



Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Diffusion characteristics of agarose hydrogel used in diffusive gradients in thin films for measurements of cations and anions

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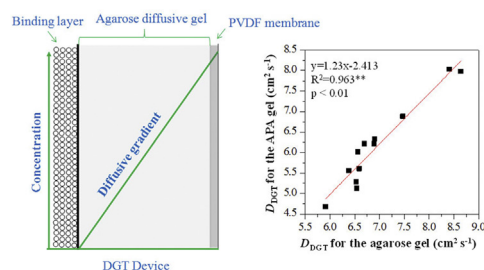
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HIGHLIGHTS

- Diffusion characteristics of agarose gel used in DGT was first investigated in depth.
- Thickness of the hydrated gel remained stable under a wide range of conditions.
- Inaccurate DGT measurements appeared at low ionic strengths due to electrostatic interactions.
- The agarose diffusion coefficients were on average 1.10 times of the reported APA values.
- The agarose gel can be used as one of the standard DGT diffusive layers.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 July 2016

Received in revised form

15 September 2016

Accepted 1 October 2016

Available online xxx

Keywords:

Agarose

Diffusion coefficient

Diffusive gel

Diffusive gradients in thin films

Cation

Anion

ABSTRACT

The agarose hydrogel has been increasingly used as a diffusive layer in diffusive gradients in thin films (DGT) measurements. However its diffusive characteristics have not been examined in detail. In this study, the performance of agarose gel was tested in DGT measurements of eight cations (Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Pb(II), and Cd(II)) and eight anions (P(V), As(V), Cr(VI), Mo(VI), Sb(V), Se(VI), V(V), and W(VI)). It was found that the thickness of agarose, a key parameter in the calculation of DGT measured concentration, remained unchanged after hydration followed by storage under the following conditions: pH 2–11, ionic strength 0–1.0 M, temperature 4–40 °C, and with the storage time extending to 300 d. Enrichment of cations and repelling of anions were observed in the gel under the ionic strengths of < 2–3 mM and < 1 mM (NaNO_3), respectively, which was attributed to the electrostatic interactions of these ions with the fixed negatively charged groups (mainly pyruvate) in the gel. The diffusion coefficients of cations and anions through the agarose gel (plus a PVDF filter membrane) were on average 1.10 ± 0.04 times of the reported diffusion coefficients through the agarose cross-linked polyacrylamide (APA) hydrogel, typically used in DGT technique. The working pH ranges for the agarose gel-assembled DGTs were 4–10 and 5–9 for anions and cations, respectively. The use of agarose gel, either individually or along with different filter membranes, affected the overall diffusion rates of cations and anions. The measured DGT concentrations of cations and anions in filtered natural freshwater and seawater were mostly in line with those measured directly. The results showed that the agarose gel

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can be used as one of the standard diffusive layers in DGT measurements for a wide range of inorganic and organic analytes.

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1. Introduction

Diffusive gradients in thin films (DGT), a passive sampling technique, was first developed by Davison and Zhang [1]. The technique was initially used as an *in situ* tool for speciation measurements of trace metals in natural waters [1,2]. DGT offered the advantage of a low detection limit over a relatively short period of time, due to its capability to preconcentrate metal ions in waters. Later on, the applications of this technique were extended to sediments, soils and sewage. The studies carried out included interpretation of the kinetics of exchange of solutes between solids and solutions [3], measurements of dissociation rate constants of complexes [4], labile and bioavailable concentrations and fluxes [5,6], speciation, bioavailability and toxicity [7–9], and chemical imaging of labile solutes at a high spatial resolution [10,11]. The analytes extended from usual inorganic metals and metalloids to sulfide [12], oxyanions [13,14], uranium [15], radium [16], technetium [17], mercury [8,18,19], nanoparticles [20,21], and organic pollutants [22–24].

DGT measurement relies on the diffusion of a chemical species through the gel layer at a measurable rate. It measures the free ions and labile complexes in solution that can dissociate in the time required to traverse the diffusive layer [25]. In soils and sediments, the measurement also incorporates the labile and mobile fractions, released from the solids during DGT deployment. The accumulated mass of the species in the binding gel (M) is related to its concentration in solution (C), according to the standard DGT equation [2]:

$$M = \frac{CA\Delta t}{\Delta g} \quad (1)$$

where, A is the exposed surface area of the DGT device, D is the diffusion coefficient of the analyte through the diffusive layer, t is the deployment time, and Δg is the thickness of the diffusive layer.

The parameters of D and Δg depend on the physicochemical properties of the diffusive gel. In order to carry out measurements accurately by DGT, D and Δg should be constant for the species of interest under various deployment conditions, permitting a wide range of ionic strengths (I) and pH values. The diffusive gel commonly used in the DGT is agarose cross-linked polyacrylamide (APA) hydrogel. This gel has an open pore size of $>5 \mu\text{m}$ and permits the diffusion of molecules with molecular weights $< 10^6$ [26]. This gel retains its stability in thickness in the pH range of 2–9 after a 3.2 times swelling due to hydration [26]. The diffusion coefficients through this gel have been reported for a number of cations and anions, but the values are inconsistent among different reports [2,25,27–30]. Additionally, inconsistent results were obtained in the case of DGT measurements of trace metals at ionic strength $< 1 \text{ mM}$ [31,32]. This was attributed to the interactions of trace metals with the APA hydrogel. These interactions were attributed to specific binding of metals to the sites and electrostatic interactions between metals and fixed charged groups in the gel [33]. The APA gel has specific binding sites with high affinities but low capacities for trace metals and their fulvic acid complexes [33]. Specific binding especially to Cu can significantly interfere with the measurement of DGT for short deployment times, by delaying the formation of a steady concentration gradient across the diffusive layer [34]. The APA gel also interacts electrostatically with metals, since it

possesses a positive charge even after exhaustive washing. This interaction can reduce the effective diffusion rate in DGT of metals at low ionic strength, by reducing the concentration at the gel-solution interface, due to formation of the Donnan potential [25,31]. The electrostatic interaction can be negligible when the ionic strength is greater than 1 mM due to the low charge density in the gel [35]. Moreover, APA gel cannot be used in DGT measurements of mercury [18,19,36,37], ammonium [38], antibiotics [22], and endocrine-disrupting chemicals [23] due to adsorption of these compounds by the functional groups in the gel.

Another type of hydrogel, agarose, is increasingly used as a diffusive gel in DGT measurements of mercury [18,19] and organic mercury [36,37], uranium [39], antibiotics [22], and bisphenols [23]. Agarose is a purified linear polysaccharide isolated from agar or agar-bearing marine algae. Structurally, it is a linear polymer consisting of alternating D-galactose and 3,6-anhydro-L-galactose units linked by α -(1 → 3) and β -(1 → 4) glycosidic bonds. Agarose gel possesses binding sites, which bear a resemblance to pyruvic and sulfonic functional groups with a maximum charge density of $-5.9 \times 10^3 \text{ C kg}^{-1}$ [40]. Weak specific binding of trace metals occurs through complexation with sulfonic functional groups [40,41]. The majority of binding sites in the gel are negatively charged pyruvate groups, which show attractive and repulsive interactions with cations and anions, respectively, due to the formation of the Donnan potential. The strength of these interactions decreases with increasing ionic strength [40,41]. Previous studies on DGT measurements reported different effects of ionic strength on the uptake of DGT using agarose gel as the diffusion layer. The lowest ionic strength capable of steady-state DGT flux was 0.1 mM for methylmercury [42], 1.0 mM for methylmercury and mercury [36], 1.0 mM for antibiotics [22], and 1.0 mM for bisphenols [23], and 5 mM for mercury [43].

In this study, the performance of agarose as a diffusive gel in DGT was tested in the measurements of cations and anions. Stability in terms of thickness and the reactivity of the gel to bind anions and cations were investigated. The diffusion coefficients for a total of eight anions and eight cations through the agarose gel were determined. The effects of ionic strength and solution pH together with the addition of different filter membranes on agarose-assembled DGT measurements were further examined, based on which optimal conditions for use of agarose gel in DGT were obtained. The use of the agarose gel-assembled DGT was finally validated through measurements in natural seawater and freshwater.

2. Experimental

2.1. Reagents, materials, and solutions

MilliQ water was obtained by purification using Millipore (resistivity of $> 18 \text{ M}\Omega \text{ cm}$). Acrylamide (ultrapure grade), N, N' -methylene bisacrylamide (ultrapure grade), Ammonium persulfate (ACS grade), N, N, N', N' -tetramethylethylenediamine (TEMED, ACS grade) were purchased from AMRESCO. Durapore® PVDF membrane (0.45 μm pore size, 100 μm thickness) was supplied by Millipore. Cellulose nitrate membrane (CN, 0.45 μm pore size, 130 μm thickness) was purchased from Whatman. Hydrophilic polyethersulfone membrane (PES, 0.45 μm pore size, 140 μm thickness, Supor 450)

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