

Characterization of sorption gels used for determination of mercury in aquatic environment by diffusive gradients in thin films technique

Research Article

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Received 16 April 2010; Accepted 8 June 2010

Abstract: The influence of pH, ionic strength and selected natural ligands on the measurement of mercury by the diffusive gradients in thin films technique (DGT) using recently introduced sorption gels was determined. Sorption gels containing Chelex 100, Spheron-Thiol, Duolite GT73 and modified Iontosorb AV resins were investigated, with the sorption capacity determined for all used sorption gels. The minimum DGT measurable concentrations were calculated from 3 times the standard deviation of mercury amount in unexposed sorption gels.

Keywords: Diffusive gradients in thin films technique • Mercury • Sorption gels • pH • Ionic strength

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1. Introduction

During the last 10 years, diffusive gradients in thin films technique (DGT) [1] was developed for determination of all common metals, some alkali metals and selected lanthanides and actinides in surface water [2,3]. In addition to that, some anions like sulphides or phosphates can be determined using DGT technique [2]. The DGT technique is based on a simple device consisting of two thin hydrogel layers protected from outside solution by filter membrane [2]. Dissolved species from aquatic system diffuse through diffusive gel and are immobilized in a layer of sorption gel containing selective resin. If the resin is not saturated, the concentration of dissolved species on the sorption gel surface is zero. This effect leads to formation of concentration gradient between the sorption gel and the outside solution, which provides the motivation for other solutes to diffuse through the diffusion gel. If Fick's first law of diffusion is applied, concentration of dissolved, kinetically labile metal species can be calculated from the accumulated mass of metal species in the sorption gel using basic DGT equation:

$$c_{\text{DGT}} = m \cdot r / A \cdot t \cdot D \quad (1)$$

where m is accumulated mass of metal species in sorption gel, r is diffusive layer thickness, A is area of exposed gel, t is deployment time and D is diffusion coefficient of metal species.

Only a little effort has been expended to measure mercury species by DGT technique, though they have attracted great attention concerning environmental contamination monitoring, due to their unique toxicity [4,5]. In the pilot study dealing with mercury determination by DGT, problems were found with commonly used polyacrylamide diffusive gel and thus, this gel was replaced with agarose diffusive gel [6]. Moreover, the iminodiacetic functional groups of Chelex 100 resin, commonly used as binding phase in sorption gel for wide range of metals, were found to capture only hydrated mercury ions and mercury bonded in labile inorganic and organic complexes [7]. On the other hand, the thiol functional groups of Spheron Thiol resin were found to be able to capture mercury bonded even in strong complexes with natural ligands. The concentrations obtained by Spheron-Thiol DGT corresponded to concentrations obtained by direct measurements of total dissolved mercury [7]. Following the concept introduced by Li and coworkers [8], simultaneous use of Chelex 100

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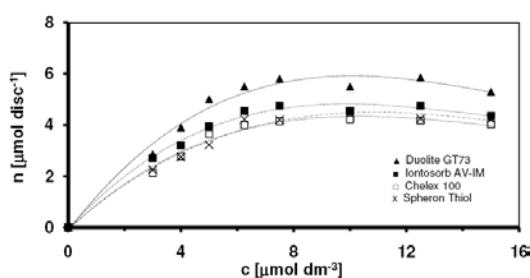


Figure 1. Sorption isotherms of all tested sorption gels

and Spheron-Thiol DGT probes can provide valuable information about speciation of mercury in studied environment. Unfortunately, Spheron-Thiol resin is no longer available at present time and for this reason, new resins have to be introduced. As an alternative to Spheron-Thiol resin, Duolite GT73 and modified Iontosorb resins were used recently [9].

This work followed the last studies [6,9] and yields new knowledge needed for application of DGT technique with recently introduced sorption gels to measure mercury species in aquatic environment. An influence of pH, ionic strength and selected natural ligands to DGT mercury measurement was studied and other parameters like sorption capacity of all prepared sorption gels and minimum DGT measurable concentrations were determined.

2. Experimental Procedure

2.1. Reagents and chemicals

All reagents were of analytical grade. Mercury nitrate solution ($1 \text{ g dm}^{-3} \text{ Hg}$, Astasol, Analytika, Czech Republic) was used as Hg standard in atomic absorption spectrometric (AAS) measurement and in the preparation of all model solution. Concentration of all test solutions was $20 \text{ } \mu\text{g dm}^{-3}$ if it is not given otherwise. For preparation of the sorption gels 0.3 g of Chelex 100 (Na form, 200-400 mesh, Biorad, USA), Duolite GT73 (Sigma, Germany), Spheron Thiol (Lachema, Czech Republic) and Iontosorb AV (Iontosorb, Czech Republic) resins were used. Iontosorb AV resin was modified by imidazole (Sigma) instead of 6-mercaptopurine according to the procedure described previously and final product was marked as Iontosorb AV-IM. Nitric acid (Analpure, Analytika) and sodium hydroxide (Penta, Czech Republic) solutions (2 mol dm^{-3}) were added to adjust the final pH of the model solutions. Sodium nitrate and potassium sulfate (Lachema) were used to set the ionic strength. In experiments focused on the

influence of natural ligands to DGT measurements, sodium chloride (Lachema) and a mixture of humic substances (Fluka, Switzerland, product No.53680) were used. Diffusive gel was prepared using agarose (Sigma), while the sorption gels were prepared using acrylamide (Sigma), patented agarose cross-linker (DGT Research), ammonium persulfate (Sigma) and N,N,N',N' tetramethylethylenediamine (Sigma). Preparation of all gels followed the procedure described previously [9].

2.2. Apparatus and instruments:

The DGT sampling units (piston type, 3.14 cm^2 exposition area) were purchased from DGT Research Ltd. All solutions were stirred at 800 rpm using magnetic stirrer. For mercury analysis in model solutions and in sorption gels, an Advance Mercury Analyser AMA 254 (Altec, Czech Republic) was used. During the sorption capacity tests an atomic absorption spectrometer with flame atomization (SpectrAA 30, Varian, Australia) was used to determine mercury at wavelength 253.9 nm , lamp current 4 mA , spectral band 0.1 nm , burner height 12 mm , air flow $3.5 \text{ dm}^3 \text{ min}^{-1}$ and acetylene flow $1.5 \text{ dm}^3 \text{ min}^{-1}$.

2.3. Sorption capacity measurement

In order to obtain the information about the equilibrium process and capacity of prepared sorption gels, the adsorption isotherm was carried out. The amount of sorbed Hg in one sorption gel disc (n) was measured as a function of Hg concentration in the initial solution (c). The concentration of mercury ranged from 3 to $15 \text{ } \mu\text{mol dm}^{-3}$ and the pH was arranged to be 6 in all solutions. After 8 hours, equilibrium concentration of mercury in model solutions was determined and from the depletion of Hg concentration, adsorbed amount of mercury was calculated. The molar amount of adsorbed Hg was plotted as a function of Hg concentration in model solutions. The adsorption capacity of the sorption gels for mercury was calculated from the Langmuir equation [10].

2.4. Effect of pH

The DGT sampling units were deployed in equilibrated model mercury solutions with different pH varied between 2 and 10 for 3 hours. After the deployment, sorption gels were extracted from DGT units and analyzed for mercury content. Calculated DGT mercury concentration (c_{DGT} , Eq. 1) was then compared with those obtained by direct analysis of mercury in model solutions (c_{AAS}). The ratio of $c_{\text{DGT}} / c_{\text{AAS}}$ is expressed as R in further text of this article.

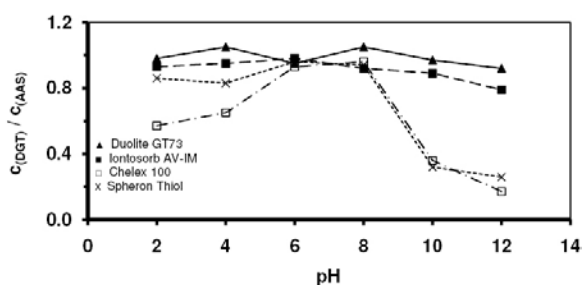


Figure 2. Influence of pH to measurement of mercury by DGT technique with various sorption gels

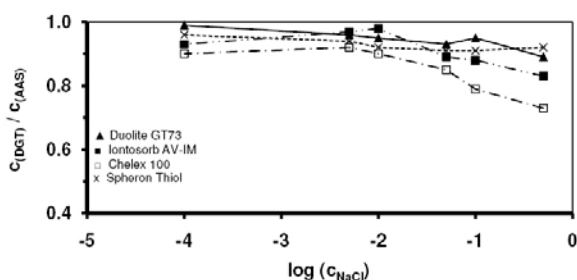


Figure 3. Influence of chloride concentration to measurement of mercury by DGT technique with various sorption gels

Table 1. Mercury mass in unexposed sorption gels with standard deviation of measurement ($n=10$) and calculated minimum DGT measureable concentrations

	Spheron Thiol	Duolite GT73	Chelex 100	Lontosorb AV-IM
Hgmass(ng)	0.53 ± 0.16	0.15 ± 0.04	0.19 ± 0.07	0.36 ± 0.11
$c_{\min DGT}(\text{ng L}^{-1})$	20	5	7	13

2.5. Effect of ionic strength and natural ligands

Three DGT sampling units were immersed stepwisely in mercury test solutions with different ionic strength in a range from 0.5 mmol dm^{-3} to 1 mol dm^{-3} for 3 hours. Subsequently, exposed sorption gels were analyzed using AMA 254 spectrometer. Similarly, experiments in mercury test solutions containing sodium chloride in concentrations range from 0.5 mmol dm^{-3} to 0.5 mol dm^{-3} were performed. In the experiment with humic substances test solutions containing $100 \text{ } \mu\text{g dm}^{-3}$ of mercury were prepared. Subsequently, humic substances were added to the solutions in concentrations 0.01, 0.1, 1 and 10 mg dm^{-3} . All solutions were left to equilibrate overnight and finally, DGT sampling units were immersed in all prepared solutions for 3 hours.

All experiments were repeated at least three times. The error bars in graphs are not shown for better transparency of the pictures. The relative standard deviation in all measurements varied from 3 to 8%.

3. Results and Discussion

Fig. 1 shows the sorption isotherms of all tested sorption gels. The total sorption capacity of the sorption gels for mercury was found to be $5.7 \text{ } \mu\text{mol}$ (Duolite GT73), $4.4 \text{ } \mu\text{mol}$ (Lontosorb AV-IM), $4.3 \text{ } \mu\text{mol}$ (Spheron-Thiol) and $3.9 \text{ } \mu\text{mol}$ (Chelex 100). It is possible that the sorption capacity of Spheron-Thiol is slightly reduced, because thiol groups can be oxidized during the storage for longer time (several years). Available sorption capacities in real aquatic systems usually reach 5-10% of total sorption capacities because, in natural systems, oversaturation of functional groups present in sorption gel by mercury is not possible. Even this, the sorption capacity of all tested sorption gels is sufficient for long time deployment in natural waters.

The investigation of Hg sorption as function of pH is shown in Fig. 2. Sorption was independent of pH ($R \sim 0.98$) in the case of Duolite GT73 and Lontosorb AV-IM sorption gels. On the other hand, similar sorption ($R \sim 0.95$) was observed by Spheron Thiol and Chelex-100 only in the pH between 6 and 8. In solutions with pH less than 6, sorption of mercury decreased ($R \sim 0.85$ for Spheron Thiol and $R \sim 0.60$ for Chelex 100). Slovák *et al.* [11] found quantitative sorption of mercury for Spheron Thiol in presence of 0.05 mol dm^{-3} hydrochloric acid. In this study, test solution was acidified with nitric acid instead of hydrochloric acid to exclude the formation of stable chloride complexes. It is thus possible that some thiol groups were oxidized during the experiment. The sorption of mercury decreased even more ($R \sim 0.35$) for both Spheron Thiol and Chelex 100 sorption gels in solutions with pH greater than 8. Decrease of the Hg sorption in the case of Chelex 100 DGT is caused by change in structure of Chelex 100 resin [12]. In solutions with pH greater than 8, hydrolysis reactions take place in Spheron-Thiol resin structure, which lead to lower sorption of mercury [13].

Effect of ionic strength on Hg sorption was negligible for all tested sorption gels. Higher concentration of chloride ions in tested solutions affected the DGT measurement mainly with the use of Chelex 100 sorption gel (Fig. 3). In the case of other tested sorption gels, recovery of mercury from test solutions fluctuated around 0.9 for all chloride concentrations. Beside chloride ions, mercury forms stable complexes with humic substances [14]. An influence of humic substances concentration to the DGT mercury measurement is shown in Fig. 4. It can be seen that only Duolite GT73 and Spheron Thiol sorption gels can effectively bond mercury present in stable humic substance complexes. On the other side,

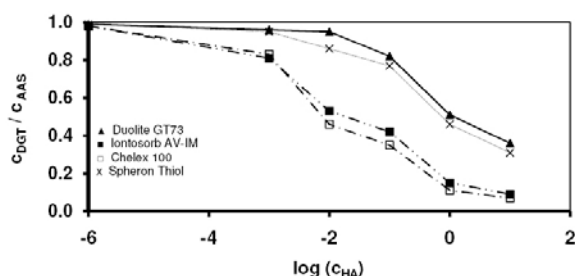


Figure 4. Influence of humic substance concentration to measurement of mercury by DGT technique with various sorption gels

stability constant of mercury-iminodiacetic complex (Chelex 100) and mercury-imidazole complex (Iontosorb AV-IM) is lower than stability constant of mercury-humic substance complex, which leads to the effect that mercury-humic substance complexes are not measured by DGT [8]. The obtained results confirmed the early founding from real aquatic system [6,7,9].

From 3 times the standard deviation of mercury amount in the unexposed sorption gels the minimum concentration measurable by DGT technique ($c_{\min DGT}$) was calculated using Eq. 1. Calculated data are valid for the deployment time of 24 hours and diffusive layer thickness 0.63 mm (thickness of commonly used agarose diffusive gel and filter membrane). As can be seen from Table 1, minimum concentration measurable by DGT technique with various sorption gels vary between 5 and 20 ng dm⁻³. Concentrations of total dissolved mercury in unpolluted natural water ranged from 0.1 to 15 ng dm⁻³ [4,15]. Taking local variations from this range into consideration, concentration up to 100 ng dm⁻³ can be found in natural waters. From this point of view, all tested sorption gels should be used for mercury determination in aquatic system, but if it is possible, longer deployment time than 24 hours (3-5 days) is recommended to measure lower mercury concentration.

4. Conclusions

The highest sorption capacity for mercury was found for Duolite GT73 sorption gel. Other tested sorption gels had lower sorption capacity. However, this capacity is sufficient for long deployment time (weeks) of DGT technique in aquatic environment. The minimum DGT measurable concentrations allow for the measurement of mercury in most natural waters. Concentrations below 5 ng dm⁻³ can be measured if deployment time of DGT sampling units is about 3 - 5 days. The Duolite GT73 sorption gel can be used to measure mercury in wider variety of aquatic systems (*i.e.*, waste waters or acid mine waters) in comparison with other tested sorption gels. This is because it works properly in wider pH range and it is capable of measuring mercury bonded even in strong complexes. All other tested sorption gels can be used for mercury measurement in aquatic systems with pH in range of 6-8 and except the Spheron-Thiol these sorption gels are able to capture only labile mercury species as inorganic ions and weak complexes. These properties can be used for speciation measurement in natural waters if combined DGT probe with different sorption gels is used.

Acknowledgements

The authors thanks the Grant agency of Czech Republic for financial support (projects no. GAČR 525/09/P583 and GAČR P503/10/2002), Hana Frišhansová for her experimental assistance and Bohumil Dočekal for help with manuscript preparation.

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