



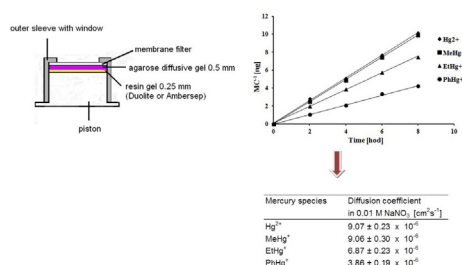
Development of the diffusive gradient in thin films technique for the measurement of labile mercury species in waters



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GRAPHICAL ABSTRACT



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ABSTRACT

The diffusive gradients in thin films (DGT) technique, utilizing resin gel with ion-exchange resin Duolite GT73 and new ion-exchange resin Ambersep GT74, was investigated for the accumulation of four mercury species (Hg²⁺, CH₃Hg⁺, C₂H₅Hg⁺, C₆H₅Hg⁺). The diffusion coefficients of mercury species in agarose gel calculated on the basis of Fick's Law were mercury species-specific. The diffusion coefficients of Hg²⁺ and CH₃Hg⁺ at 25 °C (9.07 ± 0.23 × 10⁻⁶ cm² s⁻¹ and 9.06 ± 0.30 × 10⁻⁶ cm² s⁻¹, respectively) were very similar, but the diffusion coefficients of C₂H₅Hg⁺ (6.87 ± 0.23 × 10⁻⁶ cm² s⁻¹) and C₆H₅Hg⁺ (3.86 ± 0.19 × 10⁻⁶ cm² s⁻¹) were significantly lower. Influence of experimental conditions (pH, selected cations, chlorides and humic substance) on mercury species accumulation by DGT was studied. The DGT technique was applied to river water spiked with mercury species.

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1. Introduction

Mercury can be found in the environment in various chemical forms that include elemental, inorganic and organomercury.

Abbreviations: DGT, diffusive gradients in thin films technique; DOM, dissolved organic matter; HA, humic acids; HS, humic substance.

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The form of mercury most commonly occurring in natural waters is Hg²⁺, and less often there occur methylmercury (CH₃Hg⁺), elemental mercury (Hg⁰), and dimethylmercury ((CH₃)₂Hg). Other mercury species, like phenylmercury (C₆H₅Hg⁺) and ethylmercury (C₂H₅Hg⁺), are introduced into the environment by anthropogenic activities. Mercury species' chemical forms correlate closely with their toxicity, solubility, mobility and bioavailability. The determination of individual species is therefore crucial for estimating the impact on human health [1].

However, speciation analysis of mercury in an aquatic ecosystem is very complicated. The determination is made difficult by aspects of preserving the original mercury species distribution; the various species' stability during sampling, storage and analysis; and the very low contents of mercury species in samples

[2]. In situ measurement of mercury species using the diffusive gradients in thin films (DGT) technique preserves the distribution and stability of mercury species during sampling and pre-concentrates the analytes [3]. This makes DGT technique very advantageous for measuring very low concentrations of mercury species in environmental samples.

This paper builds upon previous works dedicated to the determination of mercury in natural waters and sediments using DGT technique [4–11]. The vast majority of works published to date that deal with mercury and DGT focus on inorganic ionic mercury (Hg^{2+}). Less attention has been devoted to DGT determination of other mercury species occurring in aquatic environments. Although DGT technique using 3-mercaptopropyl functionalized silica gel has been described for methylmercury (CH_3Hg^+) determination [8–11], no application of DGT technique for determining ethylmercury ($\text{C}_2\text{H}_5\text{Hg}^+$) and phenylmercury ($\text{C}_6\text{H}_5\text{Hg}^+$) has yet been reported.

It has been shown that Hg^{2+} binds to the amide groups within polyacrylamide diffusive gel, thus making this commonly used diffusive gel unsuitable as a diffusive medium for mercury determination, and therefore this gel has been replaced by agarose diffusive gel [4]. Moreover, the iminodiacetic functional groups of Chelex 100 resin, commonly used as the binding phase in resin gel for a wide range of metals, were found to be inadequate for capturing a great part of soluble mercury species [4].

Resins containing the thiol functional groups have been found to be able to detect total dissolved mercury [12]. A group of resins with thiol groups like Spheron-Thiol [4,6], Duolite GT73 [5], and Iontosorb AV-IM [5] have been investigated and, together with such other adsorbents as 3-mercaptopropyl functionalized silica gel [7–11,13] or titanium dioxide [14], these have been tested for mercury accumulation. Titanium dioxide was determined to be unsuitable for the determination of mercury in marine waters because mercury accumulation was significantly influenced by chloride concentration [14]. Iontosorb AV-IM is not suitable for the determination of mercury in the presence of humic substance [5], and the Spheron-Thiol and Duolite resins with thiol groups are no longer commercially available. For these reasons, we sought a new and commercially available resin that would be suitable for accumulation of mercury species.

This paper deals with the application of DGT technique for determination of four mercury species (Hg^{2+} , CH_3Hg^+ , $\text{C}_2\text{H}_5\text{Hg}^+$, $\text{C}_6\text{H}_5\text{Hg}^+$). The new and commercially available ion-exchange resin Ambersep GT74 was tested. The diffusion coefficients of the mercury species in the agarose diffusive gel and various factors (pH, selected cations, chlorides and humic substance) that may affect the accumulation of mercury species by DGT were investigated.

2. Experimental

2.1. Reagents and chemicals

All reagents were of analytical grade. For dilutions, high-purity demineralized water produced by the Millipore Milli Q system (Millipore, Bedford, MA, USA) was used. An inorganic mercury calibration standard of concentration $1.000 \pm 0.002 \text{ g L}^{-1} \text{ Hg}$ in 2% v/v HNO_3 (Czech Meteorological Institute, Prague, Czech Republic) was used as the Hg^{2+} standard for preparing all model solutions. Methylmercury chloride (CH_3Hg^+) and phenylmercury chloride ($\text{C}_6\text{H}_5\text{Hg}^+$) were purchased from Sigma–Aldrich, Germany. Ethylmercury chloride ($\text{C}_2\text{H}_5\text{Hg}^+$) was purchased from Supelco, Germany. Standard solutions of CH_3Hg^+ , $\text{C}_2\text{H}_5\text{Hg}^+$ and $\text{C}_6\text{H}_5\text{Hg}^+$ ($c = 1 \text{ g L}^{-1}$) were prepared in methanol.

Nitric acid and sodium hydroxide (Penta, Chrudim, Czech Republic) were used to adjust pH. Nitric acid was purified using a

sub-boiling distillation apparatus (Type BSB-939IR, Berghof, Ennigen, Germany). Sodium nitrate ($c = 0.01 \text{ mol L}^{-1}$) was used to set the ionic strength in all experiments. In experiments focused on the influence of natural ligands and potentially competing ions, sodium chloride (Penta, Czech Republic), humic acid (Prod. Num. 53680, Fluka, a subsidiary of Sigma–Aldrich) and atomic absorption standards AgNO_3 , $\text{Cd}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ at concentration of 1 g L^{-1} of metal in $0.5 \text{ mol L}^{-1} \text{ HNO}_3$ (Merck, Germany) were used.

The reagents and materials employed for the preparation of DGT gels manufactured in-house were acrylamide (Sigma–Aldrich, Germany), ammonium persulfate (Sigma–Aldrich, Germany), tetramethylethylenediamine (Sigma–Aldrich, Germany), DGT cross-linker (DGT Research Ltd., Quernmore, Lancaster, UK), Duolite GT73 (Sigma–Aldrich, Germany), Ambersep GT74 (Rohm and Hass, Philadelphia, PA, USA), and agarose for electrophoresis (Merck, Germany).

2.2. Gel preparation

The preparation of resin gels and ion-permeable diffusive gels followed the procedure used by Zhang and Davison [15].

2.2.1. Diffusive gel

An agarose diffusive gel was used for DGT measurement of mercury species. The gel containing 1.5% agarose was prepared by dissolving agarose in an appropriate volume of 80°C deionized water. The mixture was placed in a boiling water bath and gently stirred until all the agarose was dissolved. The hot gel solution was immediately pipetted between two preheated glass plates separated by 0.5 mm plastic spacers and left to cool to its gelling temperature (36°C or below). The gel sheet was cut into disks immediately thereafter, since it would not expand (the expansion factor of agarose gel is 1) [15], and the disks were stored in demineralized water. The thickness of the prepared diffusive gel was 0.50 mm. Mercury content in the prepared diffusive gel disks was negligible ($0.082 \pm 0.01 \text{ ng disk}^{-1}$, $n = 6$).

2.2.2. Resin gels

The resin gels consisted of cation-exchange resins containing thiol functional groups (Duolite GT73 and Ambersep GT74) embedded in a polyacrylamide gel. Duolite GT73 and Ambersep GT74 are weakly acidic and have very pronounced selectivity for certain metal ions. The selectivity sequence for Ambersep GT74 and Duolite GT73 is identical, as follows: $\text{Hg} > \text{Ag} > \text{Cu} > \text{Pb} > \text{Cd} > \text{Ni} > \text{Co} > \text{Fe} > \text{Ca} > \text{Na}$ [16]. Duolite GT73 is no longer commercially available. For this reason, a similar cation-exchange resin containing thiol functional groups (Ambersep GT74) was tested for accumulation of mercury species and compared with Duolite GT73, which previously had been used only for accumulation of Hg^{2+} [5].

Both of those resins used required treatment before gel preparation. The resins were first purified using concentrated hydrochloric acid, washed with water, dried at 45°C , ground in a porcelain mortar and then sifted through a Teflon sieve. The fractions passing through the sieve ($\leq 150 \mu\text{m}$) were used for resin gel preparation. It was not possible to incorporate the original resin particles (diameter 0.450–0.700 mm) into the polyacrylamide hydrogel, as the thickness of the plastic spacers determining the resin particle diameter was 0.25 mm.

Resin gels were produced using a pre-gel solution, which was prepared by mixing aqueous solutions of 15% acrylamide and 0.3% DGT agarose-derived cross-linker. Per 2 mL of the pre-gel solution, 0.25 g of ground Duolite GT73 or Ambersep GT74 resin was added. Polymerization was initiated by adding 12 μL of freshly prepared 10% m/v ammonium persulfate water solution and 6 μL of tetramethylethylenediamine. The resulting gel solutions were pipetted

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