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Application of diffusive gradient in thin films technique (DGT) to measurement of mercury in aquatic systems

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Abstract

The diffusive gradient in thin films (DGT) technique was investigated and used to measure mercury concentration in river water. Mercury ions are covalently bound to amide nitrogen groups of commonly used polyacrylamide, which makes this gel unsuitable as a diffusive medium. In contrast, agarose gel was found as the diffusive gel for mercury measurements. Basic performance tests of agarose DGT verified the applicability of Fick's first law for DGT measurements. Two selective resins, Chelex-100 with iminodiacetic groups and Spheron-Thiol with thiol groups were used. The measured diffusion coefficient in agarose gel was close to that in water. The concentration of mercury in Svitava river measured by DGT with Speron-Thiol resin gel was higher ($0.0116 \pm 0.0009\ \mu g\ l^{-1}$) than those obtained by Chelex-100 ($0.0042 \pm 0.0005\ \mu g\ l^{-1}$). Different capture efficiencies of two adsorbents enable to estimate fractions of mercury bonded in different complexes in the river water. The concentrations of mercury found by DGT both Chelex-100 and Speron-Thiol resin gels are much lower than that measured directly in the river water ($0.088 \pm 0.012\ \mu g\ l^{-1}$). This difference indicates that DGT concerns inorganic ions and labile species only, and that it is not able to include inert organic species and colloids.

Keywords: Mercury; Diffusive gradients in thin films technique (DGT); Agarose diffusive gel

1. Introduction

This paper follows previous work [1] dedicated to diffusive equilibrium in thin films technique (DET), using hydrogels for sampling solute species in aquatic systems. Use of DET, and especially the DGT technique for the pollution monitoring and other environmental studies is increasing. In the present paper, we introduce the possibility to follow mercury transfers in aquatic systems using DGT and appropriate mercury measurement techniques.

The diffusive gradient in thin films technique, recently developed by Davison and Zhang [2] for in situ determination of kinetically labile metal species in aquatic systems has been successfully used as a means to follow the concentration of trace metals in natural waters [3–6], metal fluxes in sediments [7,8] and soils [9–11] and also to estimate the concentration of metals in pore waters [12,13]. The DGT technique employs two layers of hydrogel: a diffusive layer and a binding phase. Diffusive layer is placed in the DGT unit on the top of the binding phase and covered with a membrane (usually 0.45 μm). These three layers are sealed in the DGT unit so that only the diffusive layer covered with membrane is exposed to the solution to be analyzed [14]. Dissolved metal species, which are smaller than membrane pore size, diffuse through a hydrated polyacrylamide gel (the diffusion gel layer), of thickness Δg and area A and are accumulated by an analyte-selective adsorbent in binding phase. The use of synthetic ferrihydrite for phosphates [15], AG 50W-X cation-exchange resin for radioactive Cs and Sr [16] and silver iodide for sulfide [17] embedded in the binding phase are described. Most frequently, an iminodiacetate chelating resin, Chelex-100, is used and has been applied to a large number of divalent and trivalent metal ions [18], including heavy metals and other elements of environmental interest. After exposure of the DGT

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unit for a time t in a solution, the amount of metal ions absorbed by the resin is analyzed and the mass M of captured metals determined. The amount of metal accumulated within the binding phase under these conditions is assumed to be equivalent to the amount of metal ion passing through the diffusive layer. The time-average concentration of metal in the bulk solution, c_{DGT} can be calculated with the help of Fick's first law of diffusion as:

$$c_{\mathrm{DGT}} = \frac{M\Delta g}{tAD} \tag{1}$$

where D is the diffusion coefficient of the metal in the gel, the exposure surface area A and Δg the thickness of the gel layer. Eq. (1) is valid only if the free metal ions are in rapid equilibrium with the resin, with a large binding constant and $c_{\mathrm{binding\,phase}}$ is effectively zero providing the resin is not saturated.

The DGT technique gives useful information about a wide range of metal species but not for mercury. Mercury binding on the amide groups within polyacrylamide gel [19] rather than free diffusion does not allow use of this diffusive gel and this technique for mercury determination.

In this work, an agarose diffusive gel having different structure from polyacrylamide gel has been tested. Results obtained with agarose diffusive gel were compared with those obtained for polyacrylamide diffusive gel. In addition to testing diffusive gels, two different resins Chelex-100 and Spheron-Thiol with –SH groups prepared by Smrž and Hradil [20] and intensively studied by Dočekal and Slovák [21], were used for the mercury DGT measurement.

2. Experimental

2.1. Apparatus

DGT Research Ltd. (UK, www.dgtresearch.com) supplied DGT deployment units. Mercury in resin gels was measured using one-purpose atomic absorption spectrometer Advanced Mercury Analyser, model AMA 254 (Altec, Czech Republic) based on combustion of the sample in oxygen atmosphere and amalgamation preconcentration (www.leco.com/organic).

2.2. Reagents and materials

All the reagents were of analytical-reagent grade. For dilutions, high-purity demineralized water provided by a Milli-Q Plus filter apparatus (Millipore, USA) was used. Mercury test solutions and mercury standards were prepared from 1 g l^{-1} stock standard solution (Analytica Ltd., Czech Republic). The pH of the test solution was adjusted to 5 by addition of 0.1 mol l^{-1} NaOH (Onex, Czech Republic). A 0.1 mol l^{-1} $NaNO_3$ (Lachema, Czech Republic) medium was used in all experiments. The polyacrylamide resin gel and diffusive gel were prepared using acrylamide (Sigma-Aldrich, Germany), ammonium persulfate (Sigma-Aldrich, Germany), tetramethylethylenediamine (Sigma-Aldrich, Germany) and DGT cross-linker (DGT Research Ltd., UK). Chelex-100, Na form, 100–200 wet mesh (Bio-Rad Laboratories) and Spheron-Thiol (Lachema) resins were used. For the agarose diffusive gel preparation, a 1.5% solution of agarose (Prolabo, France) was used. To protect the outer surface of the diffusive gels, a 0.45 μm pore size membrane (Pall Corporation, USA) was placed between the diffusive gel and the plastic cap. The thickness of hydrated gels was measured using a dial micrometer.

2.3. Procedures

2.3.1. Gels preparation

2.3.1.1. Polyacrylamide gels. Preparation of resin-embedded and ion-permeable diffusive gels followed the procedure used by Zhang and Davison [14]. Firstly, the pre-gel solution was prepared by mixing aqueous solutions of 15% acrylamide and 0.3% patented agarose-derived cross-linker (DGT Research Ltd., UK). Polymerization was initiated by adding 7 μl of freshly prepared ammonium persulfate and 2.5 μl of tetramethylethylenediamine (TEMED) per millilitre of a pre-gel solution. The resulting gel solution was cast between two glass plates separated by plastic spacers and the assemblage was maintained at about 40 °C for 45 min. After removal, the gels were hydrated in demineralized water for at least 24 h to allow them to expand to a stable thickness. The thickness of hydrated gels was 0.82 ± 0.02 mm. The discs were cut using a plastic knife and stored in 0.01 mol l^{-1} $NaNO_3$.

Resin gels were prepared from a pre-gel solution of the same composition. A 0.2 g wet weight of Chelex-100 or 0.12 g wet weight of Speron-Thiol resins were added per millilitre of the pre-gel solution. The polymerization rate was decreased by adding only 6 μl of ammonium persulfate and 2 μl of TEMED per millilitre of the pre-gel solution to allow settling of the resin on one side of the gel. After hydration, the discs were cut and stored in a small volume of demineralized water. The thickness of hydrated gels was 0.43 ± 0.02 mm.

2.3.1.2. Agarose gels. A diffusive gel containing 1.5% agarose was prepared by dissolving the agarose in an appropriate volume of 80 °C warm demineralized water. The mixture was placed in a boiling water bath and gently stirred until all the agarose was dissolved and the solution became transparent. The hot gel solution was immediately pipetted between two preheated glass plates separated by plastic spacers of appropriate thickness and left to cool down to its gelling temperature (36 °C or below). The discs of agarose diffusive gels were stored in demineralized water. Their thickness was varied between 0.50 and 1.22 mm.

2.4. DGT assembly

Gels were placed on the top of the piston. The resin gel was covered by diffusive gel and by a 0.45 μm pore size cellulose nitrate membrane filter. The front cap was pressed tightly.

2.5. Diffusive gel testing

Both agarose and polyacrylamide diffusive gels were tested in a mercury solution to established if mercury was binding to the gels. The mercury test solution containing 100 μg l^{-1} of mercury in 0.01 mol l^{-1} $NaNO_3$ was stirred for 24 h to equilibrate. The DGT units, filled only with agarose and polyacrylamide diffusive gels and covered by a 0.45 μm pore size cellulose nitrate membrane filter were immersed into the equilibrated mercury solution, which was stirred using a magnetic follower. For this experiment, a 0.8 mm thick polyacrylamide diffusive gel and 0.5 mm agarose gel were used. Mercury was determined in the solution before DGT deployment and periodically during an experiment carried over 24 h. Two pistons, each filled with different diffusive gels, were removed for analysis at each testing time. The content of mercury in these gels was measured directly with the use of the AMA-254 spectrometer. When the amount of mercury in disc was more elevated than the available measurement range, the gel disc was cut for smaller pieces, and these were re-measured individually.

2.6. Basic DGT performance tests

In order to test the validity of DGT measurement for mercury analysis, the recommended tests [14] were carried out using a 100 μg l^{-1}mercury solution in 0.01 mol l^{-1} $NaNO_3$.

2.6.1. Time-dependence experiments

The DGT units were filled with resin and diffusive gels covered by membrane filter. Chelex-100 and Spheron-Thiol resin gels were combined with agarose and polyacrylamide diffusive gels and covered with membrane filters. The assembly was floated in a stirred solution for different time periods, up to 8 h. During the experiment, the concentration of mercury in the test solution was controlled. At each sampling time, three of each type of DGT units were taken from the solution, resin gels were extracted and the amount of mercury measured. Resin gel discs presenting high amount of mercury were divided into smaller pieces for measurement. The total amount of mercury in each disc was then calculated as a sum of mercury masses in all these pieces.

2.6.2. Diffusion layer thickness experiments

The other recommended test confirming the validity of the Fick's first law is the linear dependence of accumulated mass of metal in the resin on the reciprocal thickness of the diffusive gel. Agarose diffusive gels of three thicknesses (0.50, 0.72 and 1.22 mm) were used for this experiment. The DGT units with different thicknesses of diffusive gel and Chelex-100 and Spheron-Thiol resin gels were exposed for 4h to a stirred model of 100 μg l^{-1} Hg solution in 0.01 mol l^{-1} $NaNO_3$. During the experiment, the concentration of mercury in the test solution was controlled. After 4 h of exposure, DGT units were taken from the solution, resin gels were extracted and the amount of mercury measured. Resin gel discs with high amounts of mercury were divided into smaller pieces for measurements. The total amount of mercury in each disc was than calculated as a sum of the masses in all these pieces.

2.7. Field applications

DGT units were deployed in situ in the stream of Svitava river in the Husovice part of Brno. Ten DGT units, five with Chelex-100 resin and five with Spheron-Thiol and agarose diffusive gel were anchored to a nylon string. The units were suspended for 10 days in the middle of the river 0.5 m above the bottom and 0.5 m under the surface. During this time, a 1 l water sample was collected. To avoid any adsorption phenomena, this sample was stabilized by addition of potassium dichromate, nitric acid and hydrochloric acid [22]. The DGT units were rinsed with distilled water after retrieval from the river and kept in clean polyethylene bags for the transport to laboratory.

3. Results and discussion

3.1. Stability of the mercury solution

The significant adsorption of mercury on surfaces of all types of containers is a well-known phenomenon [23]. For this reason, the stability of mercury solution was checked before DGT deployment. Five litres of 100 μg l^{-1} mercury in 0.01 mol l^{-1} $NaNO_3$ was placed in an HDPE container and stirred using a magnetic follower. The concentration of mercury in this solution was periodically checked. Due to the adsorption of mercury on the bottle walls, a 10% decrease of its concentration was observed during the first hour of stirring. After saturation of the walls, this concentration remained constant for 24 h. Subsequent immersion of DGT units lowered the mercury concentration further by 50% of its adsorption on the plastic DGT units. The actual concentration of mercury was measured during experiments and was taken into consideration for the calculation of DGT mercury concentration. This decrease of mercury concentration caused by adsorption on DGT units is significant because of the small volume of model solution relative to surface area of DGT units. It is assumed that this effect does not occur in environmental systems measured in situ.

3.2. Tests of gel-diffusion equilibration times

The equilibration time for the agarose gel (thickness of 0.50 ± 0.02 mm) was measured directly by immersing it in a stirred solution of 100 μg l^{-1} Hg in 0.01 mol l^{-1} $NaNO_3$ at 22.5 °C. The amount of mercury in the gel increased with the exposure time, reaching a plateau within 8 h (Fig. 1). The concentration of mercury found in equilibrated agarose gel

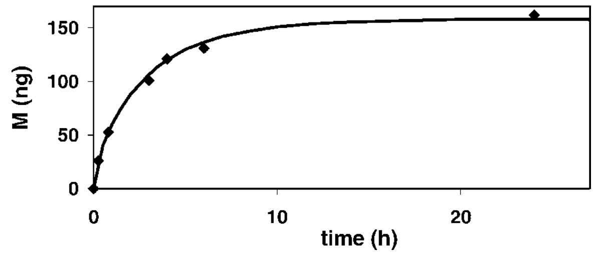

Fig. 1. Mass of mercury in agarose gel discs exposed for various periods to a test solution of 100 μg l^{-1} Hg in 0.01 mol l^{-1} NaNO$_3$.

was 450 μg l^{-1}, which is 4.5 times higher than in solution. We assume that there are some impurities in the agarose, associated with specific binding groups. After their saturation, no more mercury is collected in agarose gel. The amount of bound mercury is not large and does not affect the use of DGT units with agarose diffusive gel for mercury measurement. The amount of mercury in the polyacrylamide gel increased more dramatically with time exposure. An average of 17 μg of mercury per polyacrylamide gel discs was found. It corresponds to concentration of mercury 70 mg l^{-1}in the polyacrylamide gel. The reactivity of the amide groups towards Hg(II) is known for more than 100 years: the Hg(II) ion appears to become covalently bound to one or two amide nitrogen atoms. Special dried polyacrylamide resin has been prepared for Hg removal and recovery [19]. When polyacrylamide diffusive gel is used in DGT units, it is not possible to interpret results because there is a competition for mercury ions between two resins, Chelex-100 and polyacrylamide.

3.3. Basic DGT performance tests

Two experiments were performed to verify the applicability of Eq. (1) for DGT measurements of mercury with the systems described. The first experiment concerned the time dependence. DGT units with known agarose gel thickness were exposed for 8h to a 100 μg l^{-1} Hg stirred solution. The mass of accumulated mercury (M) normalized for mercury concentration in solution (c) was plotted against the exposure time (see Fig. 2). The two curves are linear for both Chelex-100 and Speron-Thiol sorbents and have similar slopes. Slopes obtained during the same experiment with DGT unit with polyacrylamide diffusive gel are much lower (Fig. 3) and differ for Chelex-100 and Speron-Thiol. Mercury is accumulated in the polyacrylamide gel and a competitive reaction takes place between two binding agents: the diffusive polyacrylamide gel and resin in resin gel. Spheron-Thiol resin has higher binding strength, so it can better compete with the adsorption of mercury in polyacrylamide gel structure. These competitive reactions do not allow interpretation of experimental data.

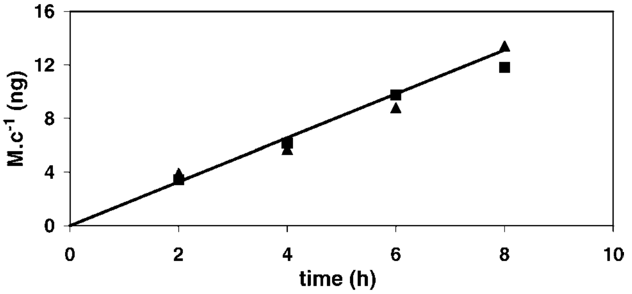

Fig. 2. Measured mass of mercury in the resin layers immersed in Hg solution (100 μg l^{-1}) for various periods. The agarose diffusive gel was used and two different resins in resin layers tested: Chelex-100 (■) and Spheron-Thiol (▲). Eq. (1) predicts the solid line.

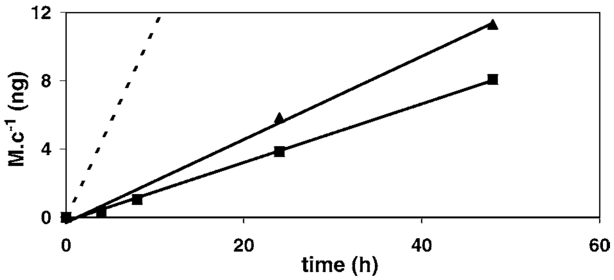

Fig. 3. Measured mass of mercury in the resin layers immersed in Hg solution (100 μg l^{-1}) for various periods. The polyacraylamide diffusive gel was used and two different resins in resin layers tested: Chelex-100 (■) and Spheron-Thiol (▲). Eq. (1) predicts the dotted line.

The diffusion coefficients were calculated from plots furnished by the time experiment. Slope k of the dependance $Mc^{-1} = f(t)$ can be expressed by Fick's first law as:

$$k = (DAt)\Delta g^{-1} \tag{2}$$

From this equation, the diffusion coefficient can be calculated:

$$D_{\text{cal}} = \frac{k\Delta g}{At} \tag{3}$$

The calculated diffusion coefficient D_{cal} of mercury in agarose gel is (8.86 ± 0.11) × 10^{-6} cm^2 s^{-1} for Chelex-100 and (9.08 ± 0.13) × 10^{-6} cm^2 s^{-1} for Spheron-Thiol. The value in water is 9.13 × 10^{-6} cm^2 s^{-1} [24].

The second recommended test experiment with DGT was also performed. The DGT units filled with agarose gels of different thickness were exposed for 4 h to a stirred solution of 100 μg l^{-1} mercury in 0.01 mol l^{-1} NaNO$_3$. The plot of the measured mass against the reciprocal gel thickness is linear (see Fig. 4). The mass in the figures is expressed as Mc^{-1},

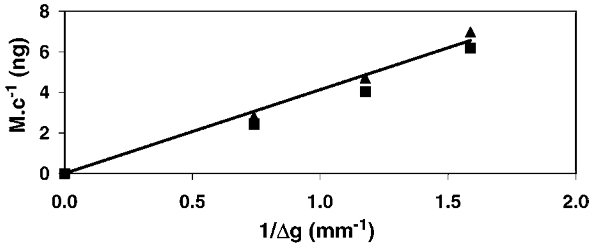

Fig. 4. Measured mass of mercury in the resin layers, (■) Chelex-100, (▲) Spheron-Thiol) immersed in Hg solution (100 μg l^{-1}) for different thicknesses of agarose gel layer. Eq. (1) predicts the solid line.

because of variable Hg concentrations in solution during experiments.

Results of both testing experiments with agarose diffusive gel confirm the validity of basic DGT principles. The DGT with agarose diffusive gel is thus possible to use for reliable mercury measurements.

3.4. Field study

In March 2004, the DGT technique was used to measure in situ mercury concentration in the Svitava river in the Husovice part of Brno, Czech Republic. Both Chelex-100 and Spheron-Thiol resin embedded in polyacrylamide gel were used, covered by agarose diffusive gel with 0.5 mm thickness. Because of the low concentration of mercury in water, the preconcentration mode proposed by the AMA-254 spectrometer was used for direct measurement of mercury in the water sample. The value of direct measurement (0.088 ± 0.012) $\mu g\, l^{-1}$ Hg was higher than the DGT measured concentrations, (0.0042 ± 0.0005) $\mu g\, l^{-1}$ for Chelex-100 resin gel and (0.0116 ± 0.0009) $\mu g\, l^{-1}$or Spheron-Thiol. The differences between direct measurement and DGT measurement may be explained by the fact that DGT measures only ionic mercury and labile mercury species and does not include inert organic species and large colloids. Chelex-100 with iminodiacetic groups enable to assess ionic mercury, and mercury related to week complexes. Spheron-Thiol has a greater affinity for mercury than Chelex-100. Thiol groups of Spheron-Thiol are capable to react with mercury bonded even in very strong complexes. Consequently, the concentration measured by Spheron-Thiol DGT unit has to be higher than those given with Chelex-100. The DGT units filled with resins having different capture efficiencies to mercury could be used to distinguish between mercury complexes with different stability and fractionate various mercury species in the sample.

4. Conclusion

DGT commonly used polyacrylamide gel is unsuitable as diffusive medium for the mercury determination. During diffusion to the resin embedded in the resin layer, mercury ions are covalently bound to amide groups of polyacrylamide diffusive gel. Competitive reactions between two adsorption agents do not allow interpretation of experimental data. On the other hand, agarose gel was found to be suitable as the diffusive gel for mercury measurements. Performing of the both recommended DGT tests has confirmed the usefulness of DGT principles. The diffusion coefficient of mercury in agarose gel calculated on the base of Fick's law was found very similar ($8.97 \times 10^{-6}\,cm^2\,s^{-1}$) to that in water ($9.13 \times 10^{-6}\,cm^2\,s^{-1}$) for both Chelex-100 and Spheron-Thiol resins, in mercury solution. Concentration of mercury in the river water measured by DGT with Speron-Thiol resin layer (0.0116 ± 0.0009) $\mu g\, l^{-1}$ was three times higher than that measured by Chelex-100 (0.0042 ± 0.0005) $\mu g\, l^{-1}$. This can be explained by the higher affinity of thiol groups to Hg(II) bound in non-labile complexes. In a real water sample, there are not only cations and small inorganic complexes of mercury, but also complexes with natural ligands as fulvic acids and humic acids. The DGT with Speron-Thiol resin measures even those species of mercury, which are more stable and are not measured by Chelex-100.

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