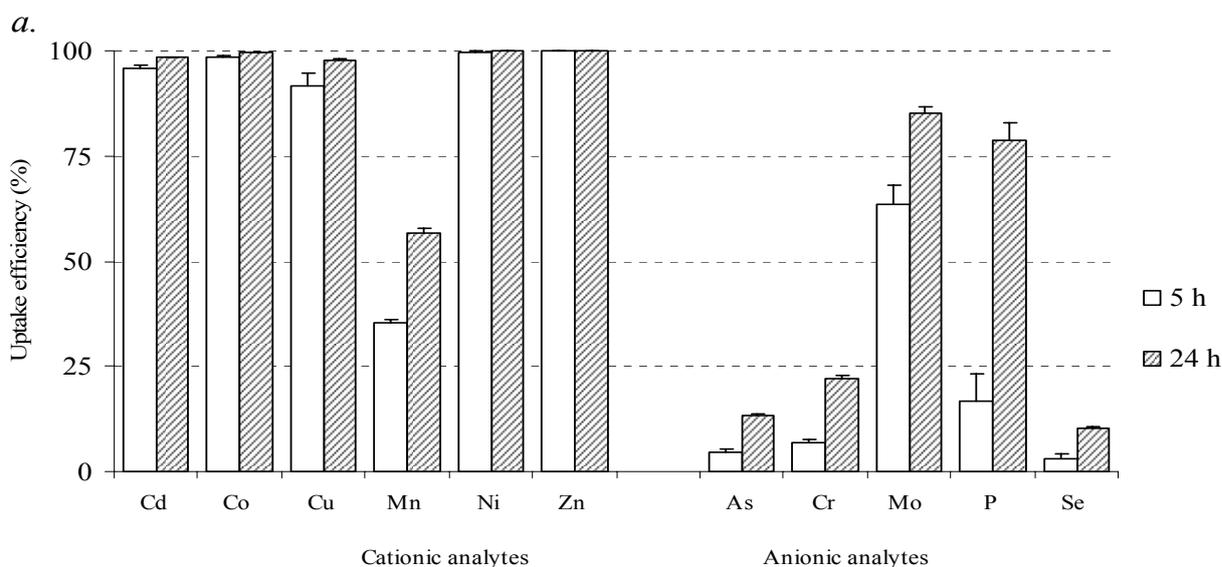
Figure 5.2.2. Kinetics of (a) cadmium and (b) molybdenum on the La-Chelex 1 resin gel. The concentration in the experimental solution before exposure of the resin gel was $0.66 \mu\text{g mL}^{-1}$ for Cd and $0.50 \mu\text{g mL}^{-1}$ for Mo. Error bars represent the standard errors.

The results of 300 min deployment time are given here to show the elution efficiency with 1mol L^{-1} HCl. The elution efficiency of La-chelex 1 resin gel was 80% for Mo, 67% for Se and only 9% for Cr. Molybdenum had the highest for the elution efficiency of all cationic and anionic analytes (Figure 5.2.1.b). For metal cations elution efficiency ranged from 71% (Cu) to 78% (Mn).

5.3. Comparison of different deployment times - La-Chelex 2 resin gel

Figure 5.3.1.a shows the uptake of analytes by the La-Chelex 2 resin-gel over time. The bar diagram for cationic analytes illustrates the rapid binding of ions to this resin. The uptake efficiencies of Ni and Zn were 100% after both 5h and 24h deployment times of immersion. Uptake of Cu, Cd and Co by La-Chelex 2 resin gel varied between 92% and 96% for 5h exposure time and between 98% and 100% for 24h exposure time respectively. Only 35% of Mn was taken up by this resin gel after 5h and 57% of Mn was taken up after 24h from test solution.

The uptake efficiency of anionic analytes varied strongly. Molybdenum and P uptake after deployment time of 24 h were 85% and 80% which are higher than other anionic analytes' efficiencies. The P uptake efficiency after 5 h was very low (17%) but 63% for Mo. The uptake efficiencies of As, Cr and Se were very low (Figure 5.3.1.a).



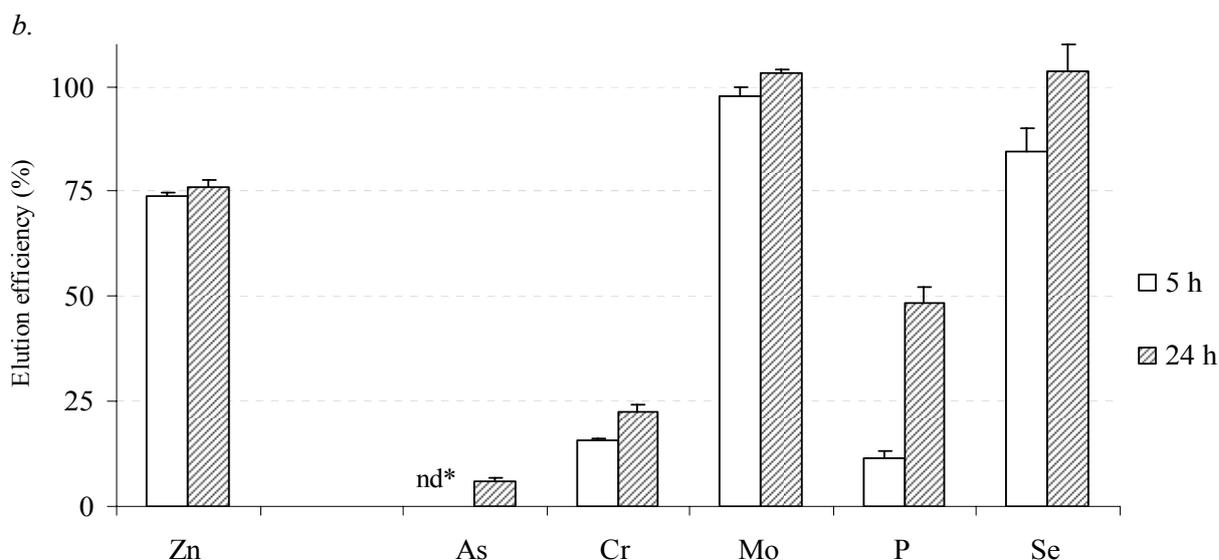


Figure 5.3.1. (a) Uptake and (b) elution efficiencies of La-Chelex 2 resin gels. Gels were deployed in the experimental solution containing cationic and anionic analytes. Deployment times were 5 h and 24 h. The acid used for elution was 1 mol L⁻¹ HCl. Error bars represent the standard errors. Some elution efficiencies were not presented here. (nd* - not determined).

The mass of the analytes that were bound to the La-Chelex 2 gel disc is presented in *Figure 5.3.2* in the *Appendix*.

The elution efficiencies of Se and Mo with 1 mol L⁻¹ HCl were the highest (*Fig 5.3.1.b*) for the resin gel discs that were exposed for 24 h. The elution efficiencies of La-Chelex 2 resin gel discs that were immersed in test solution for 5 h showed slightly lower values than discs deployed for 24 h (84% for Se and 98% for Mo). The other anionic analytes' elution efficiencies were very low (<50%). The P elution efficiency was 49% from the 24 h-deployed-resin gels. Zn was chosen to show the elution efficiency representative for cationic analytes. Seventy four percent of Zn was eluted from the disc gel deployed for 5 h. This value increased to 76% for the 24h-deployed gel discs.

5.4. La concentrations effect to produce La-Chelex 2 resin gel & elution efficiencies with different concentrations of HCl

The performance of the La-Chelex 2 was tested for binding analytes after impregnation in La solutions at different La concentrations (0.001, 0.01 and 0.1 mol L⁻¹). The gel loaded at 0.001 mol L⁻¹ solution showed higher uptake efficiency (*Figure 5.4.1*) for cationic analytes (Cd, Co, Cu, Mn, Ni and Zn). The uptake efficiency slightly decreased with the increase of La concentration. For instance, it was 92% at concentration of the 0.001 mol L⁻¹ of La solution for Cd and changed to 82% at the 0.01 mol L⁻¹ and 80% at 0.1 mol La L⁻¹ respectively. The Mn uptake by all tested gel discs were generally lower than other cationic analytes and the values varied from 56% at the 0.001

mol L⁻¹ concentration to 21% at the 0.1 mol L⁻¹ concentration of La. Anionic analytes uptake by La-Chelex 2 gel disc was generally lower than cationic analytes' uptake. Amongst the anionic species tested, Mo showed the highest uptake efficiencies of about 50% at all concentrations of La solution used to make La-Chelex 2 gel. Generally it seemed that the La concentration did not affect the uptake efficiency of the gel for anionic analytes. At 0.01 mol La L⁻¹ the mean accumulated mass of anionic analytes onto the disc gels was the highest.

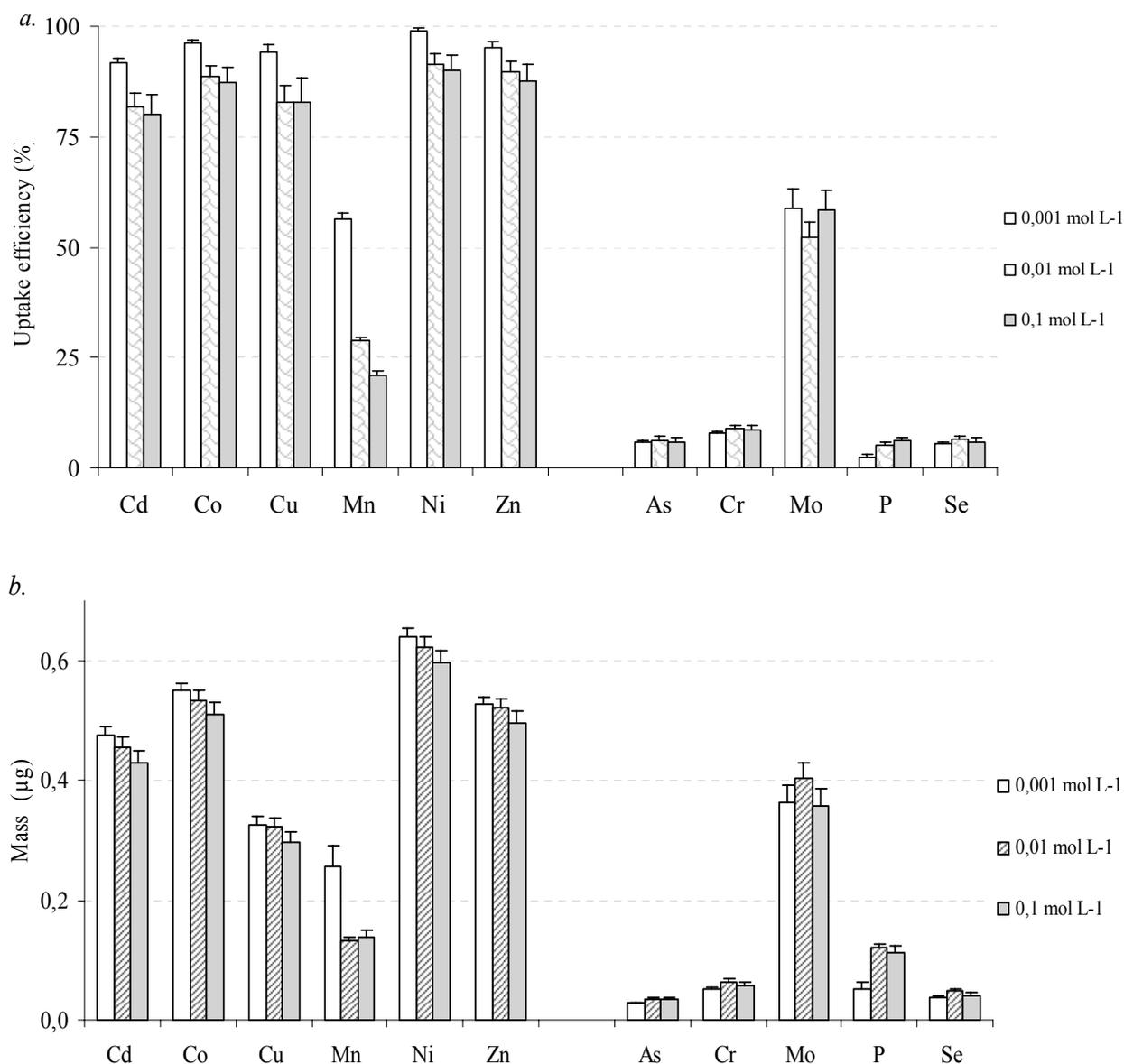


Figure 5.4.1. a) Uptake efficiency of La-Chelex 2 resin gel; b) measured mass on the La-Chelex 2 resin gel disc after deployment in the experimental solution containing cationic and anionic analytes. The La concentrations used for impregnating Chelex gels were 0.1, 0.01 and 0.001 mol L⁻¹. Deployment time was 5h. Error bars represent the standard errors.

The elution efficiency increased for cationic analytes in this experiment using the 2 mol L⁻¹ and the 5 mol L⁻¹ HCl (Figure 5.4.2). Compared to elution with HCL in the previous experiment elution of Mn from the gel disc prepared at the 0.1 mol L⁻¹ La solution was complete (100%) but decreased in the gel discs treated with lower concentrations of La. Elution efficiency of Cr was lower than for other analytes with values between 7 and 29%. Phosphorus elution efficiency using 5 mol L⁻¹ HCl showed the highest value of 66% for the gel discs with treated with the 0.1 mol L⁻¹ La solution. The highest elution efficiency by the 2 mol L⁻¹ HCl was 58% for phosphorus but the gel discs were treated by the 0.001 mol L⁻¹ La solutions. Molybdenum and Se elution efficiencies by the 2 mol L⁻¹ HCl were higher than the elution by the 5 mol L⁻¹ acid concentrations.

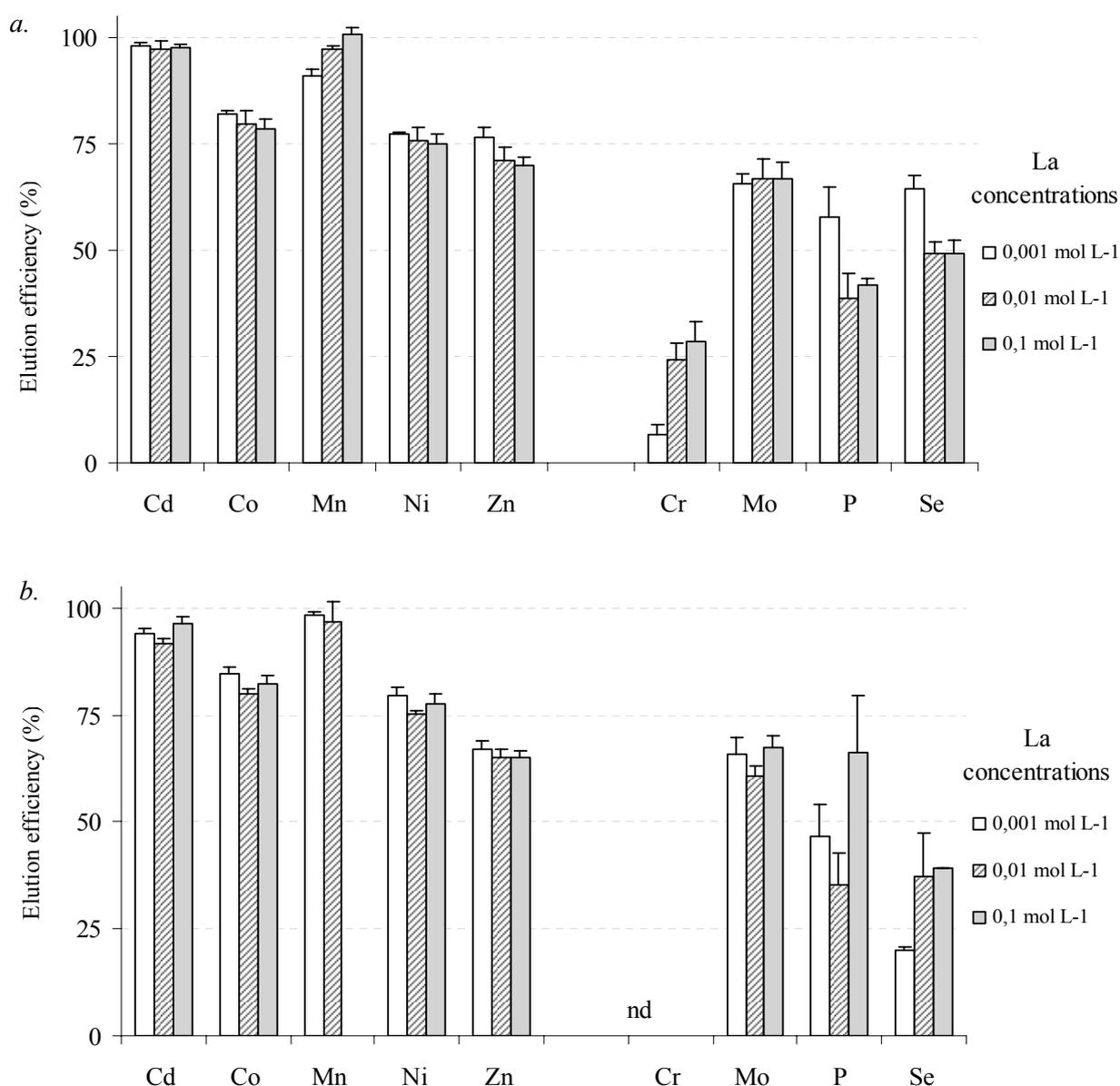


Figure 5.4.2. Elution efficiency of La-Chelex 2 resin gels after 5 h deployment in different concentrations of HCl. The concentration used for the elution was a) 2 mol L⁻¹ HCl and b) 5 mol L⁻¹ HCl. (La-Chelex 2

resin gels were prepared impregnating Chelex gels in different concentrations of La solutions.) Error bars represent the standard errors.

5.5. DGT experiment with La-Chelex 2 resin gel

This experiment was carried out to investigate the linearity of mass accumulation of cationic and anionic analytes on the La-Chelex 2 resin gels in DGT devices over 24 h (Figure 5.5.1). The concentration (C_{SOL}) of the experimental solution decreased from $182 \mu\text{g L}^{-1}$ to $173 \mu\text{g L}^{-1}$ for Mo and from $182 \mu\text{g L}^{-1}$ to $105 \mu\text{g L}^{-1}$ for Cd after 24 h deployment time.



Figure 5.5.1. The concentration of the experimental solution after different times of deployment. The values at the Y axis show the initial concentration of the solution before exposure of the DGT device.

For the calculation of C_{DGT} (Table 5.5.1) the required parameters such as V_{gel} , D , A , Δg are considered as known constants in this approach, and their values will not change under controlled conditions, except for t which is dependent on the deployment time. The elution efficiency of the La-Chelex 2 binding layers with the 2 mol L^{-1} HCl was 67% for Mo and 97% for Cd as measured in previous experiments.

Table 5.5.1. C_{dgt} concentration after different time of deployments $\mu\text{g L}^{-1}$

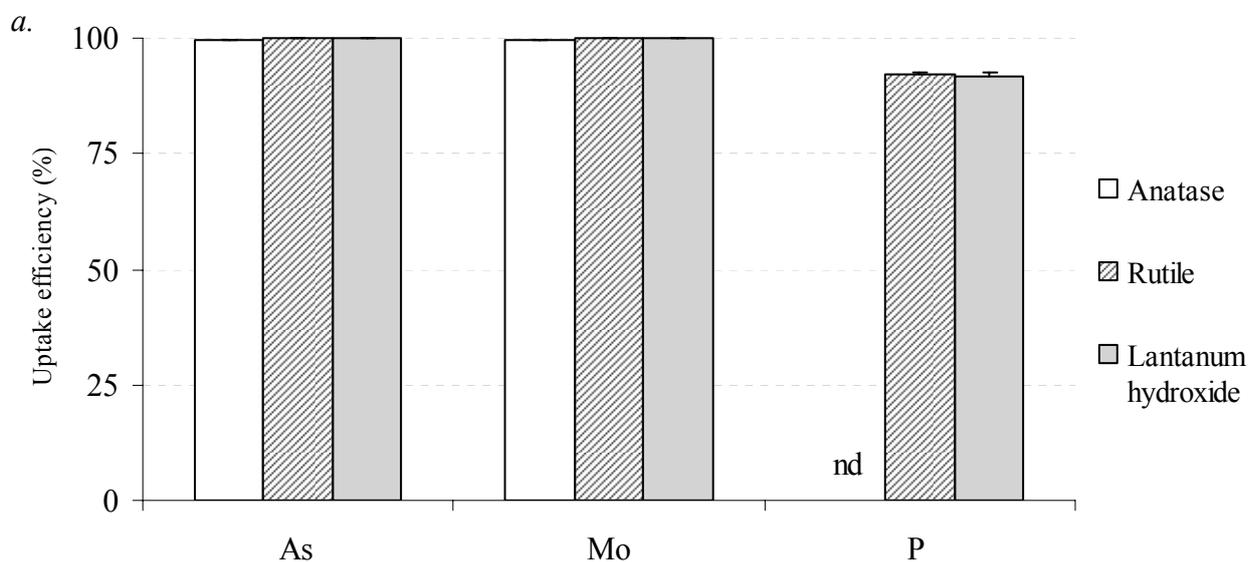
	Time of deployment	Mo	Cd
Mean	after 3 h	156	92
St.error	after 3 h	3	4
Mean	after 7 h	83	94
St.error	after 7 h	10	4
Mean	after 24 h	42.2	114
St.error	after 24 h	4	5

The ratios of C_{DGT}/C_{SOL} were 0.9 for Mo and 0.8 for Cd after 3h. It decreased from 0.5 after 7 h to 0.2 after 24 h for Mo. In contrast, the ratio increased with deployment time for Cd (0.9 after 7h and 1.0 after 24h).

5.6. Sorption test of anatase, rutile and lanthanumhydroxide resins

The minerals of anatase, rutile and lanthanumhydroxide were appropriate for use in the binding layer. These resins were strongly binding the anionic analytes species and *Fig 5.6.1* illustrates the uptake efficiencies of anatase, rutile and lanthanumhydroxide resins for the anionic analytes such as As, Mo and P.

In these initial tests the first priority was to evaluate the anion binding ability of these minerals. The uptake efficiency was calculated measuring the concentrations of As, Mo and P in the test solution after immersion. The amounts of the analytes (*Figure 5.6.1.b*) in the 10 mL solution were calculated based on the concentration measurements. As and Mo uptake efficiency by the resins were very high (~100%).



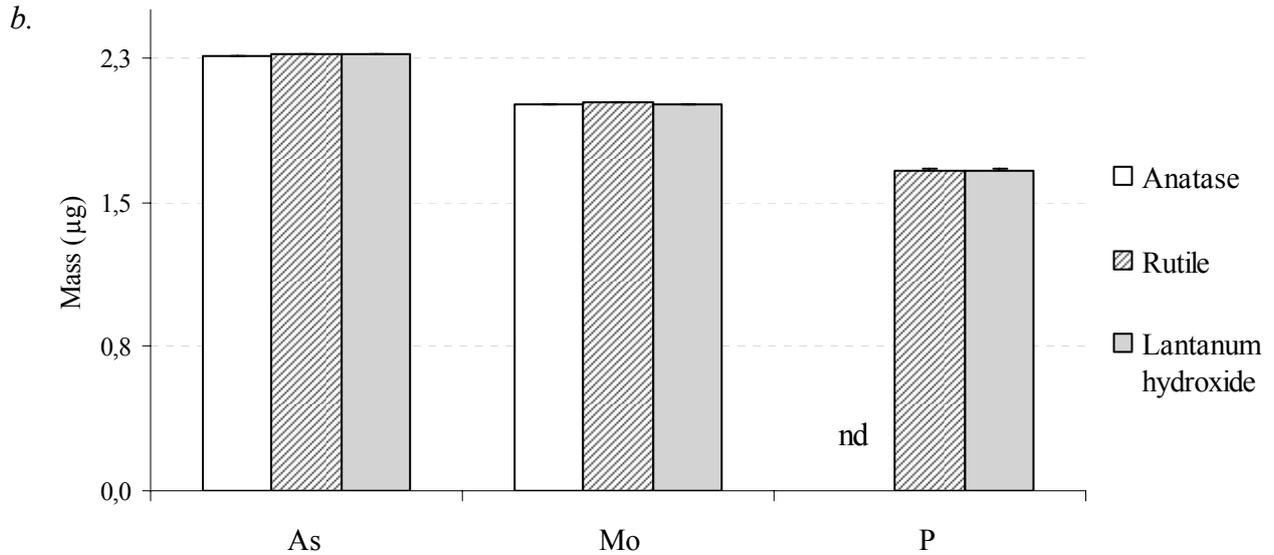


Figure 5.6.1. Uptake efficiency of different resin gels (a) containing different binding agents and measured mass on the gels (b) after deployment in the experimental solution containing cationic and anionic analytes. Anatase, rutile and lanthanumhydroxide were tested as binding resin. Error bars represent the standard errors.

The P uptake of the resins was slightly lower than for other analytes, but still sufficiently high (92%).

5.7. Sorption and elution test with anatase, rutile and lanthanumhydroxide resin gels

Due to measurement problems, only the results for lanthanumhydroxide resin gels are presented here (Figure 5.7.1). The DGT-resin gel loaded with lanthanumhydroxide showed higher uptake efficiency (90%) for As than for any other analytes. The uptake efficiency for P was 78% and was 46% for Mo. The mass bound onto the gel discs were presented in Figure 5.7.2 in Appendix.

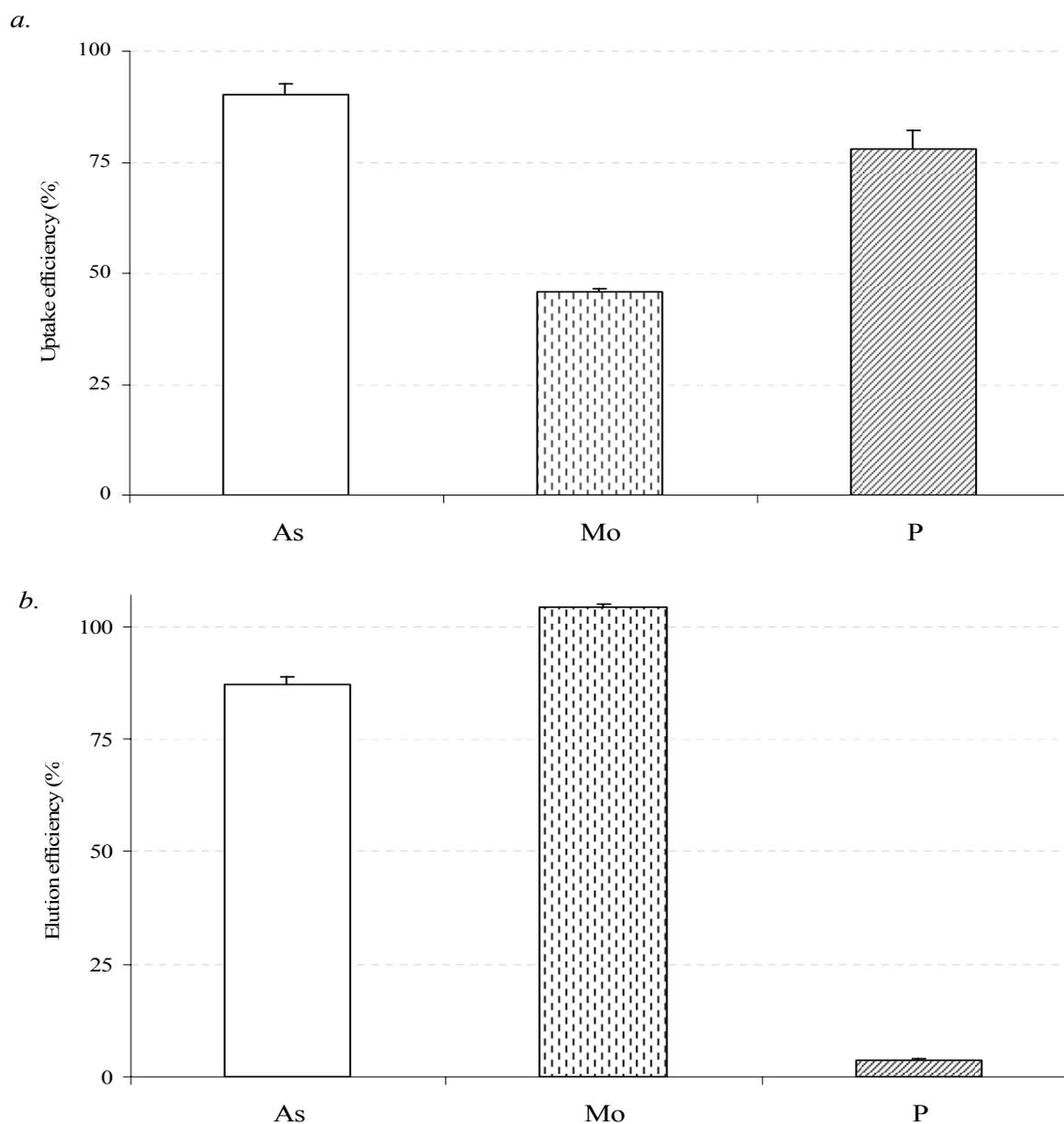


Figure 5.7.1. Uptake (a) and elution (b) efficiency of lanthanumhydroxide resin gel after deployment in the experimental solution containing anionic analytes. The eluent was $0.25 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. Error bars represent the standard errors.

As described earlier, the elution was performed with $0.25 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$. The efficiency of elution was 87% for As and 104% for Mo. The elution efficiency for P was very low (4%).

5.8. Elution of anatase and lanthanumhydroxide resin gels with 1 mol L^{-1} , 3 mol L^{-1} and 5 mol L^{-1} of HCl and H_2SO_4

Uptake and elution efficiencies were tested simultaneously by exposing anatase resin gel and lanthanumhydroxide resin gels into solutions with known amounts of As, P and Mo. The uptake efficiency of lanthanumhydroxide resin gel was 76% for P, 81% for As and 90% for Mo (Figure

5.8.1). These values were higher for the anatase resin gels (96% for P, 92% for As and 97% for Mo).

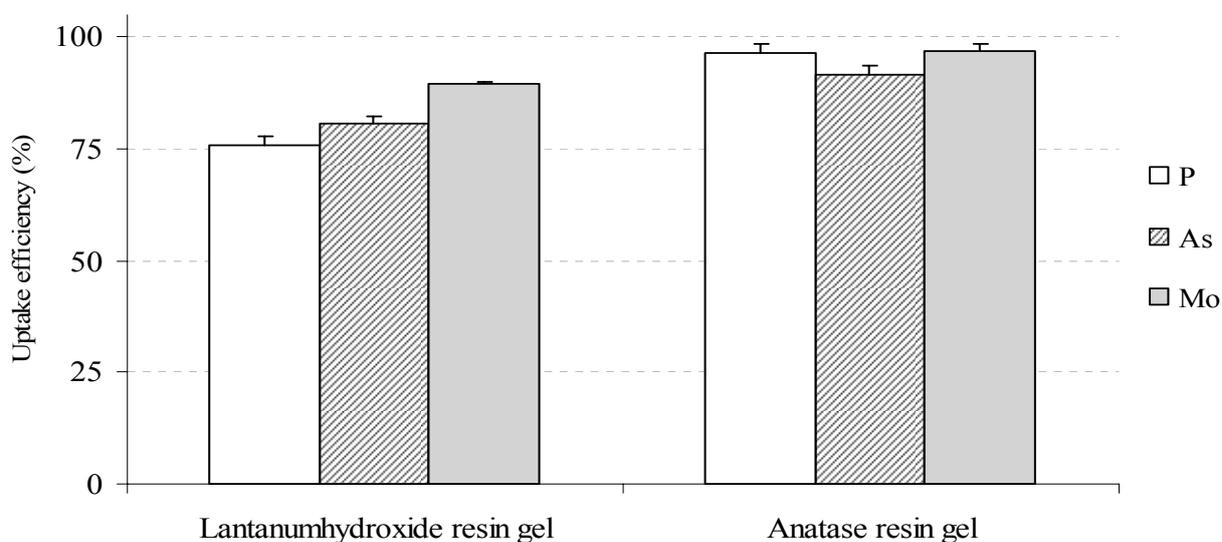


Figure 5.8.1. Uptake efficiency of lanthanumhydroxide resin gel and anatase resin gel after deployment in the experimental solution containing anionic analytes. Error bars represent the standard errors.

The species bound in these gels were eluted with the 1, 3 and 5 mol L⁻¹ HCl, and 1, 3 and 5 mol L⁻¹ H₂SO₄ respectively. In our experiment, the elutions with different concentrations of HCl and H₂SO₄ have shown altered results for each element (Figure 5.8.2).

Phosphorus elution with HCl from the lanthanumhydroxide gels was very low and the values varied from 0.3% to 1.4%. In contradiction to this result the elution efficiency increased when P was eluted from anatase resin gel discs. A proportion of 78% of P was eluted from anatase gel disc with 3 mol L⁻¹ H₂SO₄ acid whereas the 1 mol L⁻¹ H₂SO₄ eluted 58% P from same gel discs. The elution efficiencies of P from the same type of gel discs (anatase) using HCl acid were generally lower than when using H₂SO₄.

The elution of As with different concentrations of H₂SO₄ resulted in higher values than with HCl. The amount of As eluted from anatase gel discs was higher than the amount eluted from lanthanumhydroxide gel discs.

Elution efficiency of Mo from the lanthanumhydroxide resin gel was higher than from anatase gels. Elution of Mo from anatase resin gel by HCl was only sufficiently high at an eluent concentration of 5 mol L⁻¹. At 5 mol L⁻¹ H₂SO₄ >75% of Mo was eluted from both resin gels.

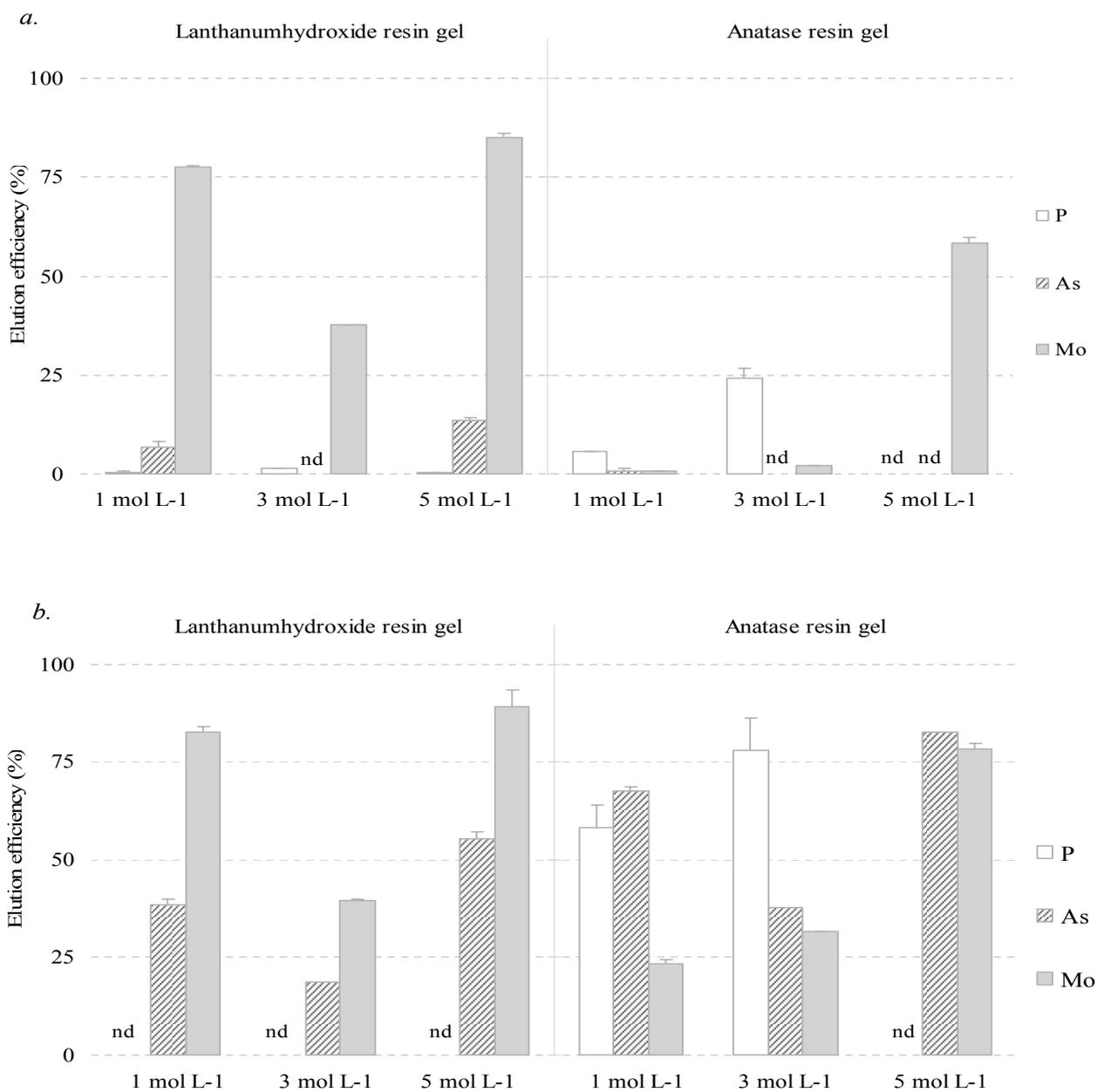


Figure 5.8.2. Elution efficiency of lanthanumhydroxide and anatase resin gels at different concentrations of HCl (a) and H₂SO₄ (b). The concentrations of the acids used for elution were 1 mol L⁻¹, 3 mol L⁻¹ and 5 mol L⁻¹. Error bars represent the standard errors.

6. Discussion

Several papers (see chapter 3.3) describing laboratory testing and field applications of DGT have been published since 1994. The metals associated with soil acidification, the heavy metals, and other elements of environmental interest were/are of high priority to be investigated. Cations and anions are not present as individual constituents but rather are in combination with other ions, the individual toxicity of a cation or anion may be masked or confounded by the associated anion or cation of the compound. The aim of this work was to produce a novel DGT binding layer that is able to measure/accumulate cations and anions simultaneously in a single assay.

As described earlier, the La was tested firstly for its anion uptake capability. The La-chelex resin was indicated by Wu et al. (2007) to be highly selective and efficient for the removal of phosphate from wastewater. They stated also that the uptake of phosphate is rapid, and it is reproducible and efficient, and there is no leakage of La. The La-Chelex resin used in our experiments showed high affinity for P when tested as resin powder. However, the affinity of La-loaded Chelex for anionic analytes decreased after incorporation of the resin in a DGT gel.

A mixture of pure Chelex and La-loaded Chelex resins showed lower anion uptake efficiency whereas this mixture showed sufficient cation uptake efficiency. This might be also connected to that the amount of this resin in the mixture was only half of the amount of La-Chelex. However, it is not necessary to mix these two resins because the La-Chelex resin alone was able to adsorb anions and cations efficiently. Generally Chelex is well known for cation adsorption (see chapter 3). The capacities of the Chelex gels are element-dependent, for example the selectivity of Chelex for Mn is lower than for Cd (Mason, 2005). Nevertheless, all cations (including Cd and Mn) after 300 min deployment were adsorbed 100% by La-Chelex in our experiment (Fig 5.2.1).

The comparison between two La-Chelex gels was made. The La content of the two gels was the same, only the method of loading La into the gels was different. La-Chelex 2 resin gels showed higher anion adsorption affinity than La-Chelex 1 resin gels. The uptake of analytes by La-Chelex 2 resin gels was tested for 5 h and 24 h. The longest deployment time to test anion uptake for La Chelex 1 resin gels was 5 h. The comparison of 5 h deployment time for Mo showed that the La-Chelex 2 resin gel has higher uptake affinity than La-Chelex 1 resin gel, demonstrating that the method of impregnation of La into the Chelex resin gels affects anion uptake ability.

Cationic analytes uptake by these two resin gels showed identical behaviour. La-Chelex 2 resin gel showed increased uptake efficiency for anionic analytes, with 79% P and 85% Mo taken up by La-Chelex 2 resin gel after 24 h exposure. Here the amount of La solution for the impregnation of the purchased Chelex resin gel was 300 ml whereas 100-150 ml La solutions were used in the previous

experiments to prepare La-Chelex resins. However the concentrations of La solution were unchanged (0.1 mol L^{-1}) and further testing of La-Chelex 1 resin gels with longer exposure times and various concentrations of La solutions could be done.

Different concentrations of La solution were investigated for La-Chelex 2 (purchased) gels to test the hypothesis that anion uptake efficiency might depend on the amount of La in the binding layer. The higher concentration of La solution could have been tested to get more effective efficiency for anion uptake of this gel. For elution 2 mol L^{-1} HCl was most practical among three different concentrations of HCL solution.

Hence La-Chelex 2 resin gel (for its superior anion uptake efficiency) and 2 mol L^{-1} HCl acid (for its higher elution efficiency) were chosen for the DGT experiment based on previous results. We compared C_{DGT} (see *Equation 6*) with the concentration in the immersion solution (C_{SOL}) obtained by ICP-MS measurement. The $C_{\text{DGT}}/C_{\text{SOL}}$ ratios should have ranged between 0.9 and 1.1 as testing DGT using standard solutions should yield results within 10% of the actual concentrations (Zhang and Davison, 1995). The quotients of concentrations of Cd determined by DGT (C_{DGT}) and the concentrations measured directly in the immersion testing solution (C_{SOL}) were not much different. The ratios of $C_{\text{DGT}}/C_{\text{SOL}}$ were 0.8 after 3h, 0.9 after 7h and 1.0 after 24h for Cd. This ratio was not within that range but varied from 0.9 to 0.2 for Mo between 3h, and 24h deployment times. Warnken et al. (2005) showed ~ 0.5 for $C_{\text{DGT}}/C_{\text{SOL}}$ when they used gels that were poorly washed of polymerization products. They explained it by a net positive charge on the gel changing the concentration of metal ions at the interface between the gel and bulk solution.

Secondly, several mineral powders were tested for their affinity of anion binding in this work. The anion uptake by anatase, rutile and lanthanumhydroxide resins varied from 92% to 100% showing their high ability to bind anions onto their surface. Different concentrations of diverse chemicals such as HCl, H_2SO_4 acids and ammonium bicarbonate (NH_4HCO_3) were tested for elution. Due to ICP-MS measurement difficulties, we did not obtain results for the elution with the 0.25 mol L^{-1} , 0.5 mol L^{-1} and 1 mol L^{-1} of NH_4HCO_3 from anatase and rutile. In this experiment, the pH was adjusted to 10 because all colloids, organic or inorganic, exhibit variable surface charges associated with OH groups. Depending on pH, both negative and positive charges may be provided from this source.

Lanthanumhydroxide resin gels took up sufficient amount of As and P. Higher elution efficiencies for As and Mo than for P were obtained when gels were eluted with 0.25 mol L^{-1} H_2SO_4 . It is not clear why the value of P elution efficiency was lower than fo As because arsenate resembles phosphate in many respects, since As and P occur in the same group of the periodic table.

Therefore an elution experiment with different acids at different concentrations was performed to elucidate this uncertainty. Bennett et al. (2010) tested also Metsorb*. Its average uptake efficiencies were 100% for As, 97% for Se, and 19% for Se and elution efficiencies by 1 mol L⁻¹ NaOH solution were 75% for As, 89% for Se^{IV}. In our last experiment we used 1 mol L⁻¹, 3 mol L⁻¹ and 5 mol L⁻¹ of HCl and H₂SO₄ for both investigated resin gels (rutile was excluded). The results of this investigation proved that both HCl and H₂SO₄ are applicable for the elution of anatase and lanthanumhydroxide resin gels with some exceptions.

The results of rutile showed lower anion uptake efficiency than anatase and lanthanumhydroxide gels. Apart from measurement problems the following explanations may be considered. Rutile and anatase have surface hydroxyl groups with different reactivities that can adsorb and retain phosphate and arsenate (Fordham & Norrisch, 1983). The amount of ions that can be adsorbed depends not only on its concentration in solution, but also on the pH of the solution. Hydroxyls and other functional groups on the surfaces of the colloidal particles that by releasing or accepting H⁺ ions can provide either negative or positive charges. Moreover, charge imbalances caused by isomorphous substitution in some mineral crystal structures of one cation by another of similar size but differing in charge may be involved. Therefore further testing of these minerals should include the effects of pH to get detailed information whether the minerals provide negative or positive charges. The points of zero charge[†] (PZC) of titanium dioxide reported in the literature range from 2 to 8.9. The PZC of anatase (average 5.9) is slightly higher than that of rutile (average 5.4) (Kosmulski, 2002). The pH_{pzc} of lanthanumhydroxide was approximately 8.75 (±0.05) and it was used for the defluoridation by Na & Park (2010). Adsorption capacity of lanthanumhydroxide in their experiment remained nearly constant up to pH_{eq}[‡] 7.5-8, and thereafter sharply decreased with increasing solution pH. Variable or pH-dependent charges formed by protonation and deprotonation of functional groups like -OH therefore could influence the adsorption of anions. Also, the so-called loading capacity, i.e. the amount of a compound adsorbed to the surface in equilibrium conditions, strongly depends on the specific surface area[§]. Here, even slight variations of the specific surface area easily overcompensate a certain difference in the adsorption enthalpies. Above mentioned arguments could apply for the adsorption of anions to all adsorbents used in this work.

Generally the effect of pH on the speciation of phosphate can be taken into account. Concerning to the research by Malati et al. (1993) at pH 5, H₂PO₄⁻ is likely to be adsorbed at the positive anatase surface sites at 25°C and as the pH is lowered H₂PO₄⁻ ions were replaced by H₃PO₄ at the

* A commercially available titanium dioxide based adsorbent

† The point of zero charge (pzc), in physical chemistry, is a concept relating to the phenomenon of adsorption, and it describes the condition when the electrical charge density on a surface is zero.

‡ a sudden change of the measured pH (pH at the equivalence point here is 7.5-8)

§ Specific surface area is defined as the surface area of particles per unit mass or unit volume of particles.

adsorption sites. However precise measurement of mobile P is necessary because excessive amounts of phosphate may cause eutrophication in water and due to its numerous forms. Also the phytoavailable P is difficult to measure in soils. Using novel binding layers as developed and tested here can significantly enhance the capabilities of the DGT technique towards simultaneous measurement of nutrients and pollutants of both cationic and anionic nature in soils, sediments and waters. Further developments and testing are required to optimize the binding layers for a wide range of chemical species and applications.

7. Conclusion

DGT technique in this work has been used as a tool for measuring time-integrated concentrations of the anions in water. All resins used in our experiments showed high affinity to adsorb anionic analytes when used as pure resins only. La-loaded chelex as well as rutile resins showed lower sorption capabilities for anions when they were incorporated in DGT gels. Anatase and lanthanumhydroxide showed high affinities for anion sorption both, as pure powders as well as after incorporation in DGT gels. These materials will therefore be further tested. The potential of this technique we investigated here offers a simultaneous measurement of cation and anions thus overcoming the need for using two independent assays. The binding layers investigated here could also become a very important part of DGT technique development for the monitoring of nutrient and pollutant bioavailabilities at high spatial resolution to elucidate their behaviour in highly variable microenvironments such as plant rhizospheres or soil aggregates.

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Appendix

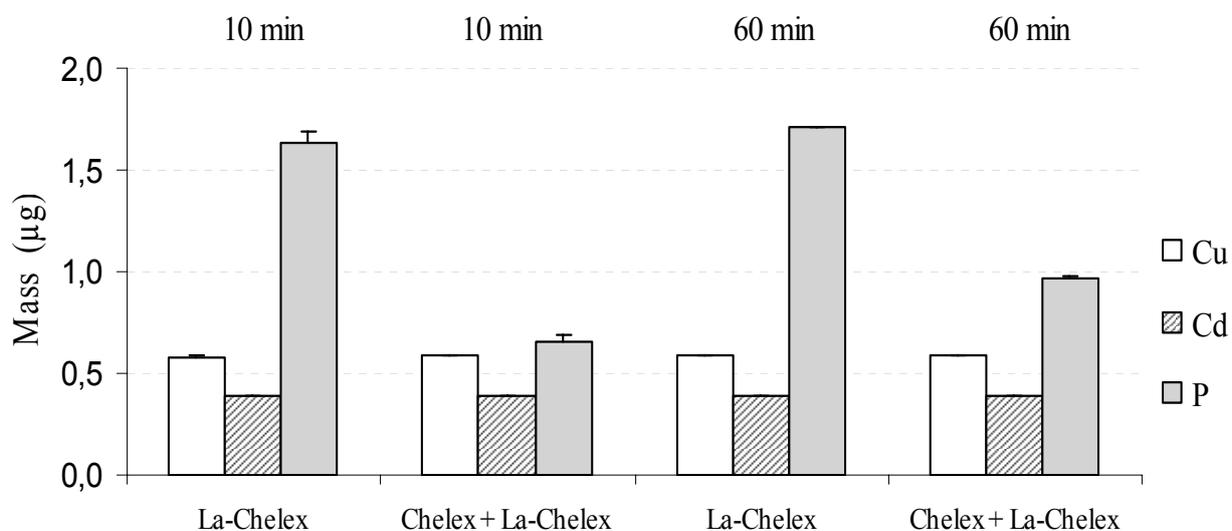


Figure 5.1.2. Measured mass of the elements on the La-Chelex and Chelex+La-Chelex resin after deployment in the experimental solution. Deployment times were 10 min and 60 min. Error bars represent the standard errors.

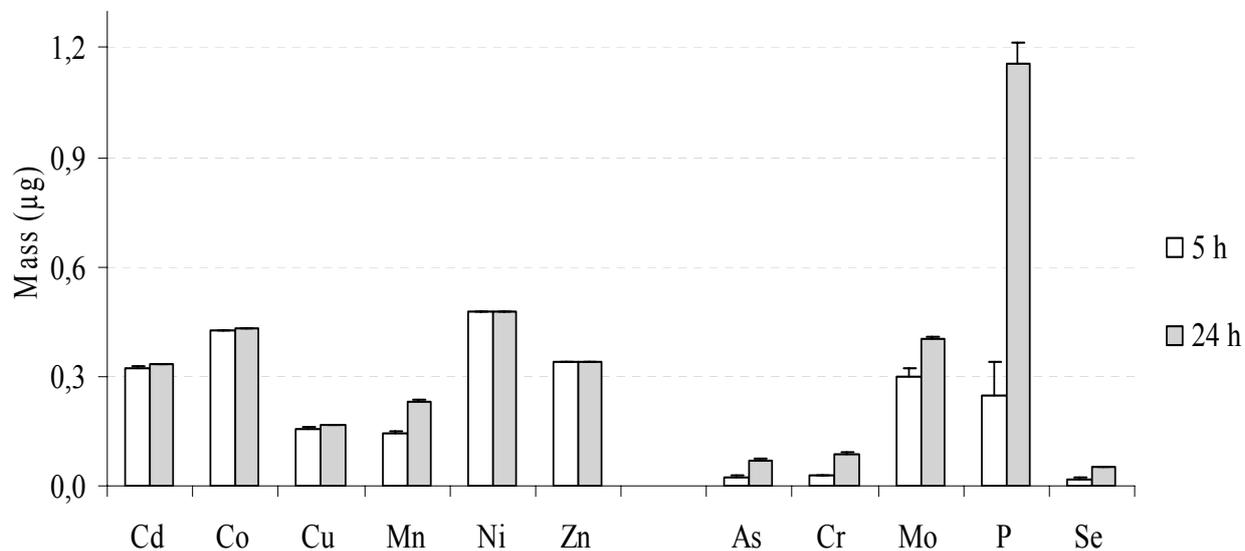


Figure 5.3.2. Measured mass of the analytes on the La-Chelex 2 resin gel disc after deployment in the test solution containing cationic and anionic analytes. Deployment times were 5h and 24h. Error bars represent the standard errors.

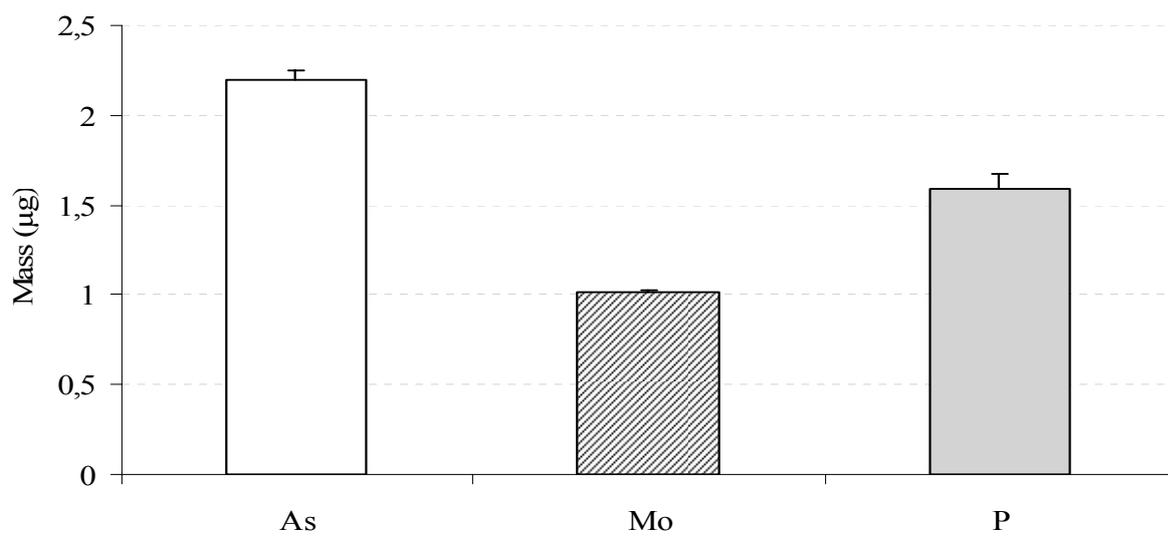


Figure 5.7.2. Measured mass of anionic analytes of lanthanumhydroxide resin gel disc after deployment in the experimental solution containing anionic analytes. Error bars represent the standard errors.