Synthesized mercaptopropyl nanoporous resins in DGT probes for determining dissolved mercury concentrations

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**Abstract**

3-Mercaptopropyl functionalized SBA-15 (SH-SBA) and 3-mercaptopropyl functionalized ethylenylene bridged periodic mesoporous organosilica (SH-PMO) were included in a Diffusive Gradients in Thin film (DGT) probe and compared to similar commercially available resins also containing thiol functional groups, such as Sumichllate Q10R (SQR) and 3-mercaptopropyl functionalized silica gel (SH-KG), and also to the Chelex-100 resin for the determination of labile Hg concentrations. An agarose gel was used as the diffusive gel because the classic polyacrylamide gel shows more than 20\% of Hg adsorption. According to our results, the Chelex-100 resin presents a much lower affinity for Hg than the thiol based resins. The non-linear accumulation profile of mercury with time for the Chelex-100 resin makes it in fact impossible to use Fick’s law for estimating the diffusion coefficient of Hg. The 4 other resins all show a linear accumulation profile of Hg with time. Although the highest accumulation rate is observed for SH-PMO followed by SQR, SH-SBA and SH-KG, these values do not differ very much.

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1. Introduction

The ambient Hg levels in natural aquatic systems, especially open ocean waters, are generally very low (ppt to ppq levels) requiring appropriate ultra-clean sampling, storage and analysis procedures. Significant improvements in instrumentation have been made, such as for example the gold trapping-atomic fluorescence technique and more recently the ICP-MS technique, allowing reliable and sensitive measurements of all Hg species, but traditional problems related to contamination mostly from in situ sampling devices, research vessels, non-quantitative recoveries, and the possibility of contamination and artifact formation during the sample preparation and separation steps still exist [1]. Therefore, it is recommended to use, whenever possible, in situ extraction and pre-concentration techniques avoiding storage of the samples and minimizing their treatment in the laboratory afterwards. One of the most effective and low-cost in situ extraction methods of trace metals such as Cd, Cu, Pb, Zn, etc. is the Diffusive Gradients in Thin film (DGT) technique, developed by Davison and Zhang [2], and in principle applicable to any ion or compound that can be trapped on an appropriate solid adsorbent.

The DGT technique is a simple sampling technique, based on the mass adsorption of solutes from the bulk solution to a backup resin, involving two hydrogel layers: commonly a polyacrylamide gel forms the first diffusive layer and is backed up by a second thin gel film layer containing a resin, generally Chelex-100 (Table 1). This system has also been applied for the determination of total Hg concentrations in the aquatic environment [3,4], but it showed several drawbacks. The polyacrylamide gel has a high affinity for mercury and was therefore replaced by an agarose gel [3]. Moreover, the adsorption efficiency of the Chelex-100 resin with regard to Hg is also controversial. Docekala and Divis [3] compared the Hg pre-concentration of a DGT containing a Chelex-100 resin with one containing a Spheron-Thiol resin [5]. They concluded that they were able to assess ionic mercury, and labile mercury complexes with both resins, but the Chelex-100 resin had less affinity for mercury than the Spheron-Thiol one. Conversely, Cattani et al. [4] reported only 50–58\% recovery of the Hg from their solution using Chelex-100 as resin gel in the DGT, whereas 83–97\% of recovery was obtained with the Spheron-Thiol resin.

Other thiol based resins such as mercaptopropyl [6–9] or dithiocarbamate [10,11] have been investigated for the pre-concentration of inorganic and organic mercury species at ng L\textsuperscript{-1} levels. All those resins (Spheron-Thiol, mercaptopropyl and dithiocarbamate) can thus in principle be used for assessing labile Hg concentrations when included in a DGT probe. However, some of those resins are not commercially available, while for other resins the beads are too large and must therefore be crushed into a fine
<table>
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<th>Resin</th>
<th>Matrix</th>
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<th>Porosity</th>
<th>Morphology</th>
<th>$S_{\text{BET}}$ $a$ (m² g⁻¹)</th>
<th>$V_p$ $b$ (mL/g)</th>
<th>$d_p$ $c$ (nm)</th>
<th>Functionality $d$ (mmol/g)</th>
<th>Capacity $e$ (mg/g)</th>
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</table>

$^a$ Specific surface area determined by the BET theory.

$^b$ Total pore volume.

$^c$ Pore diameter calculated from the adsorption branch with the BJH method.

$^d$ Total amount of functionalities determined by a silver titration.

$^e$ Mercury capacity of the various resins.

$^f$ Synthesized by the Department of Inorganic Chemistry (University of Ghent).

$^g$ Commercially available.
powder prior to their inclusion in the DGT gel. For the crushed resins there is a risk for a reduced efficiency when they are inserted in the DGT probes. Therefore we tested two recently synthesized mercaptopropyl resins of appropriate bead size.

Firstly, an adsorbent based on an SBA-15 material has been synthesized which possesses a silica matrix with a very high specific surface area and a molecular ordering of the pores [12]. This material was functionalized with mercaptopropyl units that are attached to the surface via a grafting procedure with (3-mercaptopropyl)triethoxysilane. The anchoring takes place via the silanol groups on the surface.

More recently, De Canck and Van Der Voort [13] reported a novel adsorbent, based on an ethylene bridged periodic mesoporous organosilica (PMO). This PMO material exhibits a high specific surface area (∼1000 m² g⁻¹), is highly ordered on a molecular level and possesses a narrow pore size distribution. The mercaptopropyl functionalities are anchored to the surface via a C–C bond instead of a Si–O–Si bond in the case of a functionalized SBA-15 material (see Supplementary Fig. S1). The SH-PMO material already showed some very promising results in mercury(II) ion adsorption experiments. The material exhibited an excellent structural and chemical stability after several mercury adsorption and desorption processes [13].

In this paper the 3-mercaptopropyl functionalized SBA-15 (SH-SBA) and 3-mercaptopropyl functionalized PMO (SH-PMO) were included in a DGT probe and compared to commercially available resins, also containing thiol functional groups such as the Sumichelate Q10R (SQR) and 3-mercaptopropyl functionalized silica gel (SH-KG), and also to the Chelex-100 resin for the determination of dissolved labile mercury concentrations. An agarose gel was used as the diffusive gel because the classic polyacrylamide gel possesses more than 20% of adsorption for Hg [3].

2. Materials and methods

2.1. Reagents and materials

Acetone (Fiers), acetonitrile (Acros), acrylamide solution (40%; pro analysis, Merck), agarose powder (Biorad), ammoniumpersulfate (10%, 0.1 g in 1 g of water), 1-butanol (99.9%; Sigma–Aldrich), bromine (Sigma–Aldrich), Chelex-100 (200–400 mesh, Biorad), 3-chloro-1-propanethiol (98%; Sigma–Aldrich), DGT cross-linker (DGT Research Ltd), durapore membrane filter (Millipore), hydrochloric acid (37%; Roth), HNO₃ (distilled from 65% HNO₃; pro analysis, Merck), iron(III) chloride (98%; anhydrous, Acros), magnesium (Fluka), 3-mercaptopropyl functionalized silica gel (200–400 mesh, Aldrich), (3-mercaptopropyl) triethoxysilane (92%; ABCR Gelest), mercury stock solution 1000 ppm (Alfa Aesar), MilliQ water (Millipore, >18.2 MΩ cm), NaNO₃ (Suprapur, Merck), 15L PFA bucket (Nalgene), pH indicator paper (VWR), pluronic PEO₂₀PPO₇₀PEO₂₀ (P123; Sigma–Aldrich), Sumichelate Q10R (Sumitomo, Osaka), N,N,N,N-tetraethylenediamine (99%; pro analysis, Merck), tetraethyloxyethersilicate (98%; Sigma–Aldrich), tetrahydrofuran (Rotidy ≥99.9%; Roth), thiourea (Merck), triethylamine (Sigma–Aldrich). All reagents were used as received.

2.2. Synthesis of the adsorbents SH-SBA and SH-PMO

2.2.1. 3-Mercaptopropyl SBA-15 (SH-SBA)

The first step of preparing this adsorbent was synthesizing the SBA-15 material, according to a procedure published by Zhao et al. [14]. After dissolving 4 g of P123 into 120 mL of HCl (2 M) and 30 mL of distilled water, the mixture was stirred for 1.5 h at room temperature. Next, 9 mL of tetraethyloxythiolate was added, and the temperature was raised to 45 °C for 5 h under vigorously stirring of the mixture. Subsequently, the temperature was increased to 90 °C for 16 h under static conditions. After cooling down, the white precipitate was filtered and washed with water and acetone. Finally, the material was calcinated at 550 °C for 6 h. This material was subsequently functionalized with (3-mercaptopropyl) triethoxysilane (MPTES). An amount of 10 mL of acetonitrile and 3.58 mL of triethylamine were added to 0.85 g of SBA-15 under an inert atmosphere [15]. The mixture was stirred for 2 h at room temperature, and subsequently the mixture of triethylamine and acetonitrile was removed maintaining the inert atmosphere. Next, acetonitrile (10 mL) and MPTES (6.72 mL) were added to the material. The mixture was allowed to react for 2 h at 65 °C before the solid was filtered and washed with acetonitrile and acetone. The material was then dried at 90 °C under vacuum for 16 h.

2.2.2. 3-Mercaptopropyl PMO (SH-PMO)

The ethylene bridged PMO material was prepared via the procedure previously published by Vercaemst et al. [16]. Initially, P123 (1 g), water (47.8 mL), concentrated HCl (3.42 mL) and butanol (2.45 mL) were added together. This mixture was stirred for 1.5 h. Subsequently, 1.86 mL of synthesized 100% trans 1,2-bis(triethoxysilyl)ethene was mixed [17], and the temperature was raised to 45 °C. This mixture was stirred for 4 h. Afterwards the temperature was increased to 90 °C under static conditions. Finally, the precipitate was filtered and washed with water and acetone. The template was removed by a Soxhlet extraction with acetone for 5 h. After drying, the PMO was brominated with Br₂ in gaseous phase. The physisorbed bromine was removed by drying the material at 90 °C for 24 h. This material was further modified. A mixture of Mg (0.74 g), FeCl₃ (0.54 g), and THF (30 mL) was prepared under inert atmosphere and stirred for 30 min at 50 °C. 3-Chloro-1-propanethiol (0.22 mL) was added, and this mixture was stirred for 4 h at room temperature. Immediately following, the mixture was added to a Schlenk flask containing the PMO material and stirred for 24 h at 40 °C. The solution was filtered and the filtrate was washed with THF, 2 M HCl, water, and acetone. Finally, the adsorbent was collected and dried at 90 °C for 16 h.

2.3. Preparation of the Diffusive Gradients in Thin Films (DGTs)

2.3.1. Diffusive gel

An amount of 0.3 g agarose powder was diluted in 20 mL MilliQ water and the mixture was placed in a boiling water bath, covered and gently stirred until all the agarose was dissolved and the solution was immediately pipetted into two glass plates with a spacer separating the plates. After 1 h cooling down, agarose gels were cut into 2.5 cm circles with a plexi-glass cutter.

2.3.2. Resin gels

Before including the different resins in the agarose gel, Sumichelate Q10R beads were ground into a fine powder of about 200–400 mesh, washed in 5% thiourea and rinsed three times with MilliQ water. The water was discarded by filtration and the cleaned resin was ready to be included into resin gels. All other resins, Chelex-100, 3-mercaptopropyl functionalized silica gel, SH-SBA and SH-PMO, were also cleaned in the same way.

Around 3 g of resin was added to 10 mL gel solution (15% acrylamide, 0.3% DGT cross-linker) and this solution was mixed well. The optimal amount had to be determined for each resin in order to obtain a uniform distribution of the resin in the gel. Then 50 μL 10% ammoniumpersulfate solution and 15 μL N,N,N,N-tetraethylenediamine (TEMED) were added. The solution was mixed well and cast between two glass plates with a spacer separating the plates. The assembly was placed in an oven at 45 °C for 1 h, and then hydrated in MilliQ water for at least one day until use.
2.3.3. 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 moulding 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 moulding and pressed down to the bottom of the base.

2.4. DGT performance test experiment

Performance tests with the various DGT assembly types were carried out in a 1 L mercury solution of 100 μg L$^{-1}$ containing 0.01 M NaNO$_3$. During the experiment, the accurate Hg concentration in the solution was monitored and changes were taken into account for the comparison with the DGT derived mercury concentration. The pH of the solution was adjusted to around 5. Eight DGT assemblies all facing down to the solution were plugged into the holes of a round Teflon plate. For each type of resin used in the DGTs, a Teflon plate was inserted in 100 μg L$^{-1}$ Hg solution, which was continuously stirred. After 2, 4, 8 and 24 h, 2 of the DGT assemblies were removed from the solution. The resin gels were extracted with 2 mL of 5% thiourea. Since thiourea has a strong affinity with mercury, the Hg extraction with thiourea was made in a 30% KOH solution [18].

An interference test was also performed. The various DGT assemblies were deployed in a 2 L mercury solution of 100 μg L$^{-1}$ and 0.01 M NaNO$_3$ containing a 10 times higher concentration (1 mg L$^{-1}$) of the following metals: Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Sn, and Pb. In this experiment, no interference on the mercury accumulation by the various DGT assemblies was observed.

2.5. Field deployment of DGT units in a local water pond

An amount of 12 DGT assemblies with four various resin gels were deployed in a local water pond inside the university campus for 2 days. Simultaneously, several water samples were taken from the pond and after filtration stored in a 150 mL acidiﬁed Teflon bottle with 0.5% HCl. DGT assemblies were removed from the pond after two days deployment. The resin gels were extracted with 2 mL of 5% thiourea.

2.6. Mercury analysis

All mercury solutions (standards, test solutions, resin gel extracted solutions and water samples) were analyzed by a PSA 10.035 Millennium Meriln AA instrument. Argon was used as carrier gas with a flow rate of 0.3 L min$^{-1}$ and nitrogen was used as dryer gas with a flow rate of 2.5 L min$^{-1}$. Millennium Meriln AA system was developed to be compliant with EPA Cold Vapor methods (1631) for the determination of mercury at low levels. The detection limit of the method is 0.5 ppt.

2.7. Quantification of the functional groups

The amount of reachable functional groups of the resins was determined by silver titration [19]. The thiol groups were allowed to react with a known concentration of silver nitrate, and the excess of silver was titrated with potassium thiocyanate, using FeNH$_4$(SO$_4$)$_2$·12H$_2$O in 0.3 M HNO$_3$ as indicator. Mercury capacity of the resins was determined by deployment of 0.1 g of resin in 50 mL mercury solution of 200 mg L$^{-1}$ containing 0.01 M NaNO$_3$. Hundred microlitre of solution was sampled at time intervals of 1 or 2 h and up to 24 h. Solutions were analyzed after appropriate dilution until a steady concentration was observed.

2.8. Characterization of the resins

The specific surface area, pore volume, and pore radius were determined using nitrogen adsorption desorption measurements. The isotherms were recorded on Belsorp Mini II equipment at 77 K. The samples were pretreated at 90 °C while degassing.

X-ray diffraction was performed with an ARL Xtra X-ray diffractometer of Thermo Scientiﬁc equipped with a Cu Ka1 tube and a Peltier cooled lithium drifted silicon solid stage detector.

3. Results and discussion

3.1. Characteristics of the new SBA and PMO resins

The three mesoporous functionalized silicon based materials (SH-KG, SH-SBA and SH-PMO) were characterized with nitrogen adsorption and desorption measurements to check their mesoporosity (see Supplementary Figs. S2–S4). The adsorbents showed speciﬁc surface areas between 450 and 822 m$^2$ g$^{-1}$ and their pore volumes and pore diameters are presented in Table 1. The functionalized PMO adsorbent exhibited the highest surface area and pore volume. The SH-KG material showed a very broad pore size distribution in comparison with the very narrow distribution of SH-SBA and SH-PMO.

The total amount of reachable functionalities for the thiol containing materials was determined via a silver titration and is also presented in Table 1. The functionalized PMO material contained less thiol groups than the two silica materials. The interaction between the thiol group and the mercury atoms was for all the thiol containing materials a 1:1 ratio with the mercury. The mercury capacities of the various resins are presented in Table 1: the highest capacity was observed for SQR followed by SH-PMO, SH-SBA, SH-KG and Chelex-100. All thiol containing resins showed a mercury capacity above 66 mg Hg g$^{-1}$ resin whereas Chelex-100 had a capacity of 18 mg Hg g$^{-1}$ resin.

The Chelex-100 and Sumichelate Q10R adsorbents are both macroporous polymers with a typically very low speciﬁc surface area and did not possess any ordering. Chelex-100 is a styrene-divinyl benzene polymer and contains iminodiacetate groups. This group can interact via its nitrogen and oxygen atoms with the mercury according a tridentate interaction. The Sumichelate Q10R on the other hand possesses a dithiocarbamate group which has a 1:2 ratio towards the mercury atoms.

3.2. Mercury concentrations in the bulk solution

Mercury concentrations in the 10 L bulk solution were monitored each hour by sampling 5 mL of solution and appropriate dilution. The mercury concentration decreased by about 30% during the first 4 h, most likely due to adsorption on the wall of the recipient, but became steady until the end of the experiment at a concentration of around 60 μg L$^{-1}$.

3.3. Mercury accumulation on the Chelex-100 resin gel in a DGT

Chelex-100 is a styrene-divinylbenzene resin containing iminodiacetic acid groups and it competes efﬁciently with natural ligands for divalent and trivalent metal ions. It is reported (DGT Research Ltd) that in a DGT assembly, Chelex-100 is trapping at a
continuous rate Ag, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn from the aquatic system. In most natural aquatic systems, the capacity of the resin for these metals is high enough to avoid a decrease in the trapping rate.

The adsorption efficiency of the Chelex-100 resin with regard to Hg is, however, controversial. Docerakova and Divis [3] compared the Hg pre-concentration of a DGT containing a Chelex-100 resin with one containing a Spheran-Thiol resin [5]. They concluded that they were able to assess ionic mercury, and labile mercury complexes with both resins, but apparently the Chelex-100 resin had less affinity for mercury than the Spheran-Thiol one. Conversely, Cattani et al. reported only 50–58% recovery of the Hg from their solution using Chelex-100 as resin gel in the DGT, whereas 83–97% of recovery was obtained with the Spheran-Thiol resin [4].

In our study, the Chelex-100 resin presents during the first 2 h a fast accumulation of Hg, similar to the 4 other resins but after 4 h the adsorption rate slows down (Fig. 1), while this is not the case for the other resins. This phenomenon shows that the Chelex-100 resin has a lower affinity and capacity for Hg than the thiol based ones. It is possible that the iminodiacetate functionality causes this observed affinity. The Hard Soft Acid–Base theory of Pearson [20] clearly states that mercury atoms have more affinity for sulfur atoms than nitrogen or oxygen atoms which are present in the iminodiacetate functionality.

The non-linear accumulation profile of Hg with time for the Chelex-100 resin makes it in this case impossible to use Fick’s law for estimating the diffusion coefficient of Hg. This result is opposite to the one obtained by Docerakova and Divis [3], but similar to the observations of Cattani et al. [4].

3.4. Mercury accumulation on SH-PMO, SH-SBA, SQR and SH-KG resin gels in a DGT

The 4 other resins all show a linear accumulation profile of Hg with time (Fig. 1). Despite the fact that SH-PMO has the lowest amount of thiol groups per mass unit of material, it shows a similar accumulation efficiency with Hg. The diffusion coefficient in agarose gel can be calculated with following formula:

\[ D = \frac{kA}{\Delta t} \]

with M is the accumulated mass of mercury; C is the mercury concentration in the bulk solution; D is the diffusion coefficient of Hg in agarose gel; A is the exposure area of the gel to the bulk solution; t is the deployment time; \( \Delta g \) is the thickness of the diffusive layer. When we plot the accumulated mass of mercury (M) as a function of time (t), the angular coefficient of the curve equals:

\[ k = \frac{DA}{\Delta g} \]

This angular coefficient is calculated with a least squares linear regression (Excel software) through the data points.

The diffusion coefficients for each thiol containing resin can then be calculated as:

\[ D = \frac{kA}{\Delta t} \]

Since for all the thiol containing resins the diffusion coefficients are quite similar, we calculated an average value and its standard deviation. This average Hg diffusion coefficient in agarose at 20 °C equals 8.44 ± 0.33 × 10⁻⁶ cm² s⁻¹. The diffusion coefficient of Hg in water column is 9.13 × 10⁻⁶ cm² s⁻¹ while a value of 9.08 ± 0.13 × 10⁻⁶ cm² s⁻¹ in agarose gel was reported by Docerakova and Divis [3].

3.5. Field work results

DGT assemblies with the various resin gels tested in this study, were deployed in a water pond at the VUB campus (Vrije Universiteit Brussel), for in situ mercury measurements in March 2011. Water samples and 12 eluted gel solutions obtained from the field work were analyzed by PSA 10.035 Millennium Merlin in Galahad mode, which means the cold vapor method was selected for low level Hg analysis (ppt level). The concentration of dissolved Hg in the water sample was 0.0232 ± 0.0093 μg L⁻¹ and the DGT measured concentration 0.0176 ± 0.0036 μg L⁻¹, which indicates that about 75% of mercury is present as labile species in this water pond. This labile Hg fraction is more dangerous for the micro-organisms, such as phytoplankton and microzooplankton living in this pond since the small size of that labile fraction (<10 nm) can easily pass the cell wall of those organisms. It will finally accumulate along the food chain and furthermore influence all organisms living in this small aquatic system.

4. Conclusions

Two new laboratory synthesized mercaptopropyl nanoporous resins SH-PMO and SH-SBA together with three commercial available resins SQR, SH-KG and Chelex-100 were tested as the binding layer in the DGT technique for assessing labile Hg concentrations in this study. SH-PMO, SH-SBA, SQR and SH-KG resins showed high affinity with labile Hg due to high specific surface for binding Hg and the efficient functional thiol or dithiocarbamate groups, whereas Chelex-100 presented poor binding ability with Hg due to low specific surface and less efficient functional iminodiacetate groups. With these 4 efficient Hg binding resins, slightly higher accumulation rate is observed for SH-PMO followed by SQR, SH-KG and SH-SBA. Hg diffusion coefficient in agarose at 20 °C was obtained by using these 4 resins as the binding layer in the DGT technique and the value of 8.44 ± 0.33 × 10⁻⁶ cm² s⁻¹ is comparable to the literature value of 9.08 ± 0.13 × 10⁻⁶ cm² s⁻¹. DGT assemblies with these 4 resin gels determined the labile Hg concentration in the water pond of the campus and the result of 0.0176 ± 0.0036 μg L⁻¹ is 75% of total Hg concentration in the same pond indicating the major part of Hg in this pond is labile and bioavailable species.

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Appendix A. Supplementary data


References