Talanta 120 (2014) 470–474

Contents lists available at ScienceDirect

Talanta

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

A novel method for the determination of dissolved methylmercury concentrations using diffusive gradients in thin films technique

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ARTICLE INFO

Article history:
Received 5 September 2013
Received in revised form
4 December 2013
Accepted 10 December 2013
Available online 25 December 2013

Keywords:
DGT
Agarose gel
3-Mercaptoproply functionalised silica resin gel
Acid extraction

ABSTRACT

A novel DGT probe and analysis protocol were developed for the determination of MeHg concentrations in aquatic system. The DGT probe consisted of an agarose (AG) gel as the diffusive hydrogel and a 3-mercaptoproply functionalised silica resin gel as the resin gel. The polyacrylamide (PA) hydrogel which is commonly used in DGT probes to assess trace metal concentrations in aquatic system appeared to be unsuitable for the determination of MeHg. The affinity of the PA hydrogel for MeHg is very high reducing its accumulation by the resin. In contrast, the AG hydrogel presents a by far lower affinity towards MeHg, which makes it suitable as diffusive layer in a DGT probe for MeHg determinations. Two extraction procedures to liberate MeHg from the resin were studied: one is involving thiourea as complexing agent, the other a simple acidic extraction. The extraction step was followed by an ethylation reaction of the liberated MeHg to determine low concentrations of MeHg species by Headspace-Gas Chromatography-Atomic Fluorescence (HS-GC-AFS). With the thiourea extraction method the recovery of the adsorbed MeHg compounds was extremely low while the recovery with the acid extraction method was 100%.

The reliability of the novel DGT probe and analysis protocol was studied. A linear dependency between the amount of MeHg accumulated on the resin gel and both the deployment time and the gel thickness were demonstrated. From those experiments a diffusion coefficient of MeHg in AG gel was determined: $5.1 \pm 0.20 \times 10^{-6}$ cm^2 s^{-1}. Additional experiments showed that the new DGT method can be used in most natural waters independent of the ionic strength and within a pH range of 3–8.

1. Introduction

Mercury is known as one of the most toxic trace metals in the environment. It is present in many chemical forms, but the most common ones are elemental mercury (Hg^0), inorganic (IHg or Hg^{2+}) and monomethylmercury (CH_3Hg^+, referred to as MeHg throughout this paper). Humans are exposed to Hg^0 mainly by inhalation and to IHg and MeHg mainly by ingestion of food. IHg and especially MeHg concentrations are usually very low in the environment, for example typical dissolved IHg and MeHg concentrations in the Belgian coastal zone are around 30 and 250 pg L^{-1}, respectively [1].

The determination of dissolved MeHg concentrations in the water column of rivers, estuaries or seas involves an ultra-clean sampling procedure followed by a preconcentration step, the separation of MeHg from other Hg species (mostly by GC) and atomic fluorescence spectrometry (AFS) or inductively coupled mass spectrometry (ICPMS) as detection step [2,3]. In the case of sediments, pore water has to be separated from the mineralogical part, generally by slicing the sediments and consequent centrifugation. The available volume of liquid is generally not large enough, even after a preconcentration step, for the determination of MeHg. The sampling and preconcentration procedures for the determination of dissolved MeHg either in the water column or in pore water are often the most crucial steps in the whole analysis chain. In that context, the Diffusive Gradients in Thin Films (DGT) technique has proven to be an excellent alternative since sampling and preconcentration steps are performed simultaneously, in situ and without any human intervention reducing strongly the range of uncertainty [4].

Several research groups have yet used the DGT technique to assess total mercury concentrations in natural waters and sediments [5–7]. The principle of this technique involves three key conditions: (1) the diffusive gel used in the technique should not bind with the interested solute(s); (2) the resin gel should be functional binding with the interested solute(s); (3) the elution procedure should be efficient and compatible with further steps of the analysis procedure such as the ethylation of the extracted MeHg ions.

The diffusive gels that are reported in the literature for the analysis of trace metals are agarose (AG) and polyacrylamide (PA). Earlier studies reported that PA binds mercury, possibly with its

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0039-9140/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2013.12.023

amide groups, causing it to compete with the resin gel instead of just providing a diffusive gradient, and making it impossible to get reliable results [5]. Therefore, DGT Probes including an AG diffusive gel have been proposed for the determination of total mercury [5–7]. Regarding the determination of MeHg ions in the water column and sediments, Clarisse and Hintelmann [8,9] used a DGT probe with a PA hydrogel. However, they did not take into account the possible affinity of MeHg for that hydrogel.

Common resin gels included in the DGT to bind IHg and MeHg ions are all sulfhydryl (for example 3-mercaptopropyl) functionalized silica gels. For the release of IHg species from solid materials such as sediments, hair, resins etc., several extraction solutions have been used: an acidic solution [2], a basic solution [2] and a thiourea solution [7]. For the release of MeHg ions from the resin only a thiourea solution was reported [8,9].

In this study, the binding affinity of AG and PA hydrogels towards MeHg was tested. In addition, a protocol to extract efficiently MeHg from the resin gels and to allow afterwards ethylation of the extracted MeHg ions was developed. Next, the diffusion coefficient of MeHg in the AG hydrogel was assessed as well as the influence of pH and ionic strength variability on the DGT efficiency regarding MeHg accumulation.

2. Method and materials

2.1. DGT assembly

2.1.1. Reagents and materials

Acrylamide solution (40%, pa, Merck), agarose (certified molecular biology grade, bio-rad), ammonium peroxydisulfate (APS, >98%, Merck), DGT gel crosslinker (DGT research Ltd), 3-mercaptopropyl functionalized silica gel (200–400 mesh, Aldrich), MilliQ water (Millipore, >18 MΩ cm), tetramethylethylenediamine (TEMED, >99%, Merck), sodium nitrate (suprapur, Merck). DGT pistons (DGT research Ltd).

2.1.2. Diffusive and resin gel preparation

Polyacrylamide (PA), agarose (AG) and resin gels were prepared similar to the methods reported by Gao et al. [7,10]. Briefly, for the resin gel preparation 2.5 g of 3-mercaptopropyl functionalized silica resin was added to 10 mL gel solution (15% acrylamide, 0.3% DGT cross-linker) and this solution was mixed well. Then 50 μL 10% ammoniumpersulfate solution and 15 μL *N,N,N,N*-tetraethylenediamine (TEMED) were added. The solution was mixed and cast between two glass plates with a spacer separating the plates. The glass assembly was placed in an oven at 45 °C for 1 h, and afterwards the resin gel was peeled off and hydrated in MilliQ water for at least one day until use.

2.1.3. Assembling DGT units for solution deployment

Resin gels were cut into 2.5 cm circles with a plexi-glass gel cutter. The resin gel was mounted on the DGT piston base with the resin side face up. Then the diffusive gel was placed on top of the resin gel and covered by a Millipore Durapore membrane filter (HVLP). The cap was then placed on the piston and pressed down to the bottom of the base.

2.1.4. MeHg accumulation test on diffusive gels

Twelve PA gel discs and 12 AG gel discs were separately deployed in 24 vessels with 15 mL of 40 ng L^{-1} MeHg solution. In addition, 8 control vessels containing 15 mL of 40 ng L^{-1} MeHg solution were also prepared. All those vessels were continuously shaken. After 4, 8, 24 and 48 h, 3 PA discs and 3 AG discs were each time retrieved from their deployment solution. From those 6 vessels 10 mL solution were sampled as well as from two control vessels. MeHg concentrations were assessed in all those solutions.

2.1.5. DGT performance test experiment

Performance tests of the DGT assembly were carried out in a 2 L MeHg solution of 50 μg L^{-1} containing 0.03 M $NaNO_3$. During the experiment, the MeHg concentration in the solution was monitored and used for comparison with the DGT derived MeHg concentration. The pH of the solution was around 5. Eight DGT pistons were plugged into the holes of a square housing rack. After 2, 4, 8 and 24 h, 2 of the DGT pistons were removed from the solution, the resin gel was transferred to a 20 mL FEP bottle and MeHg was extracted.

An additional experiment was carried out to study the effect of the diffusion layer thickness on the MeHg accumulation by the resin gel. DGT pistons with AG gel thicknesses from 0.04 to 0.12 cm were prepared in duplicate and deployed in a 50 μg L^{-1} MeHg solution containing 0.03 M $NaNO_3$ for 2 h. The resin gel was then treated in the same way as mentioned above.

2.1.6. pH and Ionic strength test experiments

The DGT pistons were exposed to MeHg solutions (50 μg L^{-1}) at different pH values (2 to 12) for 24 h. The pH value was adjusted using diluted HCl and NaOH. The effect of ionic strength was studied by adjusting the ionic strength of a MeHg solution (50 μg L^{-1}) with $NaNO_3$ in the range of 100 nM to 1 M. The MeHg concentration measured by DGT (C_{dgt}) was compared with that of the deployment solution (C_s).

2.2. MeHg determination

2.2.1. Reagents and standards

Acetic acid (100%, Merck), copper sulphate ($CuSO_4.5H_2O$, Merck, pa), dichloromethane (CH_2Cl_2, >99.8%, Suprasolv), hydrochloric acid (suprapur, Merck), MeHg stock solution (1000 mg L^{-1}, Chemlabpotassium Bromide (Merck, pa), potassium hydroxide (KOH pellets, Vel), sodium acetate (Merck, pa), sodium tetraethylborate ($NaBEt_4$, min 98%, Strem Chemicals), sulphuric acid (95–97%, Merck, pa), tetramethylammonium hydroxide (25% in methanol, Acros organics).

A $CuSO_4$ solution (1 M), an 18% (w/v) KBr solution and a 5% (v/v) H_2SO_4 solution were prepared from the purchased reagents in Milli-Q water. A 100 ppm MMHg stock solution is prepared from a 1000 ppm MeHg stock solution (1000 ppm, Alfa) in Milli-Q water and stored in a brown glass bottle at 4 °C. Working standard solutions of 5, 10, 20, 40 ng L^{-1} are prepared daily. One gram of sodium tetraethylborate ($NaBEt_4$, Strem Chemicals) is dissolved in a 100 mL, 2% KOH solution, which was cooled for 2 h in the deep freezer. This 1% $NaBEt_4$ solution is further diluted ten times and these solutions are stored in 20 mL FEP bottles in the deep freezer. The 0.1% $NaBEt_4$ deep frozen reagent is stable for several weeks, but once in use its lifetime is limited to one day. Acetate buffer solution is prepared in a FEP bottle by dissolving 272 g of sodium acetate and 118 mL of glacial acetic acid in 1 L Milli-Q water.

2.2.2. Extraction of MeHg from the resin gels

Twenty 3- mercaptopropyl functionalized silica resin gels were deployed separately in 10 mL of 40 ng L^{-1} MeHg solution for 48 h. Afterwards two extraction methods were applied: (1) 10 resin gels were extracted by the protocol reported by Clarisse and Hintelmann [8]. Two mL of thiourea solution (a concentration range of 0.5 to 50 mM was used) at pH 1 (0.1 M HCl) were added to each resin gel and the solution was shaken for 24 h; (2) the other 10 resin gels were extracted by a protocol that is similar to the one reported by Gao et al. [11]. Five mL of a 5% H_2SO_4 and 18% KBr mixture and 1 mL $CuSO_4$ (1 M) were added to each resin gel in a 20 mL FEP bottle and