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Simultaneous measurements of cations and anions using diffusive gradients in thin films with a ZrO-Chelex mixed binding layer

Yan Wang [a], Shiming Ding [a,*], Lei Shi [a], Mengdan Gong [a], Shiwei Xu [b], Chaosheng Zhang [c]

[a] State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China

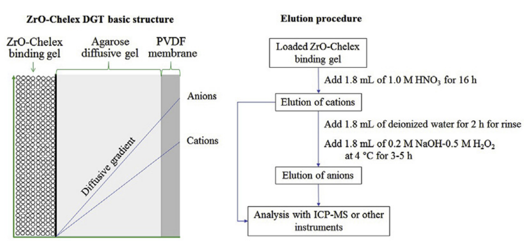
[b] Central Laboratory, Jiangsu Academy of Agricultural Science, Nanjing 210008, China

[c] International Network for Environment and Health, School of Geography and Archaeology, National University of Ireland, Galway, Ireland

HIGHLIGHTS

- Simultaneous measurements of 16 cations and anions were realized using ZrO-Chelex DGT.
- The cations and anions in the ZrO-Chelex gel were efficiently eluted using a two-step procedure.
- DGT uptake was independent of solution pH (5–9) and ionic strength (2–3 mM - 750 mM).
- ZrO-Chelex DGT had high capacities for measurements of cations and anions.
- DGT-measured concentrations agreed with freshwater and seawater measurements.

GRAPHICAL ABSTRACT



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ABSTRACT

A new method for the simultaneous measurements of eight cations [Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II)] and eight oxyanions [P(V), V(V), Cr(VI), As(III)/As(V), Se(VI), Mo(VI), Sb(V), and W(VI)] was established in this study using the diffusive gradients in thin films (DGT) technique with an improved ZrO-Chelex binding gel. The binding kinetics of each analyte in a mixed solution indicated a rapid uptake on the ZrO-Chelex gel. The anions exhibited slower absorption rates compared to the cations, which did not affect the DGT uptake. Stable elution efficiencies for these cations and anions were obtained based on a two-step extraction procedure using 1.0 M HNO_3 for elution of the cations followed by a mixed solution containing 0.2 M NaOH and 0.5 M H_2O_2 for elution of the anions. Simultaneous measurements of the cations and anions with the ZrO-Chelex DGT were validated in mixed solutions and found to be independent of solution pH (5–9) and ionic strength (2–3 mM to 750 mM). The capacities of the ZrO-Chelex DGT for single measurements of Fe(II), P(V), Cd(II), As(III), and As(V) were determined at 99.5, 127.6, 301.2, 33.3, and 87.4 μg cm^{-2}. Except for Se(VI) in seawater, accurate measurements of all of these cations and anions in natural freshwater and seawater were obtained using the ZrO-Chelex DGT. The performance of this technique for simultaneous measurements of 16 elements was also tested in sediments.

* Corresponding author.
E-mail address: smding@niglas.ac.cn (S. Ding).

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1. Introduction

Regardless of anthropogenic activities, cationic metals (Co, Ni, Cu, Zn, Cd, and Pb) and oxyanions (V, Cr, As, Se, Mo, Sb, and W) are normally detected at trace levels in natural environments [1,2]. With the development of industry, agriculture, and urbanization, increasing discharges of these heavy metal(loid)s into the environment have resulted in major environmental problems [3–5]. Heavy metal(loid)s have high toxicity, are non-degradable, and result in biological accumulation, all of which pose great risks to ecosystems and human beings [6–8]. In addition to heavy metal(loid)s, the enrichment of phosphorus (P) in natural waters and sediments is frequently a key factor affecting the trophic stage and algal bloom [9]. The redox cycling processes of Fe and Mn play a dominant role in controlling the speciation and mobility of P, As, and many other oxyanions in the environment [10,11]. All of these elements coexist in the environment and have a direct or indirect impact on one another in their biogeochemical behaviors. Accordingly, it is vitally important to be able to simultaneously measure these elements in a single assay for a better understanding of their potential couplings.

Diffusive gradients in thin films (DGT) is a dynamic passive sampling technique [12–14]. This technique is based on a diffusion flux through a well-characterized diffusion layer, in which the concentration of a solute (C_{DGT}) at the outside surface of the diffusion layer (i.e., at the surface of the DGT device) over a span of time can be quantified according to Fick's First Law [12]. In order to maintain a diffusion gradient capable of quantification, a binding phase is laid under the diffusion layer to act as a zero sink for absorbing the solute. Determination of a solute relies on the type of the binding phases employed [14]. Several binding gels have been developed to measure a range of cations and oxyanions. A binding gel impregnated with Chelex® 100 resin is a frequently used gel for measurements of cations, typically including Zn, Ni, Cu, Fe, Mn, and Cd [12–18]. Suspended particulate reagent-iminodiacetate (SPR-IDA) impregnated binding gel was developed for measurements of cationic metals on a submillimeter scale in combination with analysis by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [19]. Specific measurements of some cationic metals have been made using other binding agents (Table 1). On the other hand, the measurements of oxyanions with DGT have primarily been achieved using slurry ferrihydrite and precipitated ferrihydrite (abbreviated as SF and PF, respectively) as the binding agents for the uptake of P(V), V(V), As(V), Sb(V), and W(VI) [32,33], titanium dioxide powder (Metsorb®) for As(V), V(V), Sb(V), Mo(VI) and W(VI) [34], and zirconium oxide (Zr-oxide) for P(V), V(V), Cr(VI), As(III)/As(V), Se(VI), Mo(VI), Sb(V) and W(VI) [35]. Other binding agents have been used for selective measurement of oxyanions (Table 1).

With an increasing necessity for the simultaneous measurements of cations and anions, several DGT techniques have been developed by combining two different types of binding agents into one binding phase (Table 1). Mason et al. (2005) first developed a mixed binding gel (Chelex-ferrihydrite) using ferrihydrite slurry and Chelex® 100 as the binding agents for measurements of Cd, Cu, Mn, Mo, P, and Zn [38]. Huynh et al. (2012) extended the Chelex-ferrihydrite DGT to simultaneous measurements of As, Cd, Cu, Pb, and Zn [39]. Xu et al. (2012) developed a ZrO-Chelex mixed binding gel using Zr-oxide and Chelex® 100 as the binding agents for simultaneous measurements of Fe and P [40]. Kreuzeder et al. (2013) developed a HR-MBG mixed binding gel using zirconium hydroxide and SPR-IDA resins as the binding agents for high-resolution chemical imaging of As, P, Cd, Cu, Co, and Zn in combination with LA-ICP-MS [41]. Panther et al. (2014) developed a Chelex-Metsorb mixed binding gel using Chelex® 100 and Metsorb® as the binding agents for simultaneous measurements of trace metals and oxyanions [42]. To date, there are still a limited number of analytes (maximum a total of 12) capable of simultaneous measurement using these techniques. Additionally, the limitations of the ferrihydrite and Metsorb-based DGTs for measuring oxyanions in freshwater and seawater have been well reported, such as relatively low DGT capacity, inability in measurements of Mo(VI), long time required for elution of oxyanions from the Metsorb gel [35].

In this study, we extended the ZrO-Chelex DGT to simultaneous measurements of a total of 16 determinands including eight cations [Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II)] and eight oxyanions [P(V), V(V), Cr(VI), As(III)/As(V), Se(VI), Mo(VI), Sb(V), and W(VI)]. A series of validation experiments, including the binding kinetics of each element in mixed solutions and the tolerance of ionic strength and solution pH, were conducted to test the ZrO-Chelex DGT response under laboratory conditions. DGT capacities and field applications in natural freshwater, seawater, and sediment were also performed.

Table 1
Summary of the development of the binding layer used in DGT.

Analyte type	Binding layer (binding agent)	Analytes	Reference
Cations	Chelex® 100 resin	Zn, Ni, Cu, Fe, Mn and Cd	[12–18]
	Suspended particulate reagent-iminodiacetate (SPR-IDA)	Co, Ni, Cu, Zn, Cd and Pb	[19]
	Poly(acrylamide-*co*-acrylic acid) (PAM-PAA), Whatman P81, Poly (4-styrenesulfonate) (PSS), Polyvinyl alcohol (PVA), and sodium polyacrylate (PA)	Cu and Cd	[20–24]
	Saccharomyces cerevisiae, and thiol-polyvinyl alcohol (PVA-SH)	Cd	[25,26]
	Spheron-Thiol, Duolite GT73, and Iontosorb AV-MP resin	Hg	[27,28]
	Ammonium molybdophosphate (AMP), and copper ferrocyanide (CFCN)	Cs	[29,30]
	Spheron-Oxin® chelating ion-exchanger	U	[31]
Anions	Slurry ferrihydrite (SF), and precipitated ferrihydrite (PF)	P, V, As, Sb and W	[32,33]
	Titanium dioxide powder (Metsorb®)	As, V, Sb, Mo and W	[34]
	Zirconium oxide (Zr-oxide)	P, V, Cr, As, Se, Mo, Sb and W	[35]
	Mercapto-silica	As(III)	[36]
	N-methyl-*d*-glucamine (NMDG) functional resin	Cr	[37]
Cations and anions	Chelex-ferrihydrite (ferrihydrite slurry and Chelex® 100 resin)	Cd, Cu, Mn, Mo, P, Zn, As, Cd, Cu, Pb and Zn	[38,39]
	ZrO-Chelex (Zr-oxide and Chelex® 100 resin)	Fe and P	[40]
	HR-MBG (zirconium hydroxide and SPR-IDA resins)	As, P, Cd, Cu, Co and Zn	[41]
	Chelex-Metsorb (Chelex® 100 resin and Metsorb®)	Mn, Co, Ni, Cu, Cd, Pb, V, As, Mo, Sb, W and P	[42]