



Performance study of diffusive gradients in thin films (DGT) for 55 elements

Metals taken up by DGT samplers with Chelex absorbent

H																							He					
Li	Be																						B	C	N	O	F	Ne
Na	Mg																						Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr											
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe											
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn											
Fr	Ra	Ac																										
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu												
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr												

Not studied

pH dependant

Capacity limited

Quantitative

Not taken up

Norwegian Institute for Water Research

REPORT

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Abstract :

The technique of diffusive gradients in thin films (DGT) is a fairly new and useful tool for in situ measurement of labile metal ions in water. In this study the applicability of DGT for determining 55 elements has been investigated by comparing independently determined or estimated diffusion coefficients with DGT effective diffusion coefficients (D_{DGT}) calculated from the measured accumulation of mass by the DGT sampler. An exposure chamber was developed, where DGT could be exposed at controlled water fluid velocity. By this setup we determined D_{DGT} -values from DGT samplers exposed at controlled concentration and fluid velocity at 4 pH levels between 4.7 and 6.0. Our D_{DGT} values for the elements Co, Ni, Cu, Zn, Cd, Pb, Al, Mn and Ga were close to previously published values with some deviations for Pb and Zn. The uptake of V, Cr, Fe, U, Mo, Ti, Ba and Sr varied with pH and we recorded some experimental problems that require further investigations. We established a novel set of D_{DGT} values for the lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) that all are very consistent. The D_{DGT} values are about 10-15% lower than what can be calculated for free ions in water, and indicate that diffusion coefficients of metal ions in the agarose polyacrylamide hydrogel are 10-15% lower than in water. The high consistency of the data for the lanthanides establishes these elements as new performance test metals for the DGT sampler. The accumulation of the elements 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 was small (D_{DGT} lower than 10% of theoretical values). Furthermore we established a more efficient elution procedure using concentrated nitric acid for the absorbent gel, with elution efficiencies between 95-100 % for most metals. For deployment times of 24 hours, detection limits from 0.001-1 ng/ml were readily achieved with moderate precautions to prevent contamination.

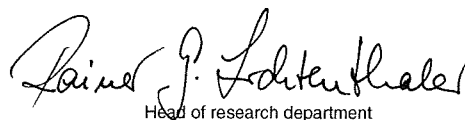
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Preface

This report is a summary of the most important results in Øyvind Aaberg Garmo's cand. scient thesis. The work was performed at Dep. of Chem., NTNU, (Norwegian University for Science and Technology), Trondheim, in the period Aug. 2000 to Dec. 2002. The work was performed in co-operation between NIVA and NTNU as a part of Oddvar Røyset's Norwegian Research Council (NRC) project MU-PROFO 140375/720, "Passive sampling of metals ions in water using DGTs". Supervisors were project partners prof. Dr. Phil. Eiliv Steinnes and ass. prof. dr. sci. Trond Peder Flaten, NTNU, and senior scientist dr. sci. Oddvar Røyset, NIVA. The undersigned thanks all participants for contributions in this work. A special thank to Øyvind Aaberg Garmo for the excellent work performed during his cand. sci. study at NTNU, and excellent contributions during the preparation of this manuscript.

Oslo, 10. December 2002

Oddvar Røyset
Project leader, NIVA.

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Summary

The technique of diffusive gradients in thin films (DGT) is a fairly new and useful tool for in situ measurement of labile metal ions in water. In this study the applicability of DGT for determining 55 elements has been investigated by comparing independently determined or estimated diffusion coefficients with DGT effective diffusion coefficients (D_{DGT}) calculated from the measured accumulation of mass by the DGT sampler. An exposure chamber was developed, where DGT could be exposed at controlled water fluid velocity. By this setup we determined D_{DGT} -values from DGT samplers exposed at controlled concentration and fluid velocity at 4 pH levels between 4.7 and 6.0. Our D_{DGT} values for the elements Co, Ni, Cu, Zn, Cd, Pb, Al, Mn and Ga were close to previously published values with some deviations for Pb and Zn. The uptake of V, Cr, Fe, U, Mo, Ti, Ba and Sr varied with pH and we recorded some experimental problems that require further investigations. We established a novel set of D_{DGT} values for the lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) that all are very consistent. The D_{DGT} values are about 10-15% lower than what can be calculated for free ions in water, and indicate that diffusion coefficients of metal ions in the agarose polyacrylamide hydrogel are 10-15% lower than in water. The high consistency of the data for the lanthanides establishes these elements as new performance test metals for the DGT sampler. The accumulation of the elements 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 was small (D_{DGT} lower than 10% of theoretical values). Furthermore we established a more efficient elution procedure using concentrated nitric acid for the absorbent gel, with elution efficiencies between 95-100 % for most metals. For deployment times of 24 hours, detection limits from 0.001-1 ng/ml were readily achieved with moderate precautions to prevent contamination.

1. Introduction

The technique of diffusive gradients in thin films (DGT), developed by Zhang and Davison (1), for passive sampling of labile metal ions in aquatic environments, has proved to be useful on account of its simplicity and wide applicability. Whereas diffusive passive samplers have become very successful in measurements of gases in air during the last 20 years, the DGT sampler is the first diffusive passive sampler for ions in water that take full advantage of diffusion theory for calculations of time-averaged concentrations. Provided that the process of mass transport is understood and quantified, such as described in some of Davison and Zhang's early works (2), the sampler gives reasonably accurate values for the time-averaged concentration during exposure. Moreover, since the technique relies on diffusion of ions through a rather narrow-pore hydrogel, the DGT technique is a new speciation tool, permitting measurements of labile (free) ions of metals in solution.

Since 1994 several papers describing laboratory testing and field applications of DGT have been published. Most of the studies have been conducted on the metals Cu, Zn, Cd, Pb, Ni, Co, Mn and Fe in the bivalent form (see Davison et al. (3) for overview). Gimpel *et al.* (4) tested the ability of DGT to concentrate Cd, Co, Mn, Zn and Cu in the pH range 2-13. They found that concentrations of Cd and Cu could be determined accurately in the pH ranges 5-10 and 2-10 respectively. Concentrations of Co, Mn and Zn could be determined accurately between pH 3.5 and 10. One of our planned applications of the DGT sampler is to study speciation and biological effects of metals in acid surface waters in Norway. We wanted to study the performance of the sampler in the pH range 4.5 to 6.0 most typical for such water types. Since we had access to HR-ICPMS and already had long experience with methods including calibration systems for 55 elements (all mixed in one solution), we decided to study the performance of the DGT technique for 55 elements in the pH range 4.7 to 6.0. The present paper describes our main results, further details are given by Garmo (5).

2. Material and methods

2.1 DGT equipment

All DGT equipment was purchased from DGT Research Ltd, Lancaster, UK (<http://www.dgtresearch.com>). The regular DGT deployment mouldings made of polyethylene were used. Diffusive agarose polyacrylamide (APA) gels were of the regular type (a formula patented by DGT Research, Ltd). Diffusive and Chelex gels were 0.80 and 0.40 mm respectively for standard experiments whereas 0.40 and 1.20 mm diffusive gels were used for diffusive boundary layer experiments (Chelex is the trade name of the iminodiacetate chelating resin produced by Bio-Rad). A cellulose nitrate filter (Sartorius, pore size 0.45 μm , thickness 0.12 mm) was placed on top of the diffusive gels in the deployment mouldings in experiments. During DBL experiments spacers of 0.40 mm were placed below the piston ring used for 1.20 mm diffusion gels. To fit the 0.4 mm diffusion gels into the deployment moulding, an extra 0.40 mm diffusive gel was placed under the Chelex gel.

2.2 Laboratory test equipment and procedure

A 50-L polyethylene bucket was used as exposure chamber. A circular rotor plate made of PVC with diameter 20 cm was mounted approximately 15 cm below the lid of the bucket and connected to a small electric motor. The rim of the rotor plate had twelve holes where DGT deployment units could be fixed (Figure 1). The motor speed was adjusted so that the rim of the rotor had a periphery velocity of 0.1 m/s, to ensure a constant fluid velocity for all DGTs tested. Before experiments the tank was carefully acid washed and filled with 50 L of deionized water (Millipore, MilliQ equipment). NaNO_3 was added to a concentration of 0.01 M and the 55 metals were added to a calculated concentration of 1.00 ng/ml (prepared by the same manufacturer as for calibration standards of HR-ICPMS, see below). After mixing the pH of the test solution was about 4.0 due to the nitric acid following from the concentrated stocks. The pH value was then adjusted to 4.7, 5.0, 5.3 or 6.0 with NaOH (p.a., Merck) and left to stabilize for 24 hours with mixing by the rotor. The DGT units were exposed in the test solution for 24, 48 and 72 hours, respectively. The water temperature was between 19 and 20 $^{\circ}\text{C}$ during the experiments. The element concentration of the test solution was controlled every 24 hours. The water samples were preserved with high purity (Merck Suprapur) HNO_3 (1% vol/vol, i.e. 0.10 ml pr 10 ml) before analysis by HR-ICPMS. After exposure the DGT units were removed from the rotor and dismantled, and the Chelex gels were transferred to acid cleaned 15 ml polypropylene tubes and 1.0 ml concentrated HNO_3 (Merck, Suprapur) was added. The tubes were swirled to assure good contact with the gel and left for 16-24 hours for complete elution of metals before adding 9.0 ml of deionized water (MilliQ). After mixing the resulting solution was decanted into a new 15 ml polypropylene tube leaving the Chelex gel in the first tube. The removal of the gel is important to prevent back absorption of metals to the Chelex gel after dilution; non-quantitative elution efficiency has been reported using 2 M HNO_3 (2). This mixing and decanting procedure took 5-10 sec for each sample. The solution was then spiked with internal standards for HR-ICPMS analysis.

2.3 HR-ICPMS procedures

A Thermo Finnigan Element HR-ICPMS (High-Resolution Inductively Coupled Plasma Mass Spectrometry) instrument was used to determine the element concentrations in the resin gel extracts and the samples from the test solution. The calibration was performed with multi-element mixtures containing 55 elements at 1, 5 or 10 ng/ml. The standards were customer designed ICPMS calibration solutions from two professional vendors of such products (high purity primary element solutions of purity 99.99% or better). They consisted of several multi-element stock solutions at 500 and 100 $\mu\text{g}/\text{ml}$ (mixed to avoid precipitation), and contained all together the elements Li, Na, K, Rb, Mg, Ca, Sr, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Cd, Al, Pb, B, Ga, Tl, P, S, As, Bi, Se, Ti, Si, Sn, Sb, Te,

Mo, Zr, Nb, Hf, Ta, W, U, Th, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. All the customer designed stock solutions were prepared free of chloride (stabilized by nitric acid only) to avoid Cl-molecular ions in the plasma during calibration and precipitation on mixing of elements like Ag. Some stock solutions contained traces of hydrofluoric acid, but when diluted to 1-10 ng/ml, the fluoride level was of the order of a few micromoles per litre or less. The acidity of calibration solutions was matched with that of the samples (10 ml conc. 65% HNO₃ per 100 ml of the DGT eluates and 1 ml conc. 65% HNO₃ per 100 ml of water samples). 5 internal standards were used containing Li-6 (95% Li-6), Sc, Ge, In and Re, and a 55 element program was designed with resolutions to meet expected molecular ion problems in ICPMS (5). The same 55 element calibration mixtures have been used at NIVA for Quadrupole ICPMS-procedures and have been thoroughly tested for stability and analytical performance. These methods comprise the basis for corresponding Quadrupole ICPMS methods at NIVA for water samples and digests of biota and sediments accredited by Norwegian Accreditation according to EN 45001. For competitive reasons more details about the calibration protocols and methods cannot be given.

3. Theoretical basis - diffusion

The diffusive flux of molecules (dm/dt) over a given distance with a concentration gradient (dC/dz) is estimated from Fick's 1st law of diffusion (eq. 1 below). The principle of diffusive sampling relies on the formation of a steady state concentration gradient and diffusion controlled mass transport. If the sampler absorbent is an efficient sink for ions (i.e. the concentration of ions at the adsorbent surface approximates zero and no back diffusion occurs), the concentration (C_o) of ions outside the sampler may be estimated by integrating equation (1), forming equation (2) for time integrated mass uptake ($m(t)$). The terms L ; D and A are constants: the diffusion coefficient (D , specific to each metal ion) and the length (L) and cross section area (A) of the diffusion membrane (which are specific to the geometry of the sampler). Eq. 2 may be solved for the time-averaged concentration (C_o) as shown in the conventional passive sampler equation (eq. 3). The L term (in eq. 2 and 3) must be expanded summing up the total length of the diffusion layer, i.e. the thickness of the gel membrane (G), the filter (f) and the diffusive boundary layer (δ) (see below), forming eq. (4). The DA/L term in equation (2) represents the uptake rate factor (cm^3/sec), which for typical D values of $5 \cdot 10^{-6} \text{ cm}^2/\text{sec}$ using the typical dimensions of the sampler gives uptake rates of $\sim 0.5 \text{ ml/h}$ or $\sim 12 \text{ ml/24h}$ at 25°C . The uptake rate is not a sampling rate in the sense we normally think of, but the volume of water “diffusively emptied” of ions per time unit.

Diffusion coefficients depend on the temperature and the viscosity of water. Adjusting the diffusion coefficient for absolute temperature (T) and viscosity (η) can be done by the Stokes-Einstein equation (eq. 5). Since the viscosity of water depends on the temperature (eq. 6), the exact temperature correction of D requires the combination of eqs. 5 and 6. The diffusive boundary layer (DBL) is a thin layer of water just outside the gel and filter where mass transport is dominated by diffusion. This diffusive boundary layer has a thickness δ that adds to the defined diffusive length of the sampler. The form and thickness of the DBL depends on the shape and dimension of the sampler. In the case of a flat plate, δ can be estimated from fluid mechanics as proposed by Levich (6). Naqvi showed that a modification of the boundary condition is sufficient to adapt Levich's analysis to a non-zero concentration at the solid-solution interface (5). Naqvi's model shown in eq. 7 was used to estimate the DBL in this work. Here, ν is the kinematic viscosity, x is the distance from the leading edge and U is the flow velocity in the free solution whereas D is the diffusion coefficient. Eq. 8 is derived by inverting eq. 4, and is used to estimate the diffusive boundary layer by the so-called reciprocal plot method, where the δ can be calculated from measurements with DGTs with at least two gel thicknesses.

Table 1.

Overview of the most common equations used to describe diffusion processes.

Flux	$Flux = \frac{dm}{dt} = -D \cdot \frac{dC}{dz}$	1
Time integrated uptake	$m(t) = C_o \cdot t \cdot D \cdot \frac{A}{L}$	2
Time averaged concentration	$C_o = \frac{m}{t} \cdot \frac{L}{DA}$	3
Time averaged concentration	$C_o = \frac{m}{t} \cdot \frac{(G + f + \delta)}{DA}$	4
Temperature correction of D (Stokes-Einstein)	$\frac{D_t \eta_t}{T_t} = \frac{D_o \eta_o}{T_o}$	5
Temperature correction of viscosity	$\log \frac{\eta_o}{\eta_t} = \frac{1,37023(t - 25) + 0,000836(t - 25)^2}{109 + t}$	6
Diffusive boundary layer (DBL) thickness	$\delta = 3.3 \cdot \sqrt[3]{\frac{D}{v}} \cdot \sqrt[2]{\frac{vx}{U}}$	7
Reciprocal mass plot for DBL estimation	$\frac{1}{m} = \frac{G + f}{D \cdot C_o \cdot At} + \frac{\delta}{D \cdot C_o \cdot At}$	8

4. Results and discussion

4.1 Exposure chamber

Using the exposure chamber shown in Figure 1, the DGT's could be exposed at the rim of the rotor plate. All the DGT's could in this way face an equal fluid velocity, which could be calculated by the periphery velocity of the rotor. Our impression was that this system performed well during the laboratory experiments. The uniform exposure conditions facilitated good precision during the experiments.

Figure 1.

Exposure chamber used for laboratory testing of DGTs.'



4.2 Stability of metal test solutions

Preparation of test solutions containing 55 elements in the pH range 4.7 to 6.0 is complicated, especially avoiding precipitation of divalent and trivalent metals with low solubility. Ions such as Fe(III) and Al(III) are problematic because of the low solubility of their hydroxides in this pH range (about 1 ng/ml at pH 5 for $\text{Fe}(\text{OH})_3$ and 5-10 ng/ml at pH 6 for $\text{Al}(\text{OH})_3$). Having access to the very sensitive HR-ICPMS technique, we could reduce the concentrations to as low as 1 ng/ml and still achieve reasonably accurate determinations in the eluates of exposed samplers. We therefore decided to prepare the multi-mixture test solutions at a concentration of 1 ng/ml. An exception was made for Al. We used concentrations of 50, 10 and 5 ng/ml for Al, as we were particularly interested in data of high quality for this element. At 1 ng/ml surface adsorption and contamination may change the concentrations during experiments. To control this problem water samples were collected daily. For some metals we observed a decrease in concentration, but in most cases not more than 10%. The elements Sn, Ti and Fe were the most problematic and we observed larger reductions in

concentrations. For the elements Zn and Cu some contamination was observed. In all cases the calculation of D values was based on the average measured concentration in the exposure chamber during the exposure period, and not the nominal calculated initial concentration of 1.00 ng/ml. The water volume of the exposure chamber was 50 L while the typical uptake rate of the samplers were around 10-20 ml/24 h. Twelve samplers simultaneously exposed will absorb 150-300 ml per 24 h, which is less than 0.5% of the total amount added to the exposure chamber. This uptake is only about 1-1.5 % during 72 h and was not corrected for in calculations of diffusion coefficients.

4.3 Determination of elution efficiency

In earlier procedures comprising 2 M HNO₃ Davison and Zhang (2) reported elution efficiencies of about 0.80 with some variability for certain metals. We believed that using concentrated HNO₃ would increase the elution efficiency and checked this by eluting exposed Chelex gels twice with concentrated HNO₃ (the procedure described in the experimental section was repeated twice for the same gel). The results are shown in Table 1 and demonstrate that 97-98% of the total extracted mass of most metals was found in the first acid extract. The low efficiencies for Fe and Cr are probably due to contamination, as the concentration in the second eluate was at the same level as for the blank. The low values for Sn, Ti, Th and Mo are due to low uptake, as the blank levels constituted a large fraction of the total amount, resulting in lower apparent elution efficiencies. The elution efficiency of the lanthanides is impressively similar, around 97.5 %, indicating very similar chemical properties of these metals. This high and reproducible elution efficiency achieved with concentrated nitric acid is important, as it proves almost quantitative elution of many metals using only one extraction step. The high reproducibility of this elution procedure also ensures that accurate and precise elution correction factors may be applied. However, we found somewhat lower elution efficiency in the range 93-97% for some important metals (Al, Zn, Cr and Ni), so the most viable procedure is probably to elute the resin twice. This will ensure a quantitative elution of all metals, and the use of inaccurate elution efficiency correction factors is avoided.

A suspected disadvantage of eluting with concentrated HNO₃ was degradation of the APA gel during extraction, producing a viscous solution. Slight degradation of the gel was observed, but it was easy to remove the gel from the extract after dilution with water. As internal standards were always used during HR-ICPMS analysis, we believe that possible changes in viscosity of the extract caused by dissolved gel material may be sufficiently corrected for.

An approach to achieve complete elution of collected metals is digestion of the complete Chelex membranes by hot concentrated HNO₃. Heating the extract in the polypropylene tubes at 120 °C removed the gel, but not the Chelex resin, while digestion in closed microwave bombs (about 170 °C at elevated pressure) removed both the gel and the Chelex resin. However, using microwave bombs for this purpose, we observed considerably higher blank levels than with cold elution with only nitric acid (Figure 1.). PFA/PTFE materials are known to have tedious memory effects for elements such as Al, Fe, Mn, Cr, Ni, Cu and Zn, yielding blanks in the 10-100 ng range (7). Even with very careful procedures to keep blanks low, ordinary microwave bombs will probably produce higher and less reproducible blanks than the values presented in Figure 2. Microwave digestions may be appropriate at high levels of metals, but not for trace levels. In the latter case, elution repeated twice with concentrated cold HNO₃ is probably the best procedure.

Table 2.

Summary of elution efficiencies obtained with concentrated HNO₃ of the Chelex gel, achieved by repeated extraction of the same exposed gel.

	Recovery in first eluate	
	%	RSD %
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y,	97.5-97.7	1.0-1.5
Cd, Co, Ag, Mn, Cu, V, Pb, Ga	98.3-98.9	0.9-1.5
Sr, Zn, U	96.2-97.0	1.3-1.9
Al	94.7	2.2
Mo	93.9	4.0
Cr	93.7	2.5
Ni	93.5	0.8
Sn	91.2	1.0
Th	89.1	2.1
Ti	88.7	6.2
Fe	80.8	10.1

4.4 Capacity of the Chelex receiving absorbent.

Assuming the thickness of the Chelex layer to be 0.1 mm in absorbent membrane, the resin bed volume is approximately 0.03 ml for a 20 mm diameter Chelex. The binding capacity of Chelex is approximately 0.5 meq/ml wet resin (8), which gives a maximum capacity of 15 µeq for the Chelex absorbent packed in the 0.4 mm resin gel. This is in good agreement with experimental maximum capacity values obtained by Davison and Zhang (2). They reported 0.56 mg Cd corresponding to about 12 µeq. At metal ion concentrations of 1 ng/ml (0.1-0.01 nmol/ml) for about 50 metals and typical uptake rates of 10 ml/24 h, a theoretical capacity of at least 300 days may be estimated, ensuring that we do not exceed capacity during our exposure experiments. However, in the field the capacity is limited by the absorption of the major cations Na, K, Ca and Mg and other abundant divalent/trivalent metal ions. In acid surface water the dominating trace element ions are Al, Fe, Mn, Cu, and Zn, at typical levels of 0.1-5 µM, summing up to a concentration of about 10 µM, which is equivalent to an exposure time around 100 days. Due to the lower selectivity of the major cations, these more loosely bound metals are exchanged during exposure with divalent and trivalent transition and other trace metal ions. Field tests in seawater have also indicated exposures times up to 100 days without saturation (2).

4.5 Accumulation of metal ions as a function of deployment time

The Chelex-100 resin is known to be a selective and efficient chelator for divalent and trivalent metal ions in the pH range 4.7-6.0 as used in our experiments (8). As long as the capacity of the Chelex resin gel is not exceeded, eq. 2 predicts linear uptake of ions with time for a DGT sampler. The amount of metal accumulated at 24, 48 and 72 hours was plotted and the linearity was examined (5). At the

concentration studied (1 ng/ml) we found good linearity up to 72 hours for most of the elements listed in Table 3. Exceptions were Ba and Sr, where a small decrease in uptake was observed above 48 hours, whereas Ag, Be, Fe, Mo and Ti showed some mixed patterns. For the elements Li, Na, K, Rb, Mg, Ca, B, Tl, P, S, As, Bi, Se, Si, Sn, Sb, Te, Zr, Nb, Hf, Ta, W and Th, linear uptake with time was not observed. We should probably have expected a linear uptake, at least initially, of the elements Mg and Ca, as Dahlquist et al. (9) showed that DGTs have a limited absorption capacity for these elements.

4.6 Estimation of the thickness of the diffusive boundary layer

One of the most problematic parameters to control using diffusive samplers for ions in water is the diffusive boundary layer formed at the solvent-solid interface. In this thin layer of solution the mass transport is conducted by diffusion and not by convection. Hence, the apparent diffusion length of the sampler is prolonged and must be corrected for to achieve accurate measurements. Estimates of the thickness of the DBL based on fluid mechanical considerations can be obtained by means of eq. 7 (5). This model relies on a rather crude approximation, because it is derived for a liquid flowing across a flat plate.

As described under Material and methods above, DBL experiments were conducted with three gel thicknesses of 0.4, 0.8 and 1.2 mm. Garmo (5) estimated δ values for different elements based on the reciprocal plot method of eq. 8. As shown in Table 1 our experimental results imply a DBL layer thickness around 100 μm . Again we get very reproducible values for δ from the lanthanides, while the values based on Cd and Mn deviate somewhat and are probably too high. Eq. 7 predicts δ values between 75 and 100 μm for ions with D values in the range $4\text{-}8 \text{ E-}6 \text{ cm}^2/\text{s}$ at a speed of 0.1 m/s (the periphery velocity of the rotor in the exposure chamber) and a distance of 1 cm (in the middle of the DGT window).

As apparent from Table 2 the estimates based on the reciprocal plot method show large standard errors, ranging from 45 to 80 μm . One reason for this problem is that the measured uptake of metals using the 1.2 mm gel was too high (giving a negative value for DBL) due to an unrecognized error. The results in Table 2 derived from reciprocal plots, were therefore only based on the result from 0.4 and 0.8 mm membranes. Because we had only two data points, the uncertainties are considerably larger than we would expect from plots with 3 points. This experiment was repeated with 5 membranes of 0.4, 0.8, 1.2, 1.6 and 2.0 mm (1.6 achieved by placing two 0.8 mm gels on top of each other and 2.0 mm by a 1.2 plus 0.8 mm gels on top of each other). Similar problems occurred in this case: the thicker membranes collected higher amounts than expected. Zhang (10) have experienced similar problems without finding any good explanation. However, the data obtained for 0.4 and 0.8 mm gels and the estimate based on eq. 7, indicate that DBL values are in the range of 80-100 μm for these experiments with a flow velocity of 0.1 m/s. As the total diffusion length of the system is about 1000 μm ($G=800$, $f=120$ and $\delta=100$), the uncertainty in the estimate of 40-80 μm contributes with a total error of 4-8% to the D values obtained. A detailed discussion of all the implications of the different methods of estimating the DBL is far beyond the scope of this work. Both the experimental problems encountered as well as the need for better understanding of how the DBL develops above the DGT surface, call for future research.

Table 3.

Estimation of DBL thickness by the reciprocal plot method and compared to values obtained with eq. 7.

	Reciprocal plot input values			Diffusive boundary layer DBL		
	Diffusion	Reciprocal	Measured	Measured by reciprocal plots		Estimated from
	coefficient cm ² /s	mass (1/m) µg ⁻¹	conc. in test ng/ml	δ, µm	Std. error, µm	model (eq. 7) δ, µm
Pb	8.0E-06	4.0648	0.81	93	45	99
Cd	6.0E-06	4.5498	1.22	152	70	90
Mn	5.8E-06	6.092	1.01	167	76	89
Co	5.7E-06	4.3909	1.05	95	57	89
Cu	5.9E-06	3.1468	1.46	100	75	90
Ni	5.8E-06	4.4726	1.08	108	74	89
Al	3.5E-06	0.7138	10.06	82	63	75
La	5.2E-06	4.8095	1.05	96	73	86
Ce	5.2E-06	6.5367	0.86	119	75	86
Pr	5.2E-06	6.1928	0.86	107	70	86
Nd	5.2E-06	5.9325	0.94	116	71	86
Sm	5.1E-06	5.9728	0.89	102	71	86
Eu	5.1E-06	5.9285	0.91	105	74	85
Gd	5.1E-06	5.4811	0.90	83	69	85
Dy	4.9E-06	5.8836	0.87	86	78	85
Ho	5.0E-06	5.8243	0.88	87	79	85
Er	5.0E-06	6.039	0.87	91	73	85
Tm	4.9E-06	5.7572	0.87	79	74	84
Yb	4.9E-06	6.2143	0.92	108	74	85
			Average	104	71	87
			Std. Dev.	22	8	4
			Maximum	167	79	99
			Minimum	79	45	75

4.7 Estimation of diffusion coefficients at different pH values

Our first application for the DGT technology was Norwegian acid surface waters with pH ranging from 4.5 to 6.0 and we therefore focused our laboratory study to this pH range. We conducted eight laboratory experiments at pH 4.7, 5.0, 5.4 and 5.9, performing both tests twice to control the stability of the tests. The effective diffusion coefficient was calculated by solving eq. 3 (Table 1) for D. All the parameters of eq. 3 were known (A, G, f and δ) or measured; the accumulated mass (x), the time (t) and the concentration C₀ of each metal ion in the test solution.

It must be realized that what we measured most precisely can be denoted DGT effective diffusion coefficients (D_{DGT}). The diffusion coefficients obtained from our experiments are a mixed expression of the diffusion rate of ions in the diffusion gel membrane, and the binding ability of the receiving Chelex adsorbent. Thus for elements for which the Chelex adsorbent has lower selectivity, back diffusion may be expected and the D_{DGT} -value obtained will be lower than what can be calculated or measured from diffusion cell measurements. Nevertheless, provided that the accumulation is linear with respect to time, we believe that this is a very viable way to achieve diffusion coefficients related to DGT, as it reveals the elements that accumulate in a quantifiable way.

The diffusion coefficient depends on the temperature and the viscosity of water. The laboratory experiments were performed at a temperature of 19-20 °C. The values were normalized to 25 °C by the Stokes Einstein relation for comparison with earlier results. Table 3 compares our results with values either estimated by Li and Gregory (11) from limiting equivalent conductivity data (D_{LEC}) or measured by Zhang and coworkers (12) in diffusion cells (D_{DC}), with the same type of APA gel as applied in these DGT experiments.

The D_{DGT} values listed in Table 3 are close to previously published values for Co, Ni, Cu, Cd, Al, Mn and Ga, while there is some deviation for Pb and Zn. For Ba and Sr the uptake is limited by the capacity and selectivity of the adsorbents, at low pH the uptake is probably reduced by competition with H^+ ions. This is probably also the case for Cd at pH 4.7. Previous studies (4) have shown that Cd is one of the trace metals for which the Chelex resin has a relatively low selectivity.

To our knowledge the performance of DGT for the lanthanides has not been reported before. The data obtained for the lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) are very consistent with D_{DGT} about 10-15% lower than estimated diffusion coefficients in water (with the exception of Gd probably being too high due to an unknown reason). The very consistent data for the rest of the lanthanides confirm that diffusion coefficients of ions in the APA hydrogel are 10-15% lower than in water. This was also suggested by Alfaro-De la Torre et al. (13), i.e. the hydrogel imposes a resistance to ionic movement of this order of magnitude.

The elements 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 showed low uptake (D_{DGT} less than 10% of theoretical values for D). These ions are not completely absorbed by the Chelex resin, as the selectivity of Chelex for the cationic forms of these elements is low, or the elements form mainly anionic forms that are not bound. It is rather surprising that Ag showed so little uptake, as Chelex is reported to have a high selectivity for this element (8).

For most of the elements there are no obvious relations between the D_{DGT} -values and pH in this range. Exceptions are Sr and Ba, which were taken up in larger amounts on the Chelex-100 resin with increasing pH values (larger D_{DGT} values at higher pH). The accumulation of the elements V, Cr, Fe, U, Mo and Ti decreased at higher pH. These elements have a rather complicated aqueous chemistry in this pH range forming hydroxy-/oxy-complexes with charge and stability highly dependent on pH. Some of the problems especially with Fe may be due to both contamination (high blanks in the gel) as well as instability problems of the test solutions. The D_{DGT} -values for Fe in table 3 are probably too low. In a field investigation of metals in river water DGT measurements were compared with the labile fraction achieved with size charge fractionation, and we found reasonably good results for Fe using Zhang's diffusion coefficients (14). More thorough investigations are needed to produce better D_{DGT} values for these elements.

Table 4.

Diffusion coefficients obtained from our experiments at pH 4.7 – 5.9 compared to values obtained from diffusion cells (Zhang (12)) and from limiting conductance data (Li and Gregory (11)). All data are temperature adjusted to 25 °C by Stokes-Einstein.

pH	4.7		5.0		5.4		5.9		All 4 tests		Li & Gregory	Zhang
N	18		16		18		20		72			
Elem.	Ave	RSD	Ave	RSD	Ave	RSD	Ave	RSD	Ave	RSD	Ref (11)	Ref (12)
(*)	D_{DGT}		D_{DGT}		D_{DGT}		D_{DGT}		D_{DGT}		D_{LEC}	D_{DC}
Ag (I)	0.5	40	0.7	35	0.8	45	1.7	69	0.92	45		
Be (II)	3.1	145	3.3	117	2.1	92	3.0	23	2.87	92		
Ba (II)	3.9	26	4.3	288	5.7	37	4.8	42	4.70	37	8.48	
Sr (II)	3.3	31	4.5	23	5.5	14	6.1	28	4.85	14	9.45	
Cd (II)	4.7	17	5.2	12	5.4	11	5.5	20	5.36	11	7.17	6.09
Co (II)	5.8	20	6.0	11	6.4	15	5.8	18	5.99	15	6.99	5.94
Cu (II)	6.6	22	6.4	11	6.5	16	5.5	167	6.25	16	7.33	6.23
Mn (II)	5.1	23	5.6	12	6.2	13	6.4	16	5.82	13	6.88	5.85
Ni (II)	6.3	21	6.3	13	6.6	17	6.0	18	6.29	17	6.79	5.77
Pb (II)	10.3	21	9.8	10	10.1	17	9.4	17	9.91	17	9.00	8.03
Zn (II)	3.8	20	4.6	18	4.6	15	4.6	24	4.38	15	7.15	6.08
Cr (III)	4.0	23	3.6	15	3.0	24	1.3	25	3.00	24	5.94	5.05
Fe(III)	2.6	69	3.2	24	2.4	74	1.4	61	2.38	74		
Al (III)	5.1	22	5.1	11	5.2	18	5.0	18	5.10	18	5.59	4.75
Ga(III)	5.8	18	6.2	12	6.9	16	6.7	20	6.38	16		
Ce (III)	4.5	16	5.1	15	4.7	12	4.2	21	4.64	12	6.19	
Dy (III)	5.6	24	5.5	12	5.6	21	4.8	20	5.38	21	5.82	
Er (III)	5.8	22	5.5	12	5.6	20	5.2	20	5.52	20	5.85	
Eu (III)	5.8	22	5.7	11	5.5	20	4.6	19	5.40	20		
Gd(III)	8.1	40	6.3	16	7.4	44	8.1	19	7.49	44		
Ho (III)	5.6	23	5.7	12	5.6	23	4.9	19	5.45	20		
La (III)	4.5	16	5.0	17	4.9	11	4.0	19	4.58	11	6.17	
Lu (III)	5.1	22	5.3	12	5.1	20	4.3	20	4.97	20		
Nd (III)	5.5	20	5.7	12	5.6	19	4.8	19	5.40	19	6.16	
Pr (III)	5.9	21	5.8	11	5.9	16	5.4	21	5.75	16	6.18	
Sm (III)	5.8	22	5.5	12	5.6	19	5.1	20	5.50	19	6.08	
Tb (III)	5.7	22	5.5	11	5.6	20	5.1	21	5.46	20		
Tm (III)	5.6	23	5.5	10	5.4	20	4.8	19	5.34	20	5.80	
Y (III)	4.8	17	4.9	14	5.1	15	4.5	19	4.82	15		
Yb (III)	5.4	23	5.3	12	5.3	21	4.4	20	5.11	21	5.82	
U (IV)	4.8	20	4.7	13	4.0	11	3.4	19	4.22	11		
V (V)	5.1	17	4.8	15	4.3	13	2.4	26	4.16	13		
Ti (IV)	2.1	24	2.0	31	1.0	40	0.7	27	1.30	53		
Mo (VII)	2.8	30	1.5	19	0.9	57	0.2	31	1.37	57		

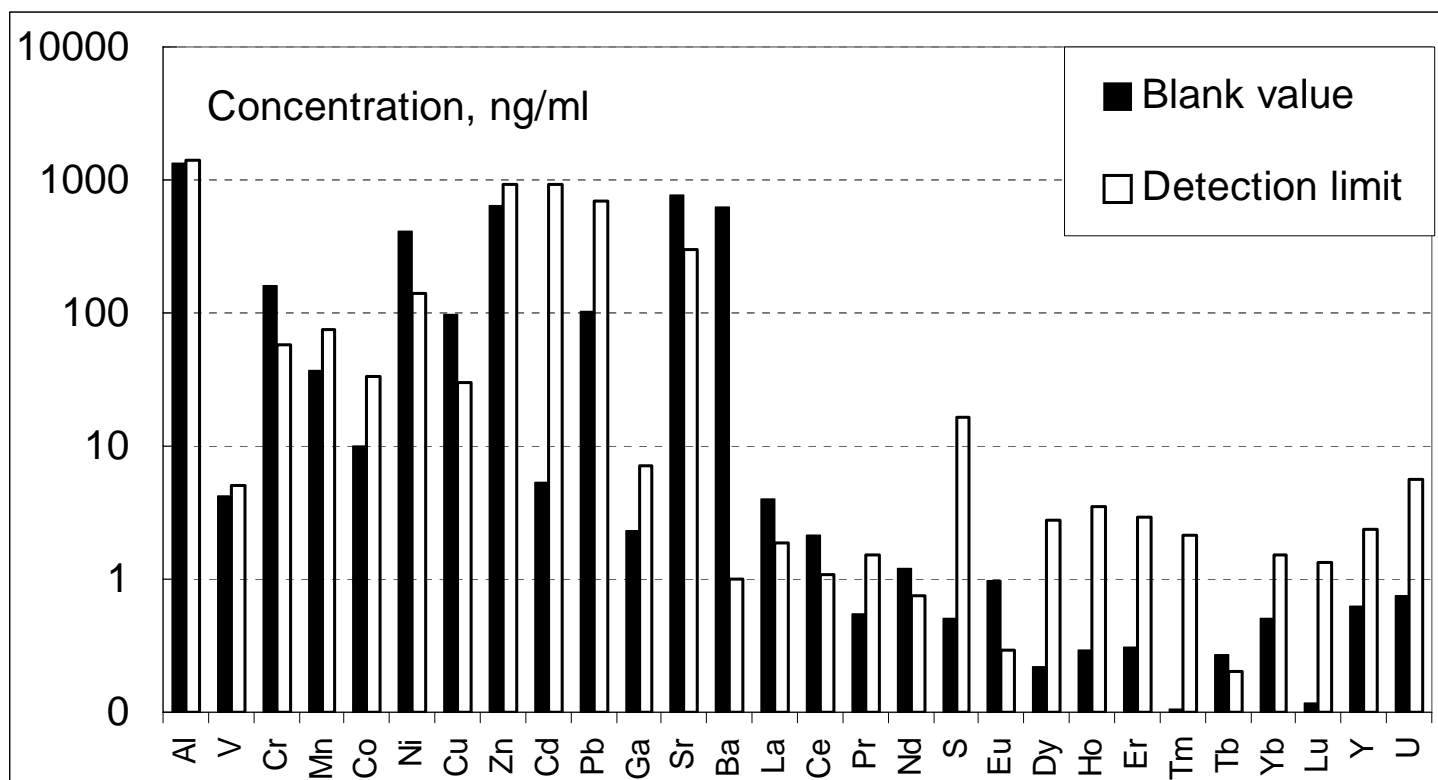
*) Most probable oxidation state of ionic species

4.8 Detection limits

Although the sampling rate by diffusion is slow, the DGT technique as employed in this work provides pre-concentration of metal ions by a factor one to two per 24 h exposure time (i.e. sampling rates of about 10-20 ml/24 h and elution volume of 10 ml). The sensitivity of HR-ICPMS is more than adequate, and the limiting factor to achieve low detection limits is the procedural blanks achieved. During the laboratory experiments a large number of blank samples were collected, and the detection limits of the DGT technique were calculated from the variance of the blank value and eq. 3. The average detection limits achieved in the laboratory experiments for a DGT deployment of 24 hours are presented in Figure 2. Detection limits in the order of 0.1-1 ng/ml were achieved for the elements most commonly associated with contamination (Al, Cu, Zn, Cr, Ba and Sr). For many trace metals detection limits in the order of 0.01-0.1 ng/ml were achieved, while for the lanthanides, where contamination is much less pronounced, detection limits were around 0.001 ng/ml. All the detection limits reported in Figure 2 were achieved with moderate precautions for contamination control. The samplers were mounted and eluted in a class 100,000 clean room, and the Chelex gels were used as delivered from the manufacturer without further cleaning. Olofson et al. (15) acid cleaned the Chelex-100 resin, made their own Chelex gels, used strict procedures for avoiding contamination and reported detection limits 1-2 orders of magnitude lower than those reported in the present work for several elements. Nevertheless, the detection limits in Figure 2 are adequate for many of our applications, e.g. the requirement for toxicological evaluations of reactive Al towards fish species are well above 1 ng/ml. Furthermore, by using typical exposure periods of 1-4 weeks, the limit of detection is lowered by about a factor of 1-2 per day, due to the preconcentration effect of the sampler.

Figure 2.

Blank values and detection limits values achieved with the DGT technique. The blanks are expressed as concentration in a 10 ml extract while the detection limits are 2 times the standard deviation of blanks normalized to a deployment time of 24 hours at 25 °C.



5. Conclusions

This study presents the most comprehensive set of diffusion coefficients achieved to date employing DGT technology. The results also give further insight into the performance of the DGT sampler for metal ions in water in the pH range 4.7 to 6.0. Of the 55 elements tested, we found good performance for about 24 elements with D_{DGT} values close to those reported by other workers, which indicate quantitative absorption by the Chelex for these metals. Additional 7 elements show significant uptake by the sampler, but the approach of this study is not suitable for obtaining reliable diffusion coefficients for these elements because they may partly exist as species that probably are unavailable for uptake in the DGT.

Figure 3 sums up the general patterns achieved. These patterns agree very well with what has become a common understanding during the research based on the selectivity and metal binding ability of the Chelex resin, as summarized in a current monograph by Vandecastelle (16). It is very promising that we get D_{DGT} values for Al which are consistent with those achieved by Zhang (12) and Li and Gregory (11). Labile reactive Al is the most important metal in acid surface waters in Norway for assessments of toxic effect towards fish. Recent results have shown that DGT labile Al is a good predictor for gill uptake of Al in salmonids (18).

Earlier studies of diffusion coefficients have either been performed in diffusion cells (12) or based on calculations from limiting conductivity data for ions in water (11). In the present work we have calculated DGT effective diffusion coefficients (D_{DGT}) where the value is obtained from exposed DGTs. The value obtained in this way is a mixture of the diffusion rate of ions in the gel, and the binding ability of the receiving absorbent (i.e. the Chelex). Where D_{DGT} values are close to the theoretical ones we may conclude that the Chelex resin is an efficient absorbent for that metal ion, while where the values are far below, the DGT with Chelex as absorbent is not useful for that ion. Our general patterns for diffusion coefficients agree closely with what is known from basic data on the chelating ability of Chelex. For elements where the binding strength is high, such as for lanthanides, the D_{DGT} values achieved are 10-15% lower than those calculated for free ions in water. This indicates that the APA hydrogel acts as a restrictor to ion movements of this order of magnitude. These data indicates that we on a general basis may conclude that D_{DGT} values are 10-15% lower than the theoretical ones for free diffusion of ions in water.

The very high elution efficiency with concentrated nitric acid establishes new knowledge. This elution procedure is nearly fully quantitative and the uncertainty of the correction factor achieved is only about 1% for most metals taken up by the sampler. With small modifications using repeated elution, the procedure may become completely quantitative.

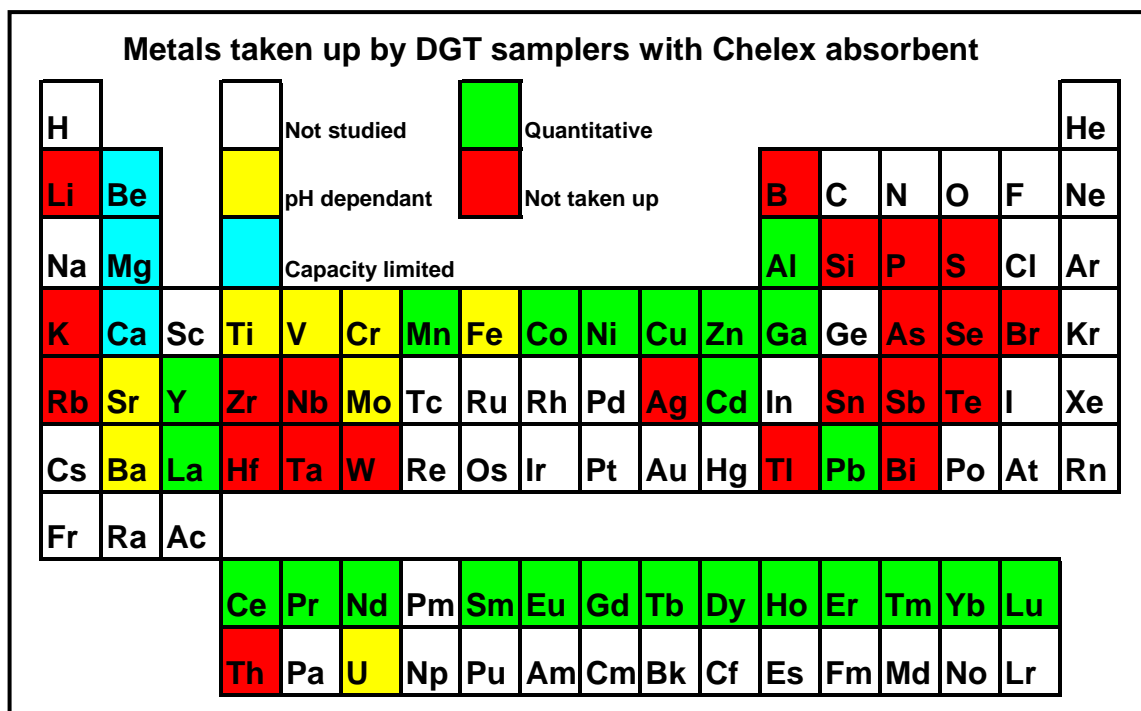
There is a need for more research on methods to estimate the diffusive boundary layer, both to get a more sophisticated fluid mechanical model for how it forms above the circular window of the sampler as well as better control with the experimental procedure using variable gel thickness. The problem of applying DGT with diffusive gels thicker than 0.8 mm should be investigated further in order to get better data for DBL. Experiments with more than three diffusive gel thicknesses at different flow velocities should be conducted and compared with theoretical models for DBL. Our experiments and theoretical predictions indicate that at water velocities around 0.1 m/s the measured and estimated thickness of the DBL layer is around 0.1 mm, i.e. about 10 % of the total diffusion length of the sampler, with an uncertainty of the estimated total diffusion length of 4-8%. At lower flow velocities the DBL will be thicker and impose larger uncertainties in the estimate of the diffusion length term, and consequently lead to correspondingly increased uncertainties of the time-averaged concentrations achieved from the DGT sampler.

Even though diffusive sampling of ions in water is a slow process, the thin membrane of the sampler facilitates high sampling rates and thereby low LODs (0.001-1 ng/ml) even at only 24 h exposure and only moderate precautions for contamination control.

This is the first study where lanthanides have been examined in such detail. Although the environmental significance of these metals is rather limited, the very good performance observed for these metals helps us to establish new performance test parameters for the DGT. The chemical properties of the lanthanides are similar: all are small trivalent cations with almost equal diffusion rates and quantitative absorption by the Chelex receiving absorbent. The lanthanides are very easily determined with both Quadrupole ICPMS and HR-ICPMS, and they may be very convenient for testing the sampler in the laboratory. They may also be used as indicators of general sampling performance *in situ*. During several field trials we have found reasonably good precision of the lanthanides even at levels of 0.1-10 ng/ml (17).

Figure 3.

Overview of properties of metal ions tested in the range 4.7 to 6.



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7. References

- (1) Davison, W.; Zhang, H. In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature*, 1994, 367, 546-548.
- (2) Zhang, H.; Davison, W. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. *Analytical Chemistry*, 1995, 67, 3391-4000.
- (3) Davison, W.; Fones, G.; Harper, M.; Teasdale, P.; Zhang, H. Dialysis, DET and DGT: In situ diffusive techniques for studying water, sediments and soils. In: In situ monitoring of aquatic systems: Chemical analysis and speciation, Buffle, J. and Horvai, G. (Ed.), John Wiley & Sons, New York, 2000, 495-569.
- (4) Gimpel, J.; Zhang, H.; Hutchinson, W.; Davison, W. Effect of solution composition, flow and deployment time on the measurement of trace metals by the diffusive gradients in thin films technique. *Analytica Chimica Acta*, 2001, 448, 93-103.
- (5) Garmo, Ø. Laboratory study of the technique Diffusion Gradients in Thin films for determination of free ions and labile species in water. Cand. Scient. thesis, Norwegian University of Science and Technology, NTNU, Trondheim, Norway, 2001.
- (6) Levich, V.G. Physicochemical hydrodynamics. Prentice Hall Inc., Englewood Cliffs, New Jersey, 1962, 9-20, 57-60, 87-91.
- (7) Røyset, O. Norwegian Institute for water Research (NIVA), Oslo, Norway, unpublished results, 2002.
- (8) Bio-Rad; Chelex-100 Chelating ion exchange resin instruction manual. Bio-Rad Laboratories, California, USA, 1993.
- (9) Dahlquist, R.; Ingri, J.; Zhang, H.; Davison, W. Performance of the diffusive gradients in thin films technique for measuring Ca and Mg in freshwater. *Analytica Chimica Acta*, 2002, 460, 247-256.
- (10) Zhang, H. Aquatic Chemistry, Environmental Science, Lancaster University, UK, pers. comm., 2002.
- (11) Li, Y.; Gregory, S. Diffusion of ions in sea water and in deep-sea sediments. *Geochimica et Cosmochimica Acta*, 2002, 38, 703-714.
- (12) Zhang, H.; Davison, W.; Teasdale, P. Multi-element determination of metal species in natural water using DGT with ICP-MS detection. In preparation, 2002.
- (13) Alfaro-De la Torre, M.C.; Beaulieu, P.Y.; Tessier, A. In situ measurement of trace metals in lakewater using the dialysis and DGT techniques. *Analytica Chimica Acta*, 2000, 418, 53-68.
- (14) Røyset, O.; Frederichsen, O.; Gunther, J.G.; Lund, W.. Passive sampling of metal ions in Norwegian freshwater, Poster, Nordic Conference on Plasma Spectrochemistry, June 2-5, 2002, Loen, Norway.
- (15) Olofsson, R.; Dahlqvist, R.; Rodushkin, I.; Ingri, J. Sector field ICP-MS combined with the technique of DGT for measurement of labile species of 37 metals in natural waters. Poster, European Winter Conference on Plasma Spectrochemistry, Lillehammer, February 2. – 7., 2001, Norway.

- (16) Vandecasteele C.; Block, C.B. Modern methods for trace element determination, John Wiley & Sons, New York, USA, 1993.
- (17) Røyset, O. Norwegian Institute for water Research (NIVA), Oslo, Norway, unpublished results, 2002.
- (18) Røyset, O.; Rosseland, B.O.; Kroglund, F.; "DGTs predicts gill uptake of Al in salmonids" in Passive sampling of metal ions in water by DGTs, oral presentation, Nordic Conference on Plasma Spectrochemistry, June 2,-5., 2002, Loen, Norway.