Chapter 4. Binding layer properties

William W. Bennett, Maja Arsic, Jared G. Panther, David T. Welsh, and Peter R. Teasdale

4.1 Introduction

The accurate measurement of solutes by DGT relies on the strength of their interaction with the binding layer. Mass transport of the analyte through the diffusive layer can only achieve a steady state when the analyte binds rapidly and irreversibly to the surface of the binding layer, so that the concentration of the solute at the interface between the binding layer and diffusive layer is effectively zero [1]. When this assumption is met, the DGT equation can be used to accurately determine the DGT-labile concentration of the analyte in the bulk solution.

The first binding layer to be used with DGT consisted of a hydrogel containing Chelex 100, a commercially available resin containing iminodiacetic acid functional groups, which strongly bind transition metal ions via chelation [2]. The selectivity of Chelex 100 for transition metals over alkali and alkaline earth metals ensures that the major ions in natural waters (i.e. Na^+ , K^+ , Mg^{2+} , Ca^{2+}) do not interfere with the measurement of transition metals typically present in much lower concentrations (i.e. trace metals) [3]. Without the high degree of selectivity that Chelex 100 exhibits for trace metals, successful measurement of these analytes in a wide variety of natural waters would not be possible, due to competition for binding sites by major ions.

Natural waters exhibit a variety of major ion concentrations and compositions, as well as a range of hydrogen ion concentrations (pH), which can affect the interaction between the binding layer and the analyte. Competition for binding sites by major ions and H^+ , which are

often present at several orders of magnitude higher concentrations than trace metals, reduce the effective capacity of the binding layer for the target analyte, and thus restrict the length of deployment times that can be used. It is essential, therefore, that binding layers are comprehensively evaluated across a range of pH and ionic concentrations, and for deployment times that are representative of actual field deployments, so that measurements in natural systems can be relied on to be both accurate and precise.

This chapter has three primary aims: 1) to provide a detailed description of the different types of binding layers utilised to date and their key features; 2) to outline the steps involved in validating a potential binding layer and to discuss examples in which satisfactory and non-ideal uptake by binding layers has been reported; and, 3) to summarise the current validation status of existing binding layers described in the literature and to suggest future developments with regard to DGT binding layers. It is hoped that this chapter will be useful for both researchers looking to develop and evaluate new DGT binding layers, and those looking to apply existing DGT techniques to measuring a particular analyte or suite of analytes in the environment.

4.2 Binding layer types and features

A variety of different materials have been described in the literature for application as DGT binding layers (Table 4.1). These layers typically consist of solid resins or powders that are incorporated into a gel matrix (e.g. polyacrylamide) to form a near homogenous binding layer, although polyacrylamide derivatized with binding functional groups, commercial membranes and liquid (polyelectrolyte) binding layers have also been described [4-6]. The initial focus was on developing DGT for measuring cationic trace metals (e.g. Cd, Cu, Co, Ni, Pb, Zn), which was achieved using the chelating ion-exchange resin, Chelex 100 [2], and

expanded through application of other resins such as AG50WX8 (a non-chelating ion exchange resin) for Cs and Sr [7]. Attention then turned to oxyanionic species, such as phosphorus, sulphide and arsenic in which different binding mechanisms were used. Phosphorus and arsenic could be accumulated by adsorption onto metal (hydr)oxide-based binding layers such as ferrihydrite (FeOOH) [8, 9] and Metsorb (TiO₂ – nano-anatase distributed within a polymer backbone)[10, 11]. Sulphide used a novel binding reaction in which HS⁻ displaced I⁻ ions from silver iodide [12], which resulted in a distinct colour change that facilitated two-dimensional measurements (see Chapter 8). The measurement of mercury with DGT was another area of considerable interest, and resulted in the application of selective binding layers containing thiol-functionalised resins, which were later evaluated for the selective measurement of As^{III} [13, 14]. In order to expand the range of analytes determined in a single DGT deployment, mixed binding layers [15, 16] or sandwich deployments [17] have also been developed. The simple process of encapsulating a solid phase binding agent in a gel matrix has facilitated the development of a great diversity of DGT techniques, and will continue to do so into the future.

To use a solid material as a binding agent within a DGT binding layer, it must be of sufficiently small particle size to allow simple incorporation into a gel matrix. The standard thickness of an unhydrated binding gel layer is 250 µm (approx. 400 µm after hydration), so the diameter of solid particles incorporated into the gel must be considerably smaller than this to allow for easy preparation (< 100 µm is recommended). Further details of the practical aspects of preparing binding gel layers are provided in Chapter 10. Many of the existing binding layers utilise commercially available materials as the binding agent, which have the advantage of widespread availability and reproducibility, although laboratory-synthesised materials have also been used successfully [6, 9, 18].

As shown by the wide variety of binding agents in Table 4.1, there are often numerous options when considering which binding layer to use for a particular purpose. The suitability of a binding layer is dependent on the matrix in which it will be deployed, with many binding layers only applicable to freshwaters due to the high concentrations of competing ions present in more complex matrices like seawater [11]. In fact, of the 46 binding layers described in Table 4.1, the majority have not been tested in seawater.

There are four key characteristics when considering a potential binding layer:

1. The binding strength, which is represented by a relevant equilibrium constant for each analyte (e.g. stability or solubility constant). Binding constants for analytes are often available when a commercial resin is used but can also be determined experimentally [19]. Generally, DGT techniques with a high binding strength for their target analytes will be more suitable for making measurements in diverse sample types.
2. The *intrinsic binding capacity* of the binding layer, which relates to the number or density (concentration) of sites able to interact with analyte species at the interface of the diffusive and binding layers, and is independent of the binding strength. Determining the binding layer capacity is an important step of the validation process. Higher binding capacities will be particularly important for DGT techniques in which binding strengths are fairly low.
3. The presence of competition effects. Competition can arise from the presence of other ions with similar or stronger binding strengths, and may be important in matrices with high concentrations of several analytes where a sizeable fraction of the total binding sites are occupied. However, competition effects are more

likely for some binding layers when DGT devices are deployed in saline and/or non-circumneutral pH (<5.5 or >7.4) waters. In these instances, major ions, H^+ and/or OH^- interact more weakly with the binding layer, but may be present at much higher concentrations than analytes. Competition has the effect of decreasing the concentration of binding sites available to interact with the analyte and may therefore result in non-ideal accumulation (i.e. not described by the DGT equation) by the binding layer. An *effective binding capacity* should be determined in the presence of competing analytes or in matrices in which competition is likely (see [20] as an example). Binding layers that use adsorption or ion exchange mechanisms are generally more prone to competition effects compared with binding by complexation.

Kinetic limitation may occur if binding of an analyte is insufficiently fast to outpace diffusional supply or dissociation of a complex (see Chapter 5) and therefore maintain a negligible concentration at the binding layer surface. Kinetic limitations may not be apparent during equilibrium characterization experiments with the binding layer alone, but could be observed during laboratory DGT deployments. The presence of kinetic limitations can be determined directly, but this has been done infrequently. Some kinetic effects have been observed due to increased competition for binding sites. For instance, uptake of Mn, Co and Cd at pH 4 and Mn at pH 5 by Chelex-DGT was non-ideal [21]. A proportion of the metals was observed to penetrate into the binding layer before being bound, due to a low rate of binding, which was considered to be most likely due to competition from H^+ resulting in a lower concentration of binding sites.

To determine the suitability of a particular binding layer for measuring an analyte, a comprehensive laboratory validation should be undertaken, as described in the following section. Typical experiments in which the above characteristics are determined will be

highlighted as well as instances of results that demonstrate satisfactory and non-ideal performance characteristics.

4.3 Laboratory validation

The process of developing and evaluating a new DGT binding layer involves a series of well-defined laboratory-based experiments. This section provides a general description of each of the recommended validation steps, as well as discussion of the common performance limitations that may be encountered. Comprehensive laboratory validation is essential to ensure new DGT binding layers perform accurately and reproducibly when deployed in the field.

4.3.1 Uptake and elution

The first step in evaluating a DGT binding layer is to determine that the binding material is capable of accumulating the analyte of interest (uptake). Some researchers also complete comprehensive kinetic studies as an extension of the uptake measurement [15]. This is useful to establish, early on in the validation process, whether the target analyte is suitable for the binding layer. Then it is necessary to find a suitable eluent solution that can quantitatively remove the analytes from the binding layer. The elution step is necessary because the majority of analytical techniques used to quantify analytes require an aqueous sample (e.g. inductively coupled plasma mass spectrometry (ICP-MS)). Solid phase measurement of DGT binding layers is discussed in Chapter 8.

In typical uptake experiments replicate binding layer gel discs are exposed to relatively small volumes of solution (5-10 mL) containing a concentration of analyte that is easily-measurable by the relevant analytical technique, while ensuring that the mass of

analyte accumulated on the binding layer is typical of masses accumulated in field deployments. These experiments are normally done over 24 h in 0.01 M NaNO₃ or NaCl to limit competition effects and adsorption losses to container walls. Following the uptake experiment the binding layer is removed from the analyte solution, rinsed thoroughly, and then placed into a small volume of eluent (typically 1 mL) for a further 24 h. Suitable eluents will vary depending on the binding layer and the mechanism by which the analyte is bound. For example, metals are removed from the Chelex 100 binding layer by a 1 M nitric acid solution [1], whereas oxyanions such as phosphate are removed from the Metsorb binding layer by a 1 M sodium hydroxide solution [11]. With the ferrihydrite binding layer, analytes are quantitatively eluted by dissolving ferrihydrite in HNO₃ or other acids [8, 9, 20]. Some analytes require more complex eluents to remove them from particular binding layers, such as the combination of sodium hydroxide and hydrogen peroxide to elute antimony from Metsorb [22]. Following analysis of the eluent by a suitable analytical technique (e.g. ICP-MS for metals, colorimetry for phosphate), typically after dilution to a matrix concentration suitable for analysis, the uptake and elution factors (often referred to as ‘efficiencies’ in the literature) can be calculated. The uptake factor, f_u , is calculated from the initial mass of analyte in the solution, M_i , and the mass of analyte remaining in solution after the experiment, M_f (equation 4.1). There is no specific value that is deemed acceptable for f_u , but values of >85% (Table 4.2) are typical of successful DGT methods.

$$f_u = \frac{M_i - M_f}{M_i} \quad (4.1)$$

The elution factor, f_e , is calculated after measuring the mass of analyte in the eluent solution, M_e , using equation 4.2.

$$f_e = \frac{M_e}{M_i - M_f} \quad (4.2)$$

Elution factors typically vary from 75 – 100% (Table 4.2). Although the reproducibility of the elution procedure is more critical to the accuracy of DGT measurements, higher values of f_e are preferred. For new binding layers, more than one eluent should be tested initially to determine an optimal elution procedure [23].

4.3.2 Linear mass accumulation over time

Following successful validation of uptake and elution factors, the potential binding layer should be tested as part of an assembled DGT sampler. The fundamental assumption of the DGT equation, of linear accumulation of the target analyte over time, should be met to ensure accurate measurements of solutes by the new technique. Typical experiments involve exposing replicate DGT samplers to a known concentration of analyte(s), for various deployment times (e.g. 6, 12, 18 and 24 h), in a solution of moderate ionic strength (0.01 M NaNO_3 or NaCl) without interfering ions. The solution should be well-stirred at a reproducible and constant rate during such experiments to minimise the diffusive boundary layer thickness [1]. Ideally, a small volume of solution should be collected whenever a set of DGT samplers is removed to monitor any changes in analyte concentration over time.

Following elution of the binding layers and analysis by an appropriate analytical technique, the linearity of the mass accumulation over time can be evaluated by a simple linear regression (Figure 4.1). Such regression lines should have $R^2 > 0.95$. Where the analyte diffusion coefficients are already known, a plot of mass versus time should be compared with a theoretical mass line calculated using the DGT equation. The experimental masses, corrected for f_e , should be very close to this theoretical line (i.e. the slope and intercept of the regression line should be very similar to the theoretical line). If the diffusion coefficients are not known, then these data can be used to calculate the effective diffusion coefficient of the

tested analyte through the diffusive gel and filter membrane (D^{mdl}) by simple rearrangement of the DGT equation (see Chapter 3 for details).

After an initial mass vs. time validation experiment, with the time periods described above, it is recommended to do longer term experiments in the same solution for time periods likely to be used for field deployments as this may help to identify non-ideal behaviour. Non-ideal accumulation of an analyte can arise due to several reasons, which are numerically simulated and discussed in chapter 5. If the rate of binding at and within the binding layer is slow, the accumulation can still be represented by steady state conditions, but the accumulation at any given time will be less than expected for rapid binding. In this case the mass accumulated still increases linearly with time but with a reduced slope compared to the theoretical case. Such non-ideal behaviour has been observed, but the most common examples of non-ideal behaviour are characterised by non-linear plots of mass versus time (Figure 4.2) [16, 24]. They are easily identified by an $R^2 < 0.95$, in which deviation from linearity increases over time (other patterns of non-linearity are likely to indicate analytical issues). This non-linearity essentially signifies that steady state conditions have not been reached, which may occur for two reasons.

Firstly, the accumulated mass is a sizeable fraction of the intrinsic binding capacity (see section below). Effectively, the concentration of the analyte species at the interface between the binding and diffusive layers is progressively increasing and the flux into the DGT samplers is decreasing over time.

Secondly, the concentration of metal that is bound is close to the concentration where it establishes equilibrium with the concentration of free metal in the solution. This non-steady

state condition can be reached when the binding layer concentration of bound metal is several orders of magnitude less than the concentration for saturation conditions.

Competition effects by other ions in solution may also promote non-linearity of mass versus time plots by decreasing the effective binding capacity for an analyte or affecting the free metal concentration in solution. Competition effects can be minimised by using a single analyte and/or changing the solution matrix or concentration.

4.3.3 Capacity

The capacity of the binding layer for the target analyte(s) needs to be determined, as established above. The *intrinsic binding capacity* is most efficiently determined by exposing binding layer discs to a high concentration of analyte, until equilibrium is reached, in the absence of any competition effects [11]. If multiple analytes are determined together then there will inevitably be competition between analytes as the capacity is approached. The capacity measurement can also be made with assembled DGT samplers rather than just the binding layers [18]; the obtained values should be quite similar, regardless of the approach used, although the DGT measurement is slower and more expensive. The effective binding capacity is determined in a similar way to the intrinsic binding capacity, but in the presence of potentially competing ions (e.g. HCO_3^+ , H^+ , SO_4^{2-} etc.), which can compete for binding sites and reduce the number available for interacting with the analyte of interest [20]. A comparison between the intrinsic and effective binding capacities for a particular analyte could be helpful in revealing the susceptibility of a binding layer to competition effects in various matrices.

A distinction should be made between the intrinsic and effective capacities of the binding layer and the mass at which linear accumulation is no longer observed under particular measurement conditions [13]. This linear accumulation capacity is determined by deploying DGT samplers in a high concentration of analyte for various deployment times, so that deviation from the predicted linear uptake is observed. The linear accumulation capacity will be lower in the presence of competing ions, which occupy binding sites on the binding layer, the extent of which is determined by their concentration in solution and/or their affinity for the binding sites. This measurement is therefore highly operational and depends largely upon competition effects in the sample matrix; it provides an operationally useful estimate of conditions under which DGT can be used reliably. As DGT is a kinetic passive sampler, which is not designed to approach equilibrium during deployment, knowledge of the linear accumulation capacity measured in this way will be more useful practically than the intrinsic capacity determined simply by making measurements in a range of solution concentrations. Unfortunately, modelling studies (Chapter 5) demonstrate that there is no simple rule that can be applied to determine the proportion of a binding layer's capacity that should not be exceeded, to ensure theoretical analyte accumulation by a DGT sampler. For this reason, we recommend a thorough investigation of the linear accumulation performance of new DGT binding layers in representative matrices, for representative deployment times, as discussed in detail in the section '*Extended deployment in representative matrices*'.

4.3.4 Ionic strength and pH

Potential binding layers must be tested to ensure accurate performance in a range of environmental conditions. Ionic strength and pH are two critical chemical parameters that vary significantly amongst natural systems, and that can impact the strength of the interaction between the analyte and the binding layer. The typical approach for evaluating the effect of

ionic strength and pH on a binding layer involves exposure of replicate DGT samplers to simple synthetic solutions containing a range of ionic concentrations (e.g. 0.0001 – 0.7 M NaNO₃) or pH (e.g. pH 3 – 8.5) that are typical of natural systems. The DGT-measured analyte concentration (c_{DGT}) is then compared to the analyte concentration measured directly in the solution by an appropriate analytical technique (c^{soln}); a ratio of c_{DGT} to c^{soln} close to unity (0.9 – 1.1) indicates that the DGT technique is accurately measuring the analyte concentration in the tested solution.

Hydrogen ions can compete with cationic species for binding sites, as evidenced by the poor performance of the Chelex 100 binding layer at pH < 4 for some analytes (Figure 4.3) [25]. Fortunately, the majority of aquatic systems have a pH > 4 and thus the Chelex 100 binding layer has been widely applied to measuring cationic trace metals in the environment. Ionic strength has minimal impact on the accumulation of most cationic trace metals by the Chelex 100 binding layer due to its high selectivity, and thus it generally performs well in matrices like seawater that contain high concentrations of competing ions.

The main caveat of this approach to assessing the impact of pH and ionic strength on a binding layer is that the experiments are typically done for no longer than 24 h. While this may be sufficient to observe significant deviations from the predicted performance, most DGT field deployments are for multiple days. It is, therefore, strongly recommended that potential binding layers are further tested in representative matrices (e.g. synthetic fresh or seawater) for deployment times similar to those that are to be used for actual field deployments, as described in the following section.

4.3.5 Extended deployment in representative matrices

The final step in the laboratory validation of a potential DGT binding layer is to test its performance in synthetic solutions that are representative of natural systems (e.g. synthetic freshwater and synthetic seawater), for deployment times that reflect those commonly used in DGT field deployments (typically < 1 week). For deployments greater than one to two weeks, it may not be feasible to perform such laboratory validation experiments, although other factors such as biofouling of the samplers may limit the use of in situ DGT deployments for these extended times [26].

Panther and co-workers [11] evaluated Metsorb and ferrihydrite DGT for measuring dissolved reactive phosphorus in both synthetic freshwater and synthetic seawater, for deployment times of up to four days. This experiment revealed that while both techniques accurately measured DRP in freshwater over a four day deployment time, only Metsorb DGT was capable of accurately measuring DRP in seawater after four days (ferrihydrite DGT underestimated the DRP concentration by 31%). This was due to competition for binding sites by bicarbonate anions (HCO_3^-), which are present at relatively high concentrations in seawater. Similar experiments [16] showed that the measurement of Mn by Chelex 100 DGT experienced similar limitations when deployed for up to four days in synthetic seawater, underestimating the Mn concentration by 49% after a four day deployment time. Interestingly, accurate measurement of Mn was possible with deployment times of up to 48 h, suggesting that the short-term validation experiments often reported in the literature (typically < 48 h) may not reveal the limitations of binding layers that only become apparent during longer deployment times. Tankéré-Muller and co-workers [24] provide a detailed explanation of the susceptibility of Mn measurements with Chelex 100 DGT to competitive interference from Ca^{2+} and Mg^{2+} ions present in high concentrations, as in seawater.

4.4 Performance characteristics of existing binding layers and future research requirements

Over 40 different DGT binding layers have been described in the literature to date for approximately 50 elements (Table 4.1). This demonstrates that the DGT technique is very well suited to elemental analysis. However, only a few studies have looked at a range of organic substances [27-29]. This is clearly an emerging area of application, the implications of which are discussed further below. The extent of validation for each binding layer varies considerably, with many only being partially validated for some analytes. As it is not feasible to present the performance characteristics of every binding layer reported in the literature, only the binding layers that have found widespread, multi-analyte, application will be addressed in detail. These are Chelex 100, ferrihydrite, Metsorb, zirconium dioxide (ZrO_2), 3-mercaptopropyl functionalised silica, AG50W-X8 and XAD18. A summary of the performance characteristics for these binding layers, determined by laboratory validations as described in Section 4.2, is presented in Table 4.2.

The effectiveness of Chelex 100 as a DGT binding layer, in selectively measuring 29 elements, is immediately apparent from Table 4.2. The success of this first commercial resin in DGT measurements was clearly instrumental in attracting other researchers to the technique. However, inspection of Table 4.2 indicates that there are many analytes for which validation data in representative matrices is missing for Chelex 100, compared to newer binding layers. Perhaps there was such confidence in the performance of Chelex-DGT that the research community moved quickly onto interesting and important applications – the nature of scientific funding undoubtedly had a role in this. To some extent the validation expectations have developed over time, as new challenges were encountered with other binding layer types.

More recently developed DGT techniques, especially those for oxyanionic species, have undergone a more comprehensive validation, particularly with respect to longer term deployments and the identification of competing ions [20, 30-32]. This has identified limitations with some analytes and binding layers, illustrating the need for this rigour. With further research some limitations have been observed for Chelex 100 too, for instance for Al and Mn [24, 30]. Although not included in Table 4.2, some of these limitations have been overcome by using mixed binding layers, for instance Chelex 100 with either ferrihydrite or Metsorb [15, 16]. These mixed binding layers have also increased the number of analytes able to be determined from single DGT binding layers, which is an important practical development and will likely make the technique more attractive to environmental consultants and regulatory users. The summary in Table 4.2 will allow researchers to establish whether sufficient validation has been done for a particular application of a DGT technique and perhaps direct research to address some of the gaps still present. Clearly, application of any DGT technique in samples with high salinity or beyond the typical pH range will require careful validation.

Despite the number of elements able to be determined by DGT, there are some important contaminants missing from the list, such as dissolved inorganic nitrogen species. There are emerging contaminants such as platinum, palladium and rare earth elements, which have only been looked at in a few studies [33-35]. The potential of the DGT technique for determination of polar organic contaminants has been demonstrated as a proof of concept but with limited detailed validation to date [27, 28]. This emerging research direction requires careful consideration, as there are actually many other passive samplers developed for various classes of organic substances. Organic contaminants are often present at ultra-trace

concentrations in waters that have required other passive samplers to be deployed for longer times than are preferred for DGT deployments (due to the difficulties associated with complex biofilm formation that affect all passive samplers) and to have sampler configurations that maximize the rates of analyte uptake. Given that many DGT techniques have been developed for application in water initially, these factors may explain why there are relatively few examples of DGT being used for organic contaminants to-date. However, DGT samplers have a configuration that is inherently flexible and may be further optimized for organic analytes, for instance by using a larger surface area and/or minimal thickness diffusive layer. For some applications, such as in industrial waste water [28] and contaminated soils and sediments [36, 37], the small size, the relatively low cost of DGT samplers and the fact that the same apparatus can be used to determine elemental contaminants may be advantageous. Furthermore, deployment in sediments and soils can make use of the extensive theory and models developed for metals [36, 37].

Various approaches have been used to prepare DGT binding layers, as described in Section 4.2. It is apparent from Table 4.2 that incorporating binding materials into a polyacrylamide hydrogel has been the most popular and successful approach. In our experience most materials (e.g. resins and powders) can readily be incorporated into polyacrylamide hydrogels. But it is worthwhile for the DGT research community to consider if there are other reasons for the dominance of this approach. Does it relate to the preferences of the most active research groups? Is it because many research groups new to the DGT field, and some perhaps with less background or interest in chemistry, prefer to purchase their binding layers commercially? Such considerations are particularly useful when we consider future directions for the DGT technique – it may be that other approaches to preparing binding layers will provide new opportunities in the future. For instance, may liquid binding

layers eventually be combined with measurement technology to develop an in situ sensor? Might use of functionalized polyacrylamide gels or membranes be useful for ultra-high resolution measurements in soils and sediments? An interesting binding layer application has been the use of *Saccharomyces cerevisiae* [38] - will incorporation of microorganisms open up interesting new applications of DGT? Will some of the new range of selective nano-materials be useful as DGT binding layers? Can the DGT technique be improved with regard to sustainability practices? We encourage the DGT research community to consider these matters – it is apparent that there remains plenty of opportunity for research in the future.

4.5 References

1. H. Zhang and W. Davison, Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution, *Anal. Chem.* **67**: (1995), 3391-3400.
2. W. Davison and H. Zhang, In situ speciation measurements of trace components in natural waters using thin-film gels, *Nature* **367**: (1994), 546-548.
3. S. C. Pai, P. Y. Whung and R. L. Lai, Pre-concentration efficiency of chelex-100 resin for heavy metals in seawater : Part 1. Effects of pH and salts on the distribution ratios of heavy metals, *Anal. Chim. Acta* **211**: (1988), 257-270.
4. B. L. Larnier and A. J. Seen, Evaluation of paper-based diffusive gradients in thin film samplers for trace metal sampling, *Anal. Chim. Acta* **539**: (2005), 349-355.
5. W. Li, H. Zhao, P. R. Teasdale and F. Wang, Trace metal speciation measurements in waters by the liquid binding phase DGT device, *Talanta* **67**: (2005), 571-578.
6. W. Li, H. Zhao, P. Teasdale, R. John and S. Zhang, Synthesis and characterisation of a polyacrylamide-polyacrylic acid copolymer hydrogel for environmental analysis of Cu and Cd, *React. Funct. Polym.* **52**: (2002), 31-41.
7. L. Y. Chang, W. Davison, H. Zhang and M. Kelly, Performance characteristics for the measurement of Cs and Sr by diffusive gradients in thin films (DGT), *Anal. Chim. Acta* **368**: (1998), 243-253.
8. J. G. Panther, K. P. Stillwell, K. J. Powell and A. J. Downard, Development and application of the diffusive gradients in thin films technique for the measurement of total dissolved inorganic arsenic in waters, *Anal. Chim. Acta* **622**: (2008), 133-142.
9. H. Zhang, W. Davison, R. Gadi and T. Kobayashi, In situ measurement of dissolved phosphorus in natural waters using DGT, *Anal. Chim. Acta* **370**: (1998), 29-38.
10. W. W. Bennett, P. R. Teasdale, J. G. Panther, D. T. Welsh and D. F. Jolley, New diffusive gradients in a thin film technique for measuring inorganic arsenic and selenium (IV) using a titanium dioxide based adsorbent, *Anal. Chem.* **82**: (2010), 7401-7407.
11. J. G. Panther, P. R. Teasdale, W. W. Bennett, D. T. Welsh and H. Zhao, Titanium dioxide-based DGT technique for in situ measurement of dissolved reactive phosphorus in fresh and marine waters, *Environ. Sci. Technol.* **44**: (2010), 9419-9424.
12. P. R. Teasdale, S. Hayward and W. Davison, In situ, high-resolution measurement of dissolved sulfide using diffusive gradients in thin films with computer-imaging densitometry, *Anal. Chem.* **71**: (1999), 2186-2191.
13. W. W. Bennett, P. R. Teasdale, J. G. Panther, D. T. Welsh and D. F. Jolley, Speciation of dissolved inorganic arsenic by diffusive gradients in thin films: selective binding of As^{III} by 3-mercaptopropyl-functionalized silica gel, *Anal. Chem.* **83**: (2011), 8293-8299.
14. H. Dočekalová and P. Diviš, Application of diffusive gradient in thin films technique (DGT) to measurement of mercury in aquatic systems, *Talanta* **65**: (2005), 1174-1178.
15. S. Mason, R. Hamon, A. Nolan, H. Zhang and W. Davison, Performance of a mixed binding layer for measuring anions and cations in a single assay using the diffusive gradients in thin films technique, *Anal. Chem.* **77**: (2005), 6339-6346.
16. J. G. Panther, W. W. Bennett, D. T. Welsh and P. R. Teasdale, Simultaneous measurement of trace metal and oxyanion concentrations in water using diffusive gradients in thin films with a chelex-metsorb mixed binding layer, *Anal. Chem.* **86**: (2014), 427-434.
17. C. Naylor, W. Davison, M. Motelica-Heino, G. A. Van Den Berg and L. M. Van Der Heijdt, Simultaneous release of sulfide with Fe, Mn, Ni and Zn in marine harbour sediment measured using a combined metal/sulfide DGT probe, *Sci. Total Environ.* **328**: (2004), 275-286.

18. S. Ding, D. Xu, Q. Sun, H. Yin and C. Zhang, Measurement of dissolved reactive phosphorus using the diffusive gradients in thin films technique with a high-capacity binding phase, *Environ. Sci. Technol.* **44**: (2010), 8169-8174.
19. W. Li, P. R. Teasdale, S. Zhang, R. John and H. Zhao, Application of a poly(4-styrenesulfonate) liquid binding layer for measurement of Cu^{2+} and Cd^{2+} with the diffusive gradients in thin-films technique, *Anal. Chem.* **75**: (2003), 2578-2583.
20. H. L. Price, P. R. Teasdale and D. F. Jolley, An evaluation of ferrihydrite- and MetsorbTM-DGT techniques for measuring oxyanion species (As, Se, V, P): Effective capacity, competition and diffusion coefficients, *Anal. Chim. Acta* **803**: (2013), 56-65.
21. J. L. Levy, H. Zhang, W. Davison, J. Puy and J. Galceran, Assessment of trace metal binding kinetics in the resin phase of diffusive gradients in thin films, *Anal. Chim. Acta* **717**: (2012), 143-150.
22. J. G. Panther, R. R. Stewart, P. R. Teasdale, W. W. Bennett, D. T. Welsh and H. Zhao, Titanium dioxide-based DGT for measuring dissolved As(V), V(V), Sb(V), Mo(VI) and W(VI) in water, *Talanta* **105**: (2013), 80-86.
23. C. M. Hutchins, J. G. Panther, P. R. Teasdale, F. Wang, R. R. Stewart, W. W. Bennett and H. Zhao, Evaluation of a titanium dioxide-based DGT technique for measuring inorganic uranium species in fresh and marine waters, *Talanta* **97**: (2012), 550-556.
24. S. Tankéré-Muller, W. Davison and H. Zhang, Effect of competitive cation binding on the measurement of Mn in marine waters and sediments by diffusive gradients in thin films, *Anal. Chim. Acta* **716**: (2012), 138-144.
25. J. Gimpel, H. Zhang, W. Hutchinson and W. Davison, Effect of solution composition, flow and deployment time on the measurement of trace metals by the diffusive gradient in thin films technique, *Anal. Chim. Acta* **448**: (2001), 93-103.
26. E. Uher, H. Zhang, S. Santos, M. H. Tusseau-Vuillemin and C. Gourlay-Francé, Impact of biofouling on diffusive gradient in thin film measurements in water, *Anal. Chem.* **84**: (2012), 3111-3118.
27. C. E. Chen, H. Zhang and K. C. Jones, A novel passive water sampler for in situ sampling of antibiotics, *J. Environ. Monit.* **14**: (2012), 1523-1530.
28. C. E. Chen, H. Zhang, G. G. Ying and K. C. Jones, Evidence and recommendations to support the use of a novel passive water sampler to quantify antibiotics in wastewaters, *Environ. Sci. Technol.* **47**: (2013), 13587-13593.
29. J. L. Zheng, D. X. Guan, J. Luo, H. Zhang, W. Davison, X.-Y. Cui, L. H. Wang and L. Q. Ma, Activated charcoal based diffusive gradients in thin films for in situ monitoring of bisphenols in waters, *Anal. Chem.* **87**: (2015), 801-807.
30. J. G. Panther, W. W. Bennett, P. R. Teasdale, D. T. Welsh and H. Zhao, DGT measurement of dissolved aluminum species in waters: comparing chelex-100 and titanium dioxide-based adsorbents, *Environ. Sci. Technol.* **46**: (2012), 2267-2275.
31. J. G. Panther, P. R. Teasdale, W. W. Bennett, D. T. Welsh and H. Zhao, Comparing dissolved reactive phosphorus measured by DGT with ferrihydrite and titanium dioxide adsorbents: Anionic interferences, adsorbent capacity and deployment time, *Anal. Chim. Acta* **698**: (2011), 20-26.
32. Q. Sun, Y. Chen, D. Xu, Y. Wang and S. Ding, Investigation of potential interferences on the measurement of dissolved reactive phosphate using zirconium oxide-based DGT technique, *J. Environ. Sci.* **25**: (2013), 1592-1600.
33. Ø. A. Garmo, O. Røyset, E. Steinnes and T. P. Flaten, Performance study of diffusive gradients in thin films for 55 elements, *Anal. Chem.* **75**: (2003), 3573-3580.
34. K. Andersson, R. Dahlqvist, D. Turner, B. Stolpe, T. Larsson, J. Ingri and P. Andersson, Colloidal rare earth elements in a boreal river: changing sources and distributions during the spring flood, *Geochim. Cosmochim. Acta* **70**: (2006), 3261-3274.

35. Ø. A. Garmo, N. J. Lehto, H. Zhang, W. Davison, O. Røyset and E. Steinnes, Dynamic aspects of DGT as demonstrated by experiments with lanthanide complexes of a multidentate ligand, *Environ. Sci. Technol.* **40**: (2006), 4754-4760.
36. C. E. Chen, W. Chen, G. G. Ying, K. C. Jones and H. Zhang, In situ measurement of solution concentrations and fluxes of sulfonamides and trimethoprim antibiotics in soils using o-DGT, *Talanta* **132**: (2015), 902-908.
37. C. E. Chen, K. C. Jones, G. G. Ying and H. Zhang, Desorption kinetics of sulfonamide and trimethoprim antibiotics in soils assessed with diffusive gradients in thin-films, *Environ. Sci. Technol.* **48**: (2014), 5530-5536.
38. A. A. Menegário, P. S. Tonello and S. F. Durrant, Use of *Saccharomyces cerevisiae* immobilized in agarose gel as a binding agent for diffusive gradients in thin films, *Anal. Chim. Acta* **683**: (2010), 107-112.
39. R. Dahlqvist, H. Zhang, J. Ingri and W. Davison, Performance of the diffusive gradients in thin films technique for measuring Ca and Mg in freshwater, *Anal. Chim. Acta* **460**: (2002), 247-256.
40. R. Cusnir, P. Steinmann, F. Bochud and P. Froidevaux, A DGT technique for plutonium bioavailability measurements, *Environ. Sci. Technol.* **48**: (2014), 10829-10834.
41. S. Tandy, S. Mundus, H. Zhang, E. Lombi, J. Frydenvang, P. E. Holm and S. Husted, A new method for determination of potassium in soils using diffusive gradients in thin films (DGT), *Environ. Chem.* **9**: (2012), 14-23.
42. K. W. Warnken, H. Zhang and W. Davison, Performance characteristics of suspended particulate reagent-iminodiacetate as a binding agent for diffusive gradients in thin films, *Anal. Chim. Acta* **508**: (2004), 41-51.
43. G. S. C. Turner, G. A. Mills, J. L. Burnett and S. Amos, Evaluation of diffusive gradients in thin-films using a Diphonix® resin for monitoring dissolved uranium in natural waters, *Anal. Chim. Acta* **854**: (2015), 78-85.
44. A. M. C. M. Rolisola, C. A. Suarez, A. A. Menegario, D. Gastmans, C. H. Kiang, C. D. Colaco, D. L. Garcez and R. E. Santelli, Speciation analysis of inorganic arsenic in river water by Amberlite IRA 910 resin immobilized in a polyacrylamide gel as a selective binding agent for As(V) in diffusive gradient thin film technique, *Analyst* **139**: (2014), 4373-4380.
45. R. W. McGifford, A. J. Seen and P. R. Haddad, Direct colorimetric detection of copper(II) ions in sampling using diffusive gradients in thin-films, *Anal. Chim. Acta* **662**: (2010), 44-50.
46. M. A. French, H. Zhang, J. M. Pates, S. E. Bryan and R. C. Wilson, Development and performance of the diffusive gradients in thin-films technique for the measurement of technetium-99 in seawater, *Anal. Chem.* **77**: (2005), 135-139.
47. J. Luo, H. Zhang, J. Santner and W. Davison, Performance characteristics of diffusive gradients in thin films equipped with a binding gel layer containing precipitated ferrihydrite for measuring arsenic(V), selenium(VI), vanadium(V), and antimony(V), *Anal. Chem.* **82**: (2010), 8903-8909.
48. H. Österlund, S. Chlot, M. Faarinen and A. Widerlund, Simultaneous measurements of As, Mo, Sb, V and W using a ferrihydrite diffusive gradients in thin films (DGT) device, *Anal. Chim. Acta* **682**: (2010), 59-65.
49. Q. Sun, S. Qin, C. Jing, Z. Hao and D. Shiming, Improved diffusive gradients in thin films (DGT) measurement of total dissolved inorganic arsenic in waters and soils using a hydrous zirconium oxide binding layer, *Anal. Chem.* **86**: (2014), 3060-3067.
50. D. X. Guan, P. N. Williams, L. Jun and J. L. Zheng, Novel precipitated zirconia-based DGT technique for high-resolution imaging of oxyanions in waters and sediments, *Environ. Sci. Technol.* **49**: (2015), 3653-3661.

51. G. S. C. Turner, G. A. Mills, P. R. Teasdale, J. L. Burnett, S. Amos and G. R. Fones, Evaluation of DGT techniques for measuring inorganic uranium species in natural waters: interferences, deployment time and speciation, *Anal. Chim. Acta* **739**: (2012), 37-46.
52. M. Leermakers, Y. Gao, J. Navez, A. Poffijn, K. Croes and W. Baeyens, Radium analysis by sector field ICP-MS in combination with the diffusive gradients in thin films (DGT) technique, *J. Anal. At. Spectrom.* **24**: (2009), 1115-1117.
53. O. Clarisse and H. Hintelmann, Measurements of dissolved methylmercury in natural waters using diffusive gradients in thin film (DGT), *J. Environ. Monit.* **8**: (2006), 1242-1247.
54. P. Diviš, R. Szkandera and H. Dočekalová, Characterization of sorption gels used for determination of mercury in aquatic environment by diffusive gradients in thin films technique, *Cent. Eur. J. Chem.* **8**: (2010), 1105-1109.
55. Y. Gao, E. De Canck, M. Leermakers, W. Baeyens and P. Van Der Voort, Synthesized mercaptopropyl nanoporous resins in DGT probes for determining dissolved mercury concentrations, *Talanta* **87**: (2011), 262-267.
56. Y. Liu, H. Chen, F. Bai, J. Gu and L. Liu, Application of sodium poly(aspartic acid) as a binding phase in the technique of diffusive gradients in thin films, *Chem. Lett.* **41**: (2012), 1471-1472.
57. D. P. Sui, H. T. Fan, J. Li, Y. Li, Q. Li and T. Sun, Application of poly(ethyleneimine) solution as a binding agent in DGT technique for measurement of heavy metals in water, *Talanta* **114**: (2013), 276-282.
58. H. Fan, T. Sun, W. Li, D. Sui, S. Jin and X. Lian, Sodium polyacrylate as a binding agent in diffusive gradients in thin-films technique for the measurement of Cu^{2+} and Cd^{2+} in waters, *Talanta* **79**: (2009), 1228-1232.
59. H. Fan, Y. Bian, D. Sui, G. Tong and T. Sun, Measurement of free copper(II) ions in water samples with polyvinyl alcohol as a binding phase in diffusive gradients in thin-films, *Anal. Sci.* **25**: (2009), 1345-1349.
60. H. T. Fan, J. X. Liu, D. P. Sui, H. Yao, F. Yan and T. Sun, Use of polymer-bound Schiff base as a new liquid binding agent of diffusive gradients in thin-films for the measurement of labile Cu^{2+} , Cd^{2+} and Pb^{2+} , *J. Hazard. Mater.* **260**: (2013), 762-769.
61. H. T. Fan, T. Sun, M. Z. Xue, G. F. Tong and D. P. Sui, Preparation of thiol-polyvinyl alcohol and its application to diffusive gradients in thin-films technique, *Chinese J. Anal. Chem.* **37**: (2009), 1379-1381.
62. H. Chen, Y. Y. Zhang, K. L. Zhong, L. W. Guo, J. L. Gu, L. Bo, M. H. Zhang and J. R. Li, Selective sampling and measurement of Cr (VI) in water with polyquaternary ammonium salt as a binding agent in diffusive gradients in thin-films technique, *J. Hazard. Mater.* **271**: (2014), 160-165.
63. H. Chen, H. Chen, M. H. Zhang, J. L. Gu and G. Zhao, Measurement of dissolved reactive phosphorus in water with polyquaternary ammonium salt as a binding agent in diffusive gradients in thin-films technique, *J. Agric. Food Chem.* **62**: (2014), 12112-12117.
64. C. D. Colaço, L. N. M. Yabuki, A. M. Rolisola, A. A. Menegário, E. De Almeida, C. A. Suárez, Y. Gao, W. T. Corns and V. F. Do Nascimento Filho, Determination of mercury in river water by diffusive gradients in thin films using P81 membrane as binding layer, *Talanta* **129**: (2014), 417-421.
65. E. De Almeida, V. F. Do Nascimento Filho and A. A. Menegário, Paper-based diffusive gradients in thin films technique coupled to energy dispersive X-ray fluorescence spectrometry for the determination of labile Mn, Co, Ni, Cu, Zn and Pb in river water, *Spectrochim. Acta, Part B* **71-72**: (2012), 70-74.
66. W. Li, H. Zhao, P. R. Teasdale, R. John and S. Zhang, Synthesis and characterisation of a polyacrylamide-polyacrylic acid copolymer hydrogel for environmental analysis of Cu and Cd, *Reactive and Functional Polymers* **52**: (2002), 31-41.

67. W. Li, H. Zhao, P. R. Teasdale and R. John, Preparation and characterisation of a poly(acrylamidoglycolic acid-co-acrylamide) hydrogel for selective binding of Cu^{2+} and application to diffusive gradients in thin films measurements, *Polymer* **43**: (2002), 4803-4809.
68. T. Huynh, H. Zhang and B. Noller, Evaluation and application of the diffusive gradients in thin films technique using a mixed-binding gel layer for measuring inorganic arsenic and metals in mining impacted water and soil, *Anal. Chem.* **84**: (2012), 9988-9995.
69. Q. Sun, L. Zhang, S. Ding, C. Li, J. Yang, J. Chen and P. Wang, Evaluation of the diffusive gradients in thin films technique using a mixed binding gel for measuring iron, phosphorus and arsenic in the environment, *Environ. Sci.: Processes Impacts* **17**: (2015), 570-577.
70. D. Xu, X. Di, C. Yifei, D. Shiming and S. Qin, Diffusive gradients in thin films technique equipped with a mixed binding gel for simultaneous measurements of dissolved reactive phosphorus and dissolved iron, *Environ. Sci. Technol.* **47**: (2013), 10477-10484.
71. Y. Zhang, S. Mason, A. Mcneill and M. J. McLaughlin, Application of the diffusive gradients in thin films technique for available potassium measurement in agricultural soils: effects of competing cations on potassium uptake by the resin gel, *Anal. Chim. Acta* **842**: (2014), 27-34.
72. Y. Zhang, S. Mason, A. Mcneill and M. J. McLaughlin, Optimization of the diffusive gradients in thin films (DGT) method for simultaneous assay of potassium and plant-available phosphorus in soils, *Talanta* **113**: (2013), 123-129.
73. Y. Gao, S. Van De Velde, P. N. Williams, W. Baeyens and H. Zhang, Two-dimensional images of dissolved sulfide and metals in anoxic sediments by a novel diffusive gradients in thin film probe and optical scanning techniques, *TrAC, Trends Anal. Chem.* **66**: (2015), 63-71.
74. S. Ding, Q. Sun, D. Xu, F. Jia, X. He and C. Zhang, High-resolution simultaneous measurements of dissolved reactive phosphorus and dissolved sulfide: the first observation of their simultaneous release in sediments, *Environ. Sci. Technol.* **46**: (2012), 8297-8304.
75. A. Stockdale, W. Davison and H. Zhang, High-resolution two-dimensional quantitative analysis of phosphorus, vanadium and arsenic, and qualitative analysis of sulfide, in a freshwater sediment, *Environ. Chem.* **5**: (2008), 143-149.
76. A. Kreuzeder, J. Santner, T. Prohaska and W. W. Wenzel, Gel for simultaneous chemical imaging of anionic and cationic solutes using diffusive gradients in thin films, *Anal. Chem.* **85**: (2013), 12028-12036.
77. C. Murdock, M. Kelly, L. Y. Chang, W. Davison and H. Zhang, DGT as an in situ tool for measuring radiocesium in natural waters, *Environ. Sci. Technol.* **35**: (2001), 4530-4535.
78. J. Dong, H. Fan, D. Sui, L. Li and T. Sun, Sampling 4-chlorophenol in water by DGT technique with molecularly imprinted polymer as binding agent and nylon membrane as diffusive layer, *Anal. Chim. Acta* **822**: (2014), 69-77.
79. W. Li, F. Wang, W. Zhang and D. Evans, Measurement of stable and radioactive cesium in natural waters by the diffusive gradients in thin films technique with new selective binding phases, *Anal. Chem.* **81**: (2009), 5889-5895.
80. M. Gregusova and B. Docekal, New resin gel for uranium determination by diffusive gradient in thin films technique, *Anal. Chim. Acta* **684**: (2011), 142-146.
81. A. Lucas, A. Rate, H. Zhang, S. U. Salmon and N. Radford, Development of the diffusive gradients in thin films technique for the measurement of labile gold in natural waters, *Anal. Chem.* **84**: (2012), 6994-7000.
82. V. E. Dos Anjos, G. Abate and M. T. Grassi, Potentiality of the use of montmorillonite in diffusive gradients in thin film (DGT) devices for determination of labile species of Cu, Cr, Cd, Mn, Ni, Pb, and Zn in natural waters, *Braz. J. Anal. Chem.* **1**: (2010), 187-193.

83. H. Ernstberger, H. Zhang and W. Davison, Determination of chromium speciation in natural systems using DGT, *Anal. Bioanal. Chem.* **373**: (2002), 873-879.
84. C. Fernández-Gómez, B. Dimock, H. Hintelmann and S. Díez, Development of the DGT technique for Hg measurement in water: Comparison of three different types of samplers in laboratory assays, *Chemosphere* **85**: (2011), 1452-1457.

Table 4.1 Binding agents used in DGT binding layers and their target analyte(s).

category	binding agent	analyte(s)	refs
cation exchange resins	Chelex 100	Al, Ca, Cd, Ce, Co, Cr(III), Cu, Dy, Er, Eu, Fe, Gd, Ho, La, Lu, Mg, Mn, Nd, Ni, Pb, Pu, Pr, Sm, Tb, Tm, U, Y, Yb, Zn	[1, 33, 39, 40]
	AG50W-X8	Cs, Sr	[7]
	Amberlite IRP69	K	[41]
	suspended particulate reagent-iminodiacetate (SPR-IDA)	Cd, Co, Cu, Ni, Pb	[42]
	Diphonix	U	[43]
anion exchange resins	Amberlite IRA 910	As(V)	[44]
	methylthymol blue adsorbed to Dowex 1X8	Cu	[45]
	TEVA resin	⁹⁹ Tc	[46]
metal (hydr)oxides	Ferrihydrite (FeOOH)	As, Mo, P, Se, Sb, U, V, W	[8, 9, 47, 48]
	Metsorb (TiO ₂)	As, Mo, P, Se, Sb, U, V, W	[10, 11, 22, 30]
	ZrO ₂	As, Mo, P, Se, Sb, V	[18, 49, 50]
	MnO ₂	Ra, U	[51, 52]
thiol-functionalised resins	3-mercaptopropyl functionalised silica	As(III), methyl-Hg	[13, 53]
	Spheron-thiol	Hg	[14]
	Duolite GT73	Hg	[54]
	Iontosorb AV-IM	Hg	[54]
	3-mercaptopropyl functionalized SBA-15	Hg	[55]
	3-mercaptopropyl functionalized organosilica	Hg	[55]
	Sumichelate Q10R	Hg	[55]
liquid binding phases	poly(4-styrenesulfonate)	Cd, Cu	[5]
	poly(aspartic acid)	Cd	[56]
	poly(ethyleneimine)	Cd, Cu, Pb	[57]
	sodium polyacrylate	Cd, Cu	[58]
	poly(vinyl alcohol)	Cu	[59]
	polymer-bound Schiff base	Cd, Cu, Pb	[60]
	thiol-poly(vinyl alcohol)	Cd	[61]
	polyquaternary ammonium salt	Cr(VI), P	[62, 63]

membranes	Whatman P81	Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn	[4, 64, 65]
modified hydrogels	poly(acrylamide-co-acrylic acid) (PAM-PAA)	Cd, Cu	[66]
	poly(acrylamidoglycolic acid-co-acrylamide) (PAAG-PAM)	Cu	[67]
mixed binding agents	Chelex 100/ferrihydrite	As, Cd, Cu, Mn, Mo, P, Pb, Zn	[15, 68]
	Chelex 100/Metsorb	As, Cd, Co, Cu, Mn, Mo, Ni, P, Pb, Sb, V, W	[16]
	Chelex 100/ZrO ₂	As, Fe, P	[69, 70]
	Amberlite IRP69/ferrihydrite	K, P	[71, 72]
	AgI/SPR-IDA	Cd, Co, Cu, Ni, Pb, S ²⁻	[73]
	AgI/ZrO ₂	As, Mo, P, S ²⁻ , Sb, Se, V	[74]
	AgI/ferrihydrite	As, Mo, P, S ²⁻ , Sb, Se, U, V, W As, V	[75]
	ZrO ₂ /SPR-IDA	As, Cd, Co, Cu, Mo, Ni, P, Pb, Sb, Se, V	[76]
other binding agents	AgI	S ²⁻	[12]
	ammonium molybdophosphate (AMP)	Cs	[77]
	molecularly imprinted polymer	4-chlorophenol	[78]
	copper ferrocyanide	Cs	[79]
	8-hydroxyquinoline functionalised Spheron-Oxin	U	[80]
	activated carbon	bisphenols, Au	[29, 81]
	montmorillonite	Cd, Cr, Cu, Mn, Ni, Pb, Zn	[82]
	XAD18	antibiotics (sulfonamides, fluoroquinolones, macrolides, ionophores, diaminopyrimidines, aminocoumarins, lincosamides)	[27, 28]
	<i>Saccharomyces cerevisiae</i>	Cd	[38]

Table 4.2 Summary of performance characteristics of commonly used binding layers. f_u and f_e are uptake and elution efficiencies, respectively.
3-MFS = 3-mercaptopropyl functionalised silica

binding layer	analyte	uptake and elution	validated pH and ionic concentration ranges	linear mass accumulation over time	representative matrix validation	comments	refs
Chelex 100	Al	$f_u > 85\%$ $f_e = 84 \pm 3\%$ (1 M HNO ₃)	pH 4.0 – 8.0 0.001 - 0.7 M NaNO ₃	96 h in 0.002 M NaNO ₃	Synthetic freshwater (96 h, ~10 µg L ⁻¹ , pH 5.4 and 6.1)	Not quantitative at pH > 8 in 0.01 M NaNO ₃ Not quantitative at pH 7.7-8.1 in synthetic freshwater Not quantitative in synthetic seawater	[30]
	Ca	$f_u > 96\%$ $f_e = 98.3 \pm 5.6\%$ (1 M HNO ₃)	pH 5.0 – 6.7	No data	Natural freshwater (6 h, 2.2 mg L ⁻¹ , pH not reported)	Not quantitative at pH < 5	[39]
	Cd	f_u – No data $f_e = 83.9 \pm 2.7\%$ (1 M HNO ₃) $f_e = 94.9 \pm 4.7\%$ (1 M HNO ₃) $f_e = 98.7 \pm 1.1$ (conc. HNO ₃)	pH 5.0 – 10.0 10 nM – 1 M NaNO ₃	72 h in 0.01 M NaNO ₃	No data	Not quantitative at pH < 5 in 0.01 M NaNO ₃	[1, 16, 25, 33]
	Co	f_u – No data $f_e = 93.0 \pm 2.0\%$ (1 M HNO ₃) $f_e = 98.6 \pm 1.2$ (conc. HNO ₃)	pH 3.5 – 10.0 No competitive effects from Ca ²⁺	72 h in 0.01 M NaNO ₃	No data		[16, 25, 33]
	Cr(III)	f_u (pH 4.4) = 99 ± 2% f_u (pH 5.3) = 94 ± 5%	pH 2.9 – 5.0	10 h in 0.01 M NaNO ₃ (pH 5.0)	No data	Not quantitative at pH 7.5 in 0.01 M NaNO ₃	[83]

		$f_e(\text{pH } 4.4) = 81 \pm 7\%$ (1 M HNO ₃) $f_e(\text{pH } 5.3) = 79 \pm 6\%$ (1 M HNO ₃)					
Cu	f_u – No data $f_e = 79.3 \pm 6.4\%$ (1 M HNO ₃) $f_e = 91.8 \pm 1.2\%$ (1 M HNO ₃) $f_e = 97.7 \pm 1.0\%$ (conc. HNO ₃)	pH 2.0 – 10.0 (0.01 M NaNO ₃) No competitive effects from Ca ²⁺	72 h in 0.01 M NaNO ₃	No data			[1, 16, 25, 33]
Fe	f_u – No data $f_e = 69.7 \pm 5.0\%$ (1 M HNO ₃) $f_e = 80.8 \pm 10.1$ (conc. HNO ₃)	No data	No data	No data	Not quantitative at pH 4.7 – 5.9		[1, 33]
Mg	$f_u > 96\%$ $f_e = 95.4 \pm 6.5\%$ (1 M HNO ₃)	pH 4.0 – 6.7	24 h in deionised water	Natural freshwater (6 h, 1.1 mg L ⁻¹ , pH not reported)	Not quantitative at pH < 4		[39]
Mn	$f_u > 99\%$ $f_e = 81.4 \pm 2.2\%$ (1 M HNO ₃) $f_e = 90.7 \pm 9.1\%$ (1 M HNO ₃) $f_e = 98.3 \pm 1.1$ (conc. HNO ₃)	pH 3.5 – 10.0 0.001 – 0.7 M NaNO ₃	24 h in 0.01 M NaNO ₃ / 0.004 M Mg(NO ₃) ₂ , pH 6.06	Synthetic freshwater (96 h, 10.9 µg L ⁻¹ , pH 7.48) Synthetic seawater (52 h, 12.7 µg L ⁻¹ , pH 8.02)	Sensitivity is reduced at pH 5-6. Competitive effects under high iron concentrations (5 mM) can be avoided by using short deployment times (<12 hours)		[1, 16, 24, 25]
Ni	f_u – No data $f_e = 81.4 \pm 2.2\%$ (1 M HNO ₃) $f_e = 92.0 \pm 2.1\%$	pH 4.7 – 6.0	24 h in 0.01 M NaNO ₃ / 0.004 M Mg(NO ₃) ₂	No data			[9, 16, 33]

		(1 M HNO ₃) $f_e = 93.5 \pm 0.8$ (conc. HNO ₃)					
	Pb	f_u – No data $f_e = 93.5 \pm 2.7\%$ (1 M HNO ₃) $f_e = 97.4 \pm 0.5$ (conc. HNO ₃)	pH 4.7 – 6.0	24 h in 0.01 M NaNO ₃ / 0.004 M Mg(NO ₃) ₂	No data		[16, 33]
	U	$f_u > 80\%$ $f_e = 80.0 \pm 6\%$ (2 M HNO ₃) $f_e = 89.0 \pm 0.8\%$ (1 M HNO ₃) $f_e = 96.2 \pm 1.3$ (conc. HNO ₃)	pH 5.0 – 9.0 0.01 – 1 M NaNO ₃	120 hours in 0.01 M NaNO ₃	Not quantitative under tested conditions	Not quantitative at pH 4.7 – 5.9 Strong competitive effects from PO ₄ ³⁻ and HCO ₃ ⁻ Poor uptake in synthetic freshwater (76%). Not quantitative in synthetic seawater	[23, 33, 51, 80]
	Zn	f_u – No data $f_e = 80.3 \pm 5.5\%$ (1 M HNO ₃) $f_e = 91.1 \pm 2.8\%$ (1 M HNO ₃) $f_e = 96.3 \pm 1.6$ (conc. HNO ₃)	pH 3.5 – 10.0	24 h in 0.01 M NaNO ₃ / 0.004 M Mg(NO ₃) ₂	No data	No competitive effects from Ca ²⁺	[9, 16, 25, 33]
Ferrihydrite	As(III)	$f_u = 100\%$ $f_e = 89 \pm 0.5\%$ (3.2 M HNO ₃) $f_e = 100 \pm 5\%$ (conc. HCl)	pH 3.0 – 8.0 0.001 – 0.2 M NaNO ₃ 5 mg L ⁻¹ fulvic acid	72 h in 0.01 M NaNO ₃	Synthetic freshwater (41 h, 90 µg L ⁻¹ , pH 8.1) Natural seawater (24 h, 100 µg L ⁻¹ , pH ~8)	No competitive effects on uptake from As(V), PO ₄ ³⁻ , V(V), Se(VI), Se(IV)	[8, 13, 20, 47]
	As(V)	$f_u > 95\%$ $f_u = 100\%$	pH 3.0 – 8.0 0.001 – 0.2 M NaNO ₃	10 h in 0.01 M NaNO ₃ 72 h in 0.01 M	Synthetic freshwater (93 h, 15 µg L ⁻¹ , pH 7.2)	Lower adsorption in presence of colloidal iron (III) hydroxide (1 – 5 mg L ⁻¹) No competitive effects on uptake from	[8, 10, 20, 22, 47, 48]

		$f_e = 78 \pm 0.48\%$ (1 M HNO ₃) $f_e = 88 \pm 0.3\%$ (3.2 M HNO ₃) $f_e = 94\% - 104\%$ (1.4 M HNO ₃ , 0.1 M HF) $f_e = 100 \pm 5\%$ (conc. HCl)	5 mg L ⁻¹ fulvic acid	NaNO ₃	Synthetic seawater (92 h, 15 µg L ⁻¹ , pH 8.3)	As(III), PO ₄ ³⁻ , V(V), Se(VI), Se(IV) in synthetic fresh or seawater	
	PO ₄ ³⁻	$f_u > 96\%$ f_u : 100% $f_e = 81 \pm 0.7\%$ (3.2 M HNO ₃) $f_e = 92 \pm 5\%$ (1 M NaOH) $f_e = 101.4 \pm 2.1\%$ (0.25 M H ₂ SO ₄)	pH 2.0 – 10.0 0.0001 – 1.0 M NaNO ₃	55 h in 0.01 M NaNO ₃	Synthetic freshwater (96 h, 47.5 µg L ⁻¹ , pH 7.2) Synthetic seawater (72 h, 95 µg L ⁻¹ , pH 8.1)	Not quantitative > 48 hours at 2.9 – 5.7 mM HCO ₃ ⁻ No competitive effects from Cl ⁻ or SO ₄ ²⁻ No competitive effects on uptake from As(III), As(V), V(V), Se(VI), Se(IV) in synthetic fresh or seawater Lower recovery at pH 1 (10.5%)	[9, 11, 20, 31]
	Se(IV)	f_u – No data $f_e = 81 \pm 0.7\%$ (3.2 M HNO ₃)	pH 4.0 – 8.0 0.001 – 0.2 M NaNO ₃	72 h in 0.01 M NaNO ₃	Synthetic freshwater (41 h, 79 µg L ⁻¹ , pH 8.1) Synthetic seawater (72 h, 40 µg L ⁻¹ , pH 8.1)	Competition for uptake by As, V and PO ₄ ³⁻	[20, 47]
	Sb(V)	$f_u > 95\%$ $f_e = 85 \pm 0.33\%$ (1 M HNO ₃) $f_e = 94\% - 104\%$ (1.4 M HNO ₃ , 0.1 M HF)	pH 3.0 – 8.0 0.001 - 0.1 M NaNO ₃	72 h in 0.01 M NaNO ₃	Synthetic freshwater (6 h, 4 µg L ⁻¹ , pH 7.2)	Slightly slower and weaker adsorption at pH > 8 Lower binding affinity than V, As, Mo and W Not quantitative in synthetic seawater Not quantitative in synthetic freshwater for deployment times > 6 h	[22, 47, 48]

	Mo(VI)	$f_u > 95\%$ $f_e = 94\% - 104\%$ (1.4 M HNO ₃ , 0.1 M HF)	pH 4.0 – 6.2	24 h in 0.01 M NaNO ₃	Synthetic freshwater (6 h, 30 µg L ⁻¹ , pH 7.2)	Slightly slower and weaker adsorption at pH > 8 Not quantitative in synthetic seawater Not quantitative in synthetic freshwater for deployment times > 6 h	[22, 48]
	V(V)	$f_u > 95\%$ $f_e = 63 \pm 0.17\%$ (1 M HNO ₃) $f_e = 91 \pm 0.4\%$ (3.2 M HNO ₃) $f_e = 94\% - 104\%$ (1.4 M HNO ₃ , 0.1 M HF)	pH 5.95 – 7.82 0.001 - 0.1 M NaNO ₃	72 h 0.01 M NaNO ₃	Synthetic freshwater (93 h, 12 µg L ⁻¹ , pH 7.2) Synthetic seawater (92 h, 13 µg L ⁻¹ , pH 8.3)	Competition effects on uptake by As(V) and PO ₄ ³⁻ at typical marine pH (~8) Reduced uptake (< 80%) at pH 3 – 4.4	[20, 22, 47, 48]
	W(VI)	$f_u > 95\%$ $f_e = 94\% - 104\%$ (1.4 M HNO ₃ , 0.1 M HF)	pH 4.0 – 8.0	24 h in 0.01 M NaNO ₃	Synthetic freshwater (93 h, 17 µg L ⁻¹ , pH 7.2)	Not quantitative in synthetic seawater	[22, 48]
Metsorb	Al	f_u (pH 4.8) > 98% f_u (pH 8.4) > 85 ± 5% $f_e = 85 \pm 6\%$ (1 M NaOH)	pH 5.0 – 8.5 0.001 – 0.7 M NaNO ₃ (pH 5.0 and 8.4)	96 h in 0.002 M NaNO ₃ (pH 5.05 and 8.35)	Synthetic freshwater (96 h, 10.2-22.6 µg L ⁻¹ , pH 5.4-8.1) Synthetic seawater (96 h, 20 µg L ⁻¹ , pH 8.15)	Not quantitative at pH < 5	[30]
	As(III)	$f_u = 100\%$ $f_e = 81.2 \pm 1.1\%$ (1 M NaOH) $f_e = 99 \pm 13\%$ (1 M NaOH)	pH 3.5 – 8.5 0.0001 – 0.75 M NaNO ₃	24 h in 0.01 M NaNO ₃	Synthetic freshwater (41 h, 90 µg L ⁻¹ , pH 8.1) Natural seawater (72 h, 50 µg L ⁻¹ , pH ~8)	No competitive effects observed with As(V) or PO ₄ ³⁻	[10, 13, 20]
	As(V)	$f_u > 98\%$ $f_u = 100\%$	pH 3.5 – 8.5 0.0001 – 0.75 M	24 h in 0.01 M NaNO ₃	Synthetic freshwater (93 h, 15 µg L ⁻¹ , pH 7.2)	No competitive effects observed with As(III) or PO ₄ ³⁻	[10, 20, 22]

		$f_e = 75.2 \pm 1.5\%$ (1 M NaOH) $f_e = 92.1 \pm 2.5\%$ (1 M NaOH) $f_e = 100 \pm 2\%$ (1 M NaOH)	NaNO ₃		Synthetic seawater (92 h, 15 µg L ⁻¹ , pH 8.3)		
	PO ₄ ³⁻	$f_u > 98\%$ $f_e = 61 \pm 9\%$ (1 M NaOH) $f_e = 92 \pm 5.0\%$ (1 M NaOH)	pH 3.9 – 8.2 0.0001 – 1.0 M NaNO ₃	55 h in 0.01 M NaNO ₃	Synthetic freshwater (96 h, 47.5 µg L ⁻¹ , pH 7.2) Synthetic seawater (96 h, 45 µg L ⁻¹ , pH 8.22)	No observed competition effects with HCO ₃ ⁻ , Cl ⁻ or SO ₄ ²⁻	[11, 20, 31]
	Se(IV)	$f_u = 96.5 \pm 0.5\%$ (1 M NaOH) $f_e = 86.2 \pm 5.6\%$ (1 M NaOH) $f_e = 94 \pm 3\%$ (1 M NaOH)	pH 3.5 – 8.5 0.0001 – 0.75 M NaNO ₃	24 h in 0.01 M NaNO ₃	Synthetic freshwater (41 h, 79 µg L ⁻¹ , pH 8.1) Synthetic seawater (48 h, 40 µg L ⁻¹ , pH 8.1)	Lower adsorption affinity compared to As(V), V(V) and PO ₄ ³⁻	[10, 20]
	Sb(V)	$f_u > 98\%$ $f_e = 90.3 \pm 4.6\%$ (1 M NaOH/ 1 M H ₂ O ₂)	pH 4.0 – 8.2 0.001 – 0.7 M NaNO ₃	24 h in 0.01 M NaNO ₃	Synthetic freshwater (93 h, 4 µg L ⁻¹ , pH 7.2) Synthetic seawater (92 h, 3 µg L ⁻¹ , pH 8.3)		[22]
	Mo(VI)	$f_u > 98\%$ $f_e = 94.8 \pm 3.6\%$ (1 M NaOH)	pH 4.0 – 8.2 0.001 – 0.7 M NaNO ₃	24 h in 0.01 M NaNO ₃	Synthetic freshwater (93 h, 30 µg L ⁻¹ , pH 7.2) Synthetic seawater (4 h, 15 µg L ⁻¹ , pH 8.3)	Not quantitative > 4 h in synthetic seawater	[22]
	V(V)	$f_u > 98\%$ $f_e = 90 \pm 5\%$	pH 4.0 – 8.2 0.001 – 0.7 M NaNO ₃	24 h in 0.01 M NaNO ₃	Synthetic freshwater (93 h, 12 µg L ⁻¹ , pH 7.2)	Possible competition effects after 24 h from As(V) and PO ₄ ³⁻ in synthetic seawater matrix	[20, 22]

		(1 M NaOH) $f_e = 90.8 \pm 2.3\%$ (1 M NaOH)			Synthetic seawater (92 h, 13 $\mu\text{g L}^{-1}$, pH 8.3)		
	U	$f_u > 90\%$ $f_u > 100 \pm 3\%$ $f_e = 83 \pm 3\%$ (1 M HNO ₃ / 1 M H ₂ O ₂) $f_e = 95.2 \pm 5\%$ (1 M NaOH/ 1 M H ₂ O ₂)	pH 3.0 – 9.0 0.001 – 1 M NaNO ₃	120 h in 0.01 M NaNO ₃	Synthetic freshwater (96 h, 14.7 $\mu\text{g L}^{-1}$, pH 8.25) Natural seawater (8 h, 26.3 $\mu\text{g L}^{-1}$, pH 7.86)	Competition affects uptake in synthetic seawater for deployments > 8 h Strong competitive effects from SO ₄ ²⁻ , PO ₄ ³⁻ or HCO ₃ ⁻ at high concentrations Addition of Ca ²⁺ increased f_u	[23, 51]
	W(VI)	$f_u > 98\%$ $f_e = 97.9 \pm 1.6\%$ (1 M NaOH)	pH 4.0 – 8.2 0.001 – 0.7 M NaNO ₃	24 h in 0.01 M NaNO ₃	Synthetic freshwater (93 h, 17 $\mu\text{g L}^{-1}$, pH 7.2) Synthetic seawater (92 h, 17 $\mu\text{g L}^{-1}$, pH 8.3)		[22]
ZrO ₂	As	$f_u = 100\%$ As(III) $f_e = 86.9 \pm 2.5\%$ (1 M NaOH) As(V) $f_e = 88.4 \pm 2.0\%$ (1 M NaOH) As (inorganic) $f_e = 96.9 \pm 1.8\%$ (0.5 M NaOH)	pH 2.0 – 9.1 0.00001 – 0.75 M NaNO ₃	72 h in 0.01 M NaNO ₃	Synthetic and natural freshwater (96 h, 50 $\mu\text{g L}^{-1}$, pH 7.2-7.6) Synthetic seawater (96 h, 200 $\mu\text{g L}^{-1}$, pH 8.2)	$f_e = 87.7\%$ used for total inorganic As(III + V) elution efficiency No competitive effects from phosphate (0.25 – 10 mg L ⁻¹)	[49, 50]
	Mo(VI)	$f_u > 85\%$ within 30 mins $f_e = 98.9 \pm 1.7\%$ (0.5 M NaOH)	pH 3.8 – 7.8 0.0001 – 0.5 M NaNO ₃	72 h in 0.01 M NaNO ₃	No data		[50]
	PO ₄ ³⁻	$f_u = 100\%$ $f_e = 95.3 \pm 2.1\%$	pH 3.0 – 10.0 0.00001 – 0.5 M	72 h in 0.01 M NaNO ₃	No data	No interferences from Cl ⁻ , SO ₄ ²⁻ , As(V) and As(III)	[18, 32, 50]

		(1 M NaOH) $f_e = 96.2 \pm 1.8\%$ (0.5 M NaOH)	NaNO ₃				
	Sb(V)	$f_u > 85\%$ within 30 mins $f_e = 101.8 \pm 0.7\%$ (0.5 M NaOH; 0.5 M NaOH/ 0.5 M H ₂ O ₂)	pH 3.8 – 7.8 0.0001 – 0.5 M NaNO ₃	72 h in 0.01 M NaNO ₃	No data		[50]
	Se(VI)	$f_u > 85\%$ $f_e = 95.3 \pm 5.2\%$ (0.5 M NaOH)	pH 3.8 – 7.8 0.001 – 0.1 M NaNO ₃	72 h in 0.01 M NaNO ₃	No data	Uptake affected at low (0.0001 M NaNO ₃) and high (0.5 M NaNO ₃) ionic strengths	[50]
	V(V)	$f_u > 85\%$ $f_e = 98.2 \pm 1.0\%$ (0.5 M NaOH)	pH 3.8 – 7.8 0.0001 – 0.5 M NaNO ₃	72 h in 0.01 M NaNO ₃	No data		[50]
3-MFS	As(III)	$f_u > 99\%$ $f_e = 85.6 \pm 1.7\%$ (1 M HNO ₃ , 0.01 M KIO ₃)	pH 3.5 – 8.5 0.0001 – 0.75 M NaNO ₃	24 h in 0.01 M NaNO ₃	Natural seawater (72 h, 100 µg L ⁻¹ , pH ~8)		[13]
	Hg	f_u – No data f_e = No data (5% thiourea) f_e = No data (aqua regia)	pH 5.0	32 h in 0.01 M NaCl	No data	No interference observed with Al, V, Mn, Cr, Fe, Co, Ni, Cu, Zn, Ag, Sn and Pb Quantitative in presence of DOM	[14, 55, 84]
	CH ₃ Hg	f_u – No data $f_e = 91 \pm 3\%$ (1.31 mM thiourea in 0.1 M HCl)	pH 3.0 – 9.0	32 h in 0.01 M NaCl	No data		[53]
AG50W-X8	Cs	$f_u = 100\%$	pH 4.0 – 9.0	No data	Synthetic freshwater (20 h, 0.03 µg L ⁻¹ , pH	Na competes effectively at > 1 mM NaCl	[7]

		$f_e = 91 \pm 0.1 \%$ (2 M HNO ₃)	1 μ M – 1 mM NaCl,		7.5)		
	Sr	$f_u = 100\%$ $f_e = 100 \pm 0.2\%$ (2 M HNO ₃)	pH 3.0 – 9.0 1 μ M – 1 mM NaCl,	No data	Natural freshwater (25 h, 16.5 μ g L ⁻¹ , pH 7.5)	Na competes effectively at > 1 mM NaCl	[7]
XAD18	SMX	f_u – No data $f_e = 97 \pm 2\%$ (methanol)	pH 6.0 – 9.0 0.001 – 0.01 M NaCl	48 h in 0.01 M NaCl	No data	Partial field validation in wastewater conducted for 40 antibiotic compounds	[27]