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Nanogold-Decorated Silica Monoliths as Highly Efficient Solid-Phase Adsorbent for Ultratrace Mercury Analysis in Natural Waters

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S *Supporting Information*

ABSTRACT: We propose a novel analytical method for mercury (Hg) trace determination based on direct Hg preconcentration from aqueous solution onto a gold nanoparticle-decorated silica monolith (AuNP@SiO$_2$). Detection of Hg is performed after thermal desorption by means of atomic fluorescence spectrometry. This new methodology benefits from reagent-free, time- and cost-saving procedure, due to most efficient solid-phase adsorbent and results in high sensitive quantification. The excellent analytical performance of the whole procedure is demonstrated by a limit of detection as low as 1.31 ng L^{-1} for only one-min accumulation duration. A good reproducibility with standard deviations ≤5.4% is given. The feasibility of the approach in natural waters was confirmed by a recovery experiment in spiked seawater with a recovery rate of 101%. Moreover, the presented method was validated through reference analysis of a submarine groundwater discharge sample by cold vapor-atomic fluorescence spectrometry resulting in a very good agreement of the found values. Hence the novel method is a very promising new tool for low-level Hg monitoring in natural waters providing easy-handling on-site preconcentration, reagent-free stabilization as well as reagent-free, highly sensitive detection.
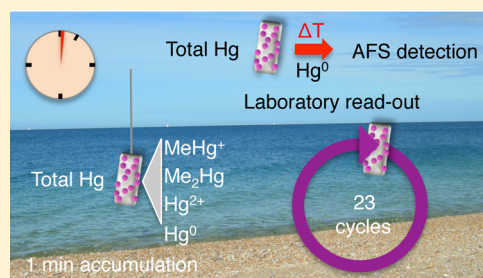
Mercury (Hg) is among the most toxic elements introduced to the environment by both anthropogenic and natural sources. It is readily transported over the atmosphere from emission hot spots and distributed over the globe. Mercury is a ubiquitous element at trace levels present in all environmental compartments. In pristine fresh waters, dissolved Hg concentrations are ranging from 1 to 5 ng Hg L^{-1}; in open ocean seawaters Hg is present in the low picomolar level.[1,2] However, Hg bioaccumulates in fish up to 1 million times as methylmercury, the most toxic species to humans, and so it enters the human food chain and affects human health. Therefore, most humans are exposed via the consumption of marine fish.[3] Consequently, monitoring of ultratrace Hg levels in the hydrosphere is mandatory. Various highly sensitive and selective analytical methods are available for this purpose. Instrumental techniques like atomic absorption spectrometry (AAS),[4] atomic fluorescence spectrometry (AFS),[5−7] and inductively coupled plasma-mass spectrometry (ICP-MS)[8] are usually applied. Typically, these techniques are coupled to an efficient separation technique, mostly chemical cold vapor generation (CV). Thereby, addition of reagents transforms Hg species into "reducible mercury" (Hg^{2+}). Subsequently, chemical reduction to gaseous elemental mercury (Hg^0) and its separation from the matrix by purging is performed. In addition, to obtain the highest sensitivity, Hg^0 vapor can be preconcentrated by an amalgamation technique (AT). Commercially available amalgamation traps are either made from silver- or gold-coated sand[9] and silica wool[10] or consist of bulk materials like gold foil strips[11] and Au/Pt gauzes.[12] Coupling CV, AT, and atomic/mass spectrometry provides high sensitivity Hg detection with detection limits in the low pg L^{-1} range.[13] Nevertheless, there are several disadvantages like time-consuming, multistep sample preparation and consumption of various reagents that result in increased risk of contamination, high blank values and consequently reduced sensitivity. Moreover, the elaborate sample preparation and bulky instrumental equipment hampers on-site application and typically transport of water samples from the sampling site into the laboratory is performed.

In recent years, considerable effort was therefore made to improve Hg trace analysis with regard to its suitability for monitoring purpose. For instance, a miniature AFS system with a lab-on-valve has been suggested in order to provide on-site measurement.[14] However, with a detection limit of 0.02 μg L^{-1},

its application is limited to contaminated waters only. Of course, sensing techniques would also perfectly meet the requirement of portability, and one research focus in Hg analysis has been the development of suitable sensors for in situ detection of Hg traces. Here, colorimetric,[15] fluorescent,[16] electrochemical,[17] and surface enhanced Raman spectroscopy[18] sensors have been suggested for detection of Hg(II) ions in aqueous solutions. These sensors often exhibit high selectivity toward Hg^{2+}; however, other naturally occurring Hg species, like, e.g., methylmercury, can generally not be detected. Moreover, their sensitivity and robustness when considering potential application for natural waters is not sufficient today. Other groups have been focusing on the enhancement of sampling and sample preparation techniques, e.g., on the development of simplified and/or reagent-free procedures. Here, passive sampling[19,20] and solid-phase extraction techniques[21−24] were recently developed in order to overcome the drawbacks of existing procedures. In a previous work, we have reported on a fully reagent-free Hg determination method based on extraction of Hg traces onto nanogold-coated silica material for preconcentration.[25,26] The method is based on the catalytic activity of nanogold that transforms dissolved Hg species (Hg^{2+}, CH_3Hg^+, $C_2H_5Hg^+$, $PhHg^+$, $(CH_3)_2Hg$) and their labile complexes into elemental mercury (Hg^0), which is then amalgamated. The adsorption behavior of dissolved mercury species had been studied in detailed and a mechanism was proposed.[27] The loose adsorbent was packed into a column that was implemented into a portable flow injection system (FIS) for in situ preconcentration of Hg from natural waters. However, on-site application involved transportation of the FIS including a battery to run the pumps. Moreover, random contamination events were observed when exchanging preconcentration columns in the field. Therefore, the objective of this study was the development of a suitable passive sampler that allows highly efficient, reagent-free and easy-handling preconcentration of Hg from natural waters by dipping the sampler into the water rather than apply extraction procedure.

■ EXPERIMENTAL SECTION

Silica Monolith Synthesis. Mesoporous−macroporous silica monoliths were prepared according to a slight modification of the method described by Smått et al.[28] To a mixture of polyethylene glycol (PEG, 35000) dissolved in 12.7 mL of water was added 10.0 g of tetraethyl orthosilicate (TEOS), and to the resulting mixture was added 1.65 mL of 65% aqueous HNO_3 solution. The sol was subsequently stirred at room temperature until a clear solution was obtained. Then, cetyltrimethylammonium bromide ($C_{16}TAB$) was added to the sol, while stirring was continued until the surfactant was completely dissolved. The final molar ratio of the solution was $TEOS/C_{16}TAB/PEG = 1/0.0502/0.5395$. The sols were left to gel at 40 °C (8−10 h) and subsequently aged for 48 h at 60 °C. Further aging of the monoliths was performed in a 1 M NH_4OH solution for 10 h at 90 °C. The as obtained monoliths were then neutralized with a 0.1 M HNO_3 solution and washed several times with ethanol (25 wt %) under continuous flow. The monoliths were dried under supercritical conditions in CO_2 for 12 h, then calcined at 550 °C for 5 h under air (heating ramp 1 K min^{-1}).

Preparation of AuNP@SiO₂. Silica (SiO_2) monolith fragments were used as the substrate for gold nanoparticle (AuNP) deposition. The size of the fragments varied from 5 to 15 mm in length and width. The deposition of AuNPs onto

SiO_2 was achieved by in situ reduction of Au(III) ($HAuCl_4$ in 2 M HCl; 1000 mg Au L^{-1}, Sigma-Aldrich, St. Louis, USA) to Au(0). The initial pH (<1) of the Au(III) solution was adjusted to 12−13 by slowly adding 7 M sodium hydroxide aqueous solution (NaOH, Merck, Darmstadt, Germany). The SiO_2 monolith was then immersed in 10 mL of this alkaline solution having a Au concentration of approximately 4×10^{-3} M. To this solution 2.5 mL of a 0.22 M hydroxylamine hydrochloride aqueous solution were added ($NH_2OH*HCl$, Merck, Darmstadt, Germany). The container was closed and placed on a shaker at 150 rpm for 15 min. The reduction of Au(III) to Au(0) started immediately after addition of $NH_2OH·HCl$ solution. The colorless solution turned to purple and the formation of aggregates of AuNPs was observed. The AuNP@ SiO_2 monolith appeared dark purple and was thoroughly rinsed with ultrapure water (UPW). Then, the AuNP@SiO₂ was calcined in ambient air applying a heating rate of approximately 1 °C min^{-1} and holding a maximum temperature of 500 °C for 2 h. After calcination the AuNP@SiO₂ showed a light pink color.

Characterization of AuNP@SiO₂. The imaging studies of the prepared AuNP@SiO₂ sorbent were performed on a Hitachi S-5200 cold field emission scanning electron microscopy (SEM; Hitachi, Tokio, Japan) instrument. The sample was attached to a stainless steel sample holder and covered with a few nm thick conductive layer of carbon (2400 V, 90 mA) to overcome charging effects. Imaging was performed at an acceleration voltage of 10 kV and emission current of 10 μA.

The surface area, the pore diameter, and volume of the noncoated as well as of the AuNP@SiO₂ material were calculated from N_2 sorption measurements carried out at 77 K using a Quadrasorb Si sorptometer (Quantachrome Instruments) after outgassing the samples at 425 K for 6 h.

The Au amount on AuNP@SiO₂ monoliths was determined by total reflection X-ray fluorescence analysis (TXRF) after extracting and dissolving Au from the monolith by immersing it in freshly prepared aqua regia overnight. The extraction solution was diluted with UPW and spiked with 1 mg L^{-1} vanadium standard solution (NH_4VO_3 in 0.5 M HNO_3, 1000 mg L^{-1}; Merck, Darmstadt, Germany) for internal calibration. After thorough mixing, 10 μL of the sample was applied onto a silicone-coated quartz glass carrier. The liquid was evaporated at 60 °C on a heating plat and the carrier was analyzed by TXRF with an S2 Picofox instrument (Bruker, Berlin, Germany) equipped with a molybdenum tube and a silicon drift detector. The measurement was performed at a tube voltage of 50 kV, a current rating of 600 μA, and a lifetime of 1000 s. The limit of detection (LOD) for Au was 0.17 μg L^{-1}.

Procedure for Mercury Accumulation onto AuNP@ SiO₂ Monolith. AuNP@SiO₂ monolith was exposed to either 4 mL or 4 L of a sample solution, respectively, using a batch procedure at room temperature. Accumulation times of 1, 3, 5, 7, 10, 30, 60, 1125, and 1135 min were investigated. After exposure to Hg solution, the AuNP@SiO₂ was rinsed thoroughly with UPW and placed in a quartz tube for thermal desorption. As sample solutions for development and optimization of the procedure Hg(II) model solution in 0.06 M hydrochloric acid (HCl) were used. Accordingly, 0.06 M HCl served as a blank sample. Moreover, Hg(II)-spiked and nonspiked natural waters were investigated by the same procedure. For all experiments performed at 4 mL sample volume, a precleaned glass vessel with snap-on cap was used
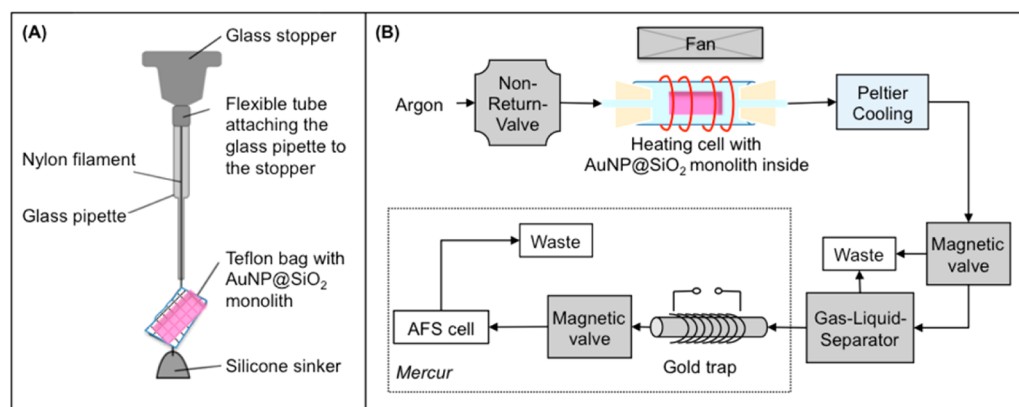
Figure 1. (A) Schematic illustration of the sampling device used for accumulation experiments in 4 L sample volume. (B) Flow injection system for Hg desorption and detection by atomic fluorescence spectrometry (AFS).

and the AuNP@SiO$_2$ adsorbent was placed in the container without any auxiliary means. To simulate turbulent conditions the vessel was placed on an orbital shaker at 150 rpm during accumulation. For the simulation of infinite water body, the sorbent was exposed to 4 L of the respective solution under stirring. For these experiments, a special sampling device was designed in order to keep the monolith centered in the 4 L round-bottomed flask during the duration of accumulation. A scheme of this setup is depicted in Figure 1A. The AuNP@SiO$_2$ was put inside a custom-made Teflon net carrier bag which was attached to a glass pipet with a nylon filament. On the other end of the filament a silicone stopper was attached as a sinker to prevent AuNP@SiO$_2$ from floating on the surface of the solution. This holding device was attached to a glass stopper that fitted the 4 L flask.

After Hg preconcentration, the AuNP@SiO$_2$ was rinsed with UPW and subsequent Hg desorption and detection was carried out as described in the following section.

Reagents, Instrumentation, and Methods for Hg Analysis. Mercury trace analysis requires specific working and cleaning conditions. Thus, all measurements were conducted in a special trace-clean laboratory equipped with an air exchange system to keep constantly low atmospheric Hg levels. Mercury solutions with a concentration higher than 1 μg L^{-1} were handled in another laboratory in order to avoid cross-contamination in the ventilated room. Mercury model solutions and natural water samples were prepared in glass vessels that were specially precleaned as described in Leopold et al.[29] All Hg solutions were made from a stock standard solution (Hg(NO$_3$)$_2$ in 2 M HNO$_3$, 1000 mg Hg L^{-1}, Sigma-Aldrich, St. Louis, USA) by dilution of adequate volumes in dilute HCl (p.a., [Hg]$_{max}$ = 0.001 mg L^{-1}, Merck, Darmstadt, Germany). Standards containing 10 mg Hg L^{-1} or more were prepared monthly, concentrations below 100 μg Hg L^{-1} weekly, and solutions with concentrations below 1 μg Hg L^{-1} were prepared freshly before use. High-purity water from a Synergy UV ultrapure water system (Merck Millipore, Billerica, USA) with a resistivity of 18.2 MΩ was used for preparation of all aqueous solutions and cleaning procedures.

Mercury detection by AFS was performed with a Mercur instrument (Analytik Jena AG, Jena, Germany) at 253.7 nm and a detector voltage of 391 V. As a reference method, samples were analyzed by CV-AFS according to the United States Environmental Protection Agency (US EPA) standard method 1631.[30] Bromine chloride solution (BrCl) in 12 M HCl for

oxidation of Hg compounds and organic matrix decomposition in natural water samples was prepared from potassium bromide (KBr, Merck, Darmstadt, Germany) and potassium bromate (KBrO$_3$, Merck, Darmstadt, Germany). For Hg decontamination, the two salts were heated to 150 °C for 2 h before dissolving in 36 % (w/v) HCl. Stannous chloride (SnCl$_2$·2 H$_2$O, p.a., [Hg]$_{max}$ = 10^{-6} % (m/m), Merck, Darmstadt, Germany) was used as a reducing agent and NH$_2$OH·HCl (p.a., [Hg]$_{max}$ = 10^{-6} % (m/m), Merck, Darmstadt, Germany) as a prereductant. Both were applied without further purification.

For Hg detection after accumulation onto herein-described AuNP@SiO$_2$ monoliths, a flow injection system (FIS) was setup and coupled to an AFS. A scheme of this computer-controlled FIS is shown in Figure 1B. After Hg preconcentration, the sorbent is placed in a quartz glass tube and Hg^0 is thermally desorbed and transported by an argon carrier stream (p = 4 bar) into the flow-through detection cell of the AFS. A custom-made heating coil prepared from a Cr/Al/Fe wire surrounds the quartz glass tube (L = 75 mm; ID = 8.5 mm; wall thickness = 1 mm). Removable silicone plugs allow introduction of AuNP@SiO$_2$ into the tube and provide sealed connection to the tubing (modified fluoralkoxy, MFA, ID = 1 mm) of the FIS. The tube serves as flow-through heating cell for thermal Hg desorption. The stepwise temperature program for this purpose is given in Table 1.

Table 1. Temperature Program for Drying and Thermal Hg Desorption from AuNP@SiO$_2$ Monolith in the Heating Cell of the FIS

time [s]	temperature[a] [°C]
10	20
30	82
50	178
70	606
90	614
110	614

[a]As measured at inner quartz glass tube wall.

Stepwise heating of the cell from room temperature to maximum 614 °C leads first to release of water vapor and then to thermal desorption of Hg^0. A Peltier cooling device (Analytik Jena AG, Jena, Germany) in connection with a gas–liquid-separator (GLS) ensures condensation and separation of water that is set free during this process. Magnetic valves allow

automatic control of the gas flow within the FIS. During the drying step the gas flow contains significant amount of water droplets and is directed to the waste. When thermal desorption of Hg^0 starts at temperatures above 350 °C, the gas flow is passed over the GLS and transported through a Nafion water-permeable drying membrane toward the AFS detection cell. Thereby, residual humidity in the gas stream is removed, which guarantees that quenching of the Hg fluorescence signal by water is avoided. For rapid cooling of the heating cell upon thermal desorption, a fan was installed above it.

The FIS was also applied for removal of Hg contamination from freshly prepared $AuNP@SiO_2$ monoliths by successive thermal desorption until constant and low signal intensity ($I <$ 0.0008) was obtained.

Calibration for Mercury Quantification. To quantify the accumulated mass of Hg on the $AuNP@SiO_2$ monolith the AFS was calibrated by a previously developed method using loose Au-coated silica for quantitative Hg adsorption from a defined sample volume. The preparation of the sorbent and the setup of the collector was described in detail elsewhere.[25] Hg(II) standard solutions were prepared in 0.06 M HCl with concentrations of 1, 10, 25, and 50 ng L^{-1}, which results in absolute Hg masses of 3, 28, 69, and 138 pg when applying 2.76 mL sample volume. The fluorescence intensity (I) resulting from 0.06 M HCl without Hg(II) spike was used for blank correction. The obtained calibration function was $I = 0.00043 \times m(Hg) - 0.000\,14$ with $R^2 = 0.9984$. Further analytical figures of merit for this calibration are listed in Table S1 in the Supporting Information.

For determination of Hg concentration in unknown sample solutions, calibration experiments with $AuNP@SiO_2$ monoliths were performed. For this purpose Hg(II) standard solutions in 0.06 M HCl with Hg concentration of 2, 5, 10, and 15 ng L^{-1} were prepared and the $AuNP@SiO_2$ monolith was exposed to 4 mL of the respective sample solutions for 1 min under turbulent conditions. After rinsing it with UPW, the sorbent was placed in the heating cell for desorption and detection of atomic fluorescence. The calibration function obtained was $I = 0.00023 \times [Hg] + 0.000\,09$ with $R^2 = 0.9763$.

Collection of Natural Waters. Natural water dedicated to Hg(II) trace detection was sampled on 13th of March 2011 from Font Estramar (42° 51′ 31.73″N 2° 57′ 30.776″E), which is a submarine groundwater discharge (SGD) located at Salses-le-Château (Pyrénées Mountains) at the edge of Corbières Mountains (France). SGDs are typically enriched in trace metals, including Hg, and have a low particle load. An unfiltered sample was taken and stored into a 2 L Teflon fluorinated ethylene propylene (FEP) bottle. Chloride concentration in this water was 34 mM and dissolved organic carbon (DOC) concentration was 1.2 mg L^{-1}. Water temperature of 17.5 °C and pH of 7.4 was measured on-site. The sample was acidified with double distilled HCl (0.4% v/v).

A second set of samples was taken in the Black Sea. Research vessel *Pelagia* occupied 12 full depth stations in the Black Sea along an east–west transect from 13th to 25th of July 2013 during the Dutch-led Mediterranean/Black Sea GEOTRACES cruise. High resolution vertical profiles were sampled using an ultraclean titanium frame[31] equipped with 24 × 24 L polyvinylidene fluoride bottles. The sample for this study was taken on July 18th 2013 in the eastern gyre (38.684°E; 42.349°N) of the Black Sea at 69 m depth. The sample was filtered (0.2 μm, Sartobran 300), drawn directly into individual

precleaned 1 L Teflon FEP bottle and acidified with double distilled HCl (0.4% v/v).

Recovery Experiments in Natural Waters. The applicability of the proposed method was proved by the investigation of two natural water samples. In the first recovery experiment, acidified seawater sample from the Black Sea was spiked with 2, 5, 10, and 15 ng Hg(II) L^{-1}. $AuNP@SiO_2$ monolith was exposed to 4 mL of the respective sample solution for 1 min under turbulent conditions. After it was rinsed with UPW, the sorbent was placed in the heating cell for desorption and detection of Hg. This complete analysis cycle was repeated 3-fold for each concentration. Calibration was performed analogously as described in the previous section. Original Hg concentration of this seawater sample was determined to be 0.56 ± 0.014 ng L^{-1} (as measured by AFS measurement according to Leopold et al.[25]). Hence, found Hg concentrations were corrected by this value in order to obtain meaningful recovery. The resulting recovery function including 12 data points is depicted in Figure S1 of the Supporting Information. For statistical evaluation, a confidence level of $P = 95\%$ was used.

In a second recovery experiment, the Hg concentration of a nonspiked SGD water sample was analyzed by the proposed method in analogous manner to the above-described experiment and by two reference methods. CV-AFS measurement according to U.S. EPA method 1631[30] was performed at Institute for Analytical and Bioanalytical Chemistry (University of Ulm, Germany). In parallel, the sample was analyzed for total Hg by modified U.S. EPA method 1631 as described by Heimbürger et al.[32] at the Géosciences Environnement Toulouse laboratory (France). All measurements were repeated three times and a confidence level of $P = 95\%$ was applied for statistical evaluation of uncertainty.

■ RESULTS AND DISCUSSION

Characterization of $AuNP@SiO_2$. In this study, meso-porous–macroporous silica monoliths were used as a substrate for AuNP deposition that serve as a selective solid-phase adsorbent for Hg trace level from natural waters. The thermal stability of silica and its chemical inertness should minimize interferences during preconcentration and thermal desorption of Hg in the analytical procedure. Furthermore, the well-defined porous structure of the SiO_2 monolith provides a large surface area and high number of adsorption sites and supports disperse and reproducible load of AuNPs. Moreover, in contrast to loose silica material, the modified monolith can simply be dipped into and removed from the sample solution for Hg trace accumulation without the necessity of further equipment.

The immobilization of AuNPs onto mesoporous–macroporous silica monoliths was performed via reduction of Au(III) (chloroauric acid) to Au(0) in alkaline aqueous solution in the presence of the monolith. A dark purple color of the monolith indicates immobilized AuNPs in a size range from 20 to 200 nm exhibiting surface plasmon resonance absorption in the visible light spectrum.[33,34] Because of the absence of any stabilizing agent in the presented synthesis, the in situ formed AuNPs are highly instable and therefore adsorb readily at the silica monolith surface. The dark purple color of the silica monolith slightly fades to a pink color after calcination at 500 °C for 2 h. The textural properties of the original silica monolith "Blank-SiO_2" and gold nanoparticle-decorated silica monolith "$AuNP@SiO_2$" are summarized in Table 2.

Table 2. Surface Characteristics of Blank-SiO$_2$ Monolith and AuNP@SiO$_2$

	surface area[a] [m^2 g^{-1}]	pore volume[b] [cc g^{-1}]	mean mesopore diameter Dv(d) [nm]
Blank-SiO$_2$	613	0.62	5.7
AuNP@SiO$_2$	404	0.50	6.0

[a]As derived from linear isotherm approach. [b]As derived from nonlocal density function theory method.

Both the specific surface area and the specific pore volume decreased markedly upon Au impregnation, while the mesopore diameter remained virtually constant. Furthermore, the adsorption−desorption hysteresis of H2-type remained unaffected by Au incorporation, which suggests that the Au nanoparticles are present on top of the mesoporous silica walls and do not penetrate into the mesopores. This is to be expected, as the size of the Au nanoparticles greatly exceeds that of the mesopore diameter. However, the decrease in specific pore volume and the specific surface area is larger than what would be expected merely taking the increase in mass upon Au loading into account (see below), which can be due to partial blocking of mesopores by the Au nanoparticles, and also due to partial hydrolytic degradation of the silica during Au loading and/or due to capillary action upon subsequent drying.

The morphology of AuNP@SiO$_2$ after calcination was studied by scanning electron microscopy (SEM). Figure 2A depicts an exemplary secondary electron image with a magnification of 5000× times. The corresponding back-scattered electrons (BSE) emitted from the gold nanoparticles are shown in Figure 2B. The average size of the NPs, evaluated from three individual images, is 67 ± 51 nm (N = 1719). An exemplary BSE image for size determination of NPs with a magnification of 30 000× times is shown in Figure 2C. The corresponding particle size distribution is shown in Figure 2D. From previous investigations of our group, it is known that AuNPs in this size range are able to enhance adsorption of different Hg species from waters. The catalytic activity of the nanogold provides elimination of complexing ligands, stripping of alkyl groups, reduction of Hg(II) to Hg(0) and formation of Hg−Au alloy.[25,26]

The Au load and size distribution of the NPs is controlled by several factors including the concentration of HAuCl$_4$, volume to mass ratio of HAuCl$_4$ to support, base type, reaction time, temperature, washing/drying steps, and calcination temperature.[35] Under the conditions applied here, a homogeneous AuNP distribution with clear interparticle spacing is achieved as can be seen in the BSE image in Figure 2B. For further characterization of the material, the amount of deposited Au was determined via TXRF analysis after extracting the Au into aqua regia. The average Au load on silica monolith was found to be 1.92 ± 0.12 μg Au per mg SiO$_2$.

The stability of the AuNPs on the silica substrate is essential for its application as adsorbent in Hg preconcentration. Here, the addition of dilute HCl is common for stabilization of calibration standards and natural water samples. Hence, another extraction experiment was carried out immersing the AuNP@SiO$_2$monolith in dilute HCl at room temperature for 10 min or 6.5 h, respectively. The Au concentration in the supernatant was checked by TXRF measurement and was found to be below the limit of detection of 0.17 μg L^{-1}. Hence, stability of AuNPs on the monoliths under these conditions was successfully proven.
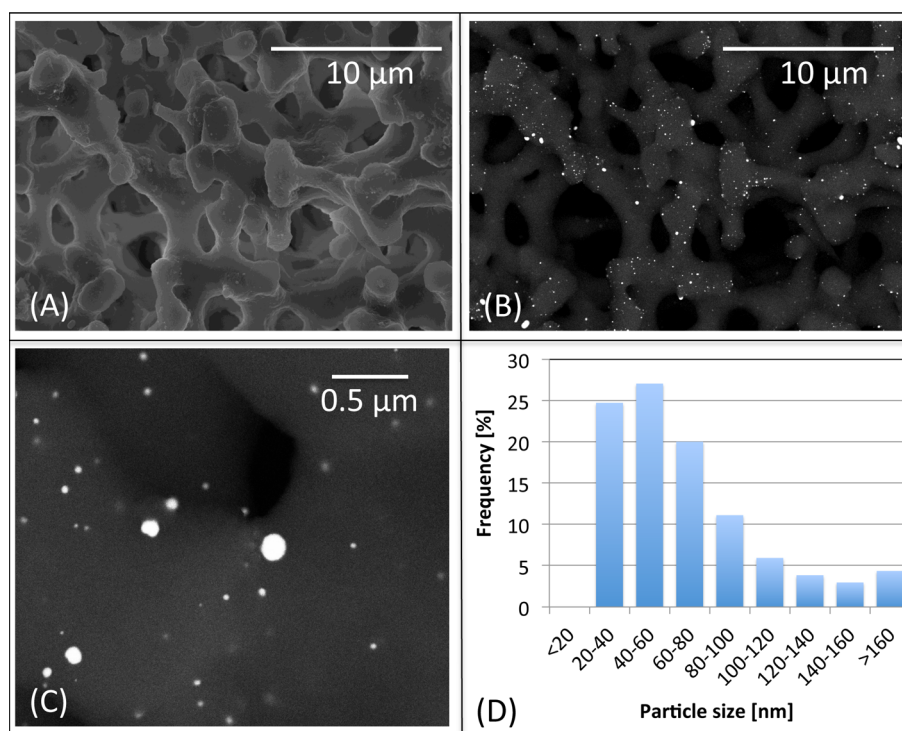
Figure 2. Exemplary scanning electron microscopy (SEM) images of AuNP@SiO$_2$ after calcination at 500 °C. (A) Visualization of porous structure by secondary electron detection. (B) Visualization of AuNPs on porous structure by backscattered electron detection. (C) Visualization of AuNPs for particle size determination (D) Particle size distribution of AuNPs on SiO$_2$ monolith (N = 1719; particle size given as major particle length).

General Procedure for Accumulation, Desorption, and Detection of Mercury. The novel AuNP@SiO$_2$ was applied as passive sampler for Hg traces from natural water samples. For optimization of the procedure, however, AuNP@SiO$_2$ was exposed to aqueous Hg(II) model solutions under varying conditions. Afterward AuNP@SiO$_2$ was rinsed with ultrapure water and Hg was released by thermal desorption in a custom-made heating device which was set up in a closed flow injection system (FIS) coupled online to an AFS for Hg detection (Figure 1B). Complete release of Hg^0 from the adsorbents was checked by performing thermal desorption several times for one and the same AuNP@SiO$_2$ monolith. The fluorescence intensity detected for the second (and third) desorption always equaled the blank value (i.e., the fluorescence intensity obtained for unused monolith) confirming quantitative release.

To obtain quantitative information from AFS measurements calibration is required. In this work, two different calibration strategies were applied. For quantification of the (absolute) Hg mass on a monolith after accumulation the AFS was calibrated by introducing a Hg collector that is able to quantitatively adsorb Hg from a defined sample volume. The resulting calibration function gives the correlation of the atomic fluorescence intensity to the Hg mass released by thermal desorption from a monolith. However, to be able to determine the Hg concentration of the original sample, i.e., an unknown concentration in a solution, it is necessary to perform a calibration experiment with the AuNP@SiO$_2$ monolith itself.

Accumulation of Mercury from Aqueous Model Solutions. First, time-dependent Hg accumulation onto AuNP@SiO$_2$ was investigated at concentrations of 10 and 100 ng Hg L^{-1}, respectively. A broad time range from 1 min to 19 h was covered in these experiments. Table 3 summarizes the proportion of Hg on the sampler after distinct time periods in percent of the initial amount present in the sample solution.

Table 3. Time-Depending Proportion of Accumulated Mercury from Aqueous Hg(II) Model Solutions

	proportion of accumulated Hg [%]	
time [min]	[Hg]$_0$ = 10 ng L^{-1}	[Hg]$_0$ = 100 ng L^{-1}
1	5	4
5	8	6
10	12	13
30	12	23
60	20	25
19 h	101	92

Within the first 10 min, rapid and nearly linear increase of Hg accumulation was observed at both tested initial concentrations. Hence, within this time period calibration of the system is easily possible. Quantitative Hg adsorption was reached after accumulation duration of approximately 1 day. These results indicate an irreversible and fast adsorption process. Obviously, adsorption of Hg(II) is followed by formation of very stable Au amalgam as discussed above and described by Zierhut et al.[26,36] The most important information deriving from this experiment in regard to the analytical applicability is, however, that the amount of Hg adsorbed after only 1 min is more than sufficient for subsequent reagent-free AFS detection. This is a clear advantage of the proposed method compared to common passive samplers that have typically to be deployed for at least a few hours up to several days in the water body before sufficient

preconcentration is obtained. Hence, problems like fouling and low time-resolution do not occur with this novel approach. Moreover, recovery experiments in natural waters confirm that the matrix does not affect adsorption kinetics within this short time interval (see below). Consequently, the proposed sampler is rather a "test stick" that is briefly dipped into the sample than a passive sampler that is deployed in the field.

In a proceeding series of experiments, the uptake rate of this novel adsorbent was determined in a manner that is consistent with calibration of, e.g., Chemcatcher, devices.[37] To simulate real conditions and to compare the obtained rate with values from literature, the sample volume was increased to 4 L, mimicking an infinite natural water body. Figure 3 presents the
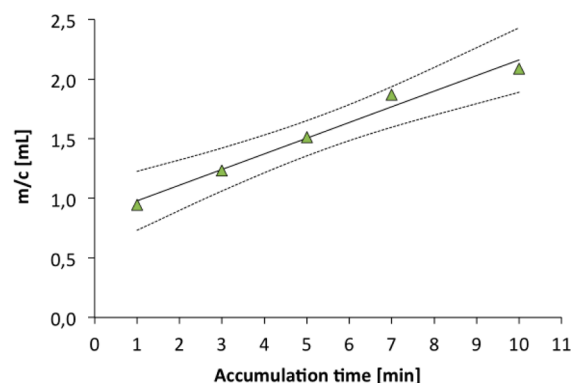
Figure 3. Determination of Hg uptake rate as slope of the mass to concentration ratio over a time range from 1 to 10 min (sample volume, 4 L; initial [Hg], 10 ng L^{-1}, room temperature, turbulent conditions; linear regression, m/c = 0.1312 mL min^{-1} × t + 0.8475 mL, R^2 = 0.9801).

uptake of Hg given as mass to concentration ratio over a time range from 1 to 10 min. Evaluation of the linear regression results in an uptake rate of 7.87 ± 2.06 mL h^{-1}. This is in the same range as for examples reported for a passive sampler consisting of thiol-functionalized silica sol–gel material proposed by Zhou et al.[19] (uptake rate: 8.78 mL h^{-1}). However, in the later approach digestion of the functionalized sol–gel in aqua regia for 24 h was mandatory prior to Hg detection by CV-AFS. In contrast, the herein presented method provides reagent-free, easy and fast Hg quantification after thermal desorption. Furthermore, multiple use of the AuNP@SiO$_2$ sampler is possible. Lifetime of the AuNP@SiO$_2$ monoliths was determined by repeating an analytical cycle consisting of immersing the monolith in a sample, rinsing, drying, and desorption of mercury until the monolith broke. This was performed with 4 individual AuNP@SiO$_2$ monoliths resulting in an average lifetime of 23 cycles.

The efficiency of the novel adsorbent material was investigated by concentration-dependent 1 min accumulation experiments. This was performed with both, AuNP@SiO$_2$ monolith and pristine Blank-SiO$_2$ monolith, in model solutions in a range from 1 to 50 ng Hg(II) L^{-1}. The obtained results confirm what was to be expected: The AFS signal intensity (I) increases linearly with the Hg concentration when applying AuNP@SiO$_2$ monolith (I = 0.0002 × [Hg] + 0.0013; R^2 = 0.9837). In contrast, the signal intensity obtained after thermal desorption of Hg from Blank-SiO$_2$ monolith follows a flat logarithm function, i.e., it increases slightly with Hg concentration up to 10 ng L^{-1} and then remains constant at the low value of I = 0.0012. These results prove that the

immobilized AuNPs on the silica monolith substrate exhibit specific adsorption efficiency for Hg from water, whereas the silica monolith provides only low adsorption capacity.

Accumulation of Mercury from Natural Waters and Validation. For proof of principle of the presented approach, the procedure was applied to seawater and SGD water samples. The seawater originates from the Black Sea (38.684°E; 42.349°N) and was used for recovery experiments with Hg(II) spikes in a concentration range from 2 to 15 ng L^{-1}. The recovery function obtained for replicate measurement ($n = 3$) of 4 different spike concentrations was $y = 1.0108x - 0.9173$ ($R^2 = 0.9701$; see Figure S1 in the Supporting Information). Hence, an excellent recovery rate of 101.1 ± 12.5% and unbiased blank value (0.9173 ± 1.1756 ng L^{-1}) were achieved revealing the absence of any matrix effects. This successful recovery experiment confirms the applicability of the novel approach for accurate Hg trace determination in seawater.

Moreover, the feasibility of the new methodology for determination of total dissolved Hg in a (nonspiked) SGD water sample was also tested. The water was collected from a karstic spring, namely Font Estramar (42° 51′ 31.73″N 2° 57′ 30.776″E). The result for the total Hg concentration found by dipping the AuNP@SiO$_2$ monolith 1 min into the SGD water and successive detection by AFS was compared with the result obtained from U.S. EPA method 1631[30] (oxidative digestion followed by CV-AFS). In addition, the sample was analyzed for total Hg by U.S. EPA method 1631 modified as described by Heimbürger et al.[32] at the Géosciences Environnement Toulouse laboratory (France). All results are summarized in Table 4.

Table 4. Total Dissolved Mercury Concentration in SGD Water Found by Application of Different Analytical Methods

method	Hg concentration [ng L^{-1}]
this work	7.97 ± 0.70[a]
standard U.S. EPA method 1631[30]	6.90 ± 0.33[a]
modified U.S. EPA method 1631[32]	9.43 ± 0.94[b]

[a]Measured after several month of storage. [b]Measured several days after collection; $n = 3$, $P = 95\%$).

The value found by application of the herein presented novel method agrees well with the Hg concentrations found by the standard method U.S. EPA method 1631. Calculation of the extended uncertainty ($U_\Delta = 1.55$; coverage factor $k = 2$) and comparison with the absolute difference ($\Delta_m = 1.07$) confirms that there is no significant difference between these values.

Analogously statistical evaluation of the difference between the values obtained by this method and modified U.S. EPA method 1631 method reveal no significant difference. Hence, comparability of the quantitative Hg trace determination in the natural water matrix by the proposed method is given. However, an apparently lower Hg concentration was found with the standard U.S. EPA method in comparison to modified EPA method. This significant difference is most probably attributed to a loss of analyte during sample storage for several months, even though storage conditions and addition of stabilization reagents were selected with great care (for details, see the Experimental Section).

Evaluation of accuracy of the proposed method by application of certified reference material was not possible, due to the oxidizing reagents that are added for stabilization of natural water matrices and their interference with the nanogold of the sampler.

Analytical Figures of Merit. Finally, the most important analytical figures of merit for the proposed method were determined and are summarized in Table 5.

The presented solid-phase sampler consisting of AuNP@SiO$_2$ monolith as specific Hg adsorbent provides a LOD as low as 1.31 ng Hg L^{-1}. Moreover, this value was achieved after only 1 min of accumulation. Hence, prolonging this time interval can obviously further lower it. Together with the fact that the linear working range covers at least 4 orders of magnitude, the application of this method to pristine natural waters as well as to contaminated waters is possible. Furthermore, the trueness and comparability of the obtained results was confirmed for freshwater as well as for seawater matrixes.

■ **CONCLUSIONS**

A highly sensitive and selective novel solid-phase sampler for in situ Hg preconcentration from natural waters has been developed. The novel sorbent consists of a mesoporous–macroporous silica monolith decorated with gold nanoparticles. For accumulation of dissolved Hg traces from natural waters, immersing the sampler for only 1 min into the sample was sufficient to obtain a detection limit as low as 1.31 ng Hg L^{-1}. Quantification of Hg was performed after thermal desorption of Hg by means of AFS detection and external calibration. Combination of extremely short exposure time (1 min) with the fully reagent-free analytical procedure provides several unbeatable advantages. The proposed sampler can serve as a "test stick" that is briefly dipped into the sample rather than deployed in the field. Thereby, common disadvantages of passive samplers (e.g., fouling) are overcome. Easy-handling

Table 5. Analytical Figures of Merit for 1 min Accumulation Time

linear working range[a]	1.31−10 000 ng L^{-1}
regression coefficient (R^2)	0.9763
method standard deviation	10.56%
detection limit as derived from calibration function[38]	1.31 ng L^{-1}
accumulation rate	7.87 mL h^{-1}
relative standard deviations ($n = 3$)	
for blank solution (0.06 M HCl)	3.57%
for standard solution with 10 ng Hg L^{-1}	4.34%
for seawater spiked with 10 ng Hg L^{-1}	5.37%
lifetime of AuNP@SiO$_2$ monolith	ca. 23 cycles

[a]Sample volume, 4 mL; calibration range, 2−15 ng Hg L^{-1}; higher concentrations than 10 000 ng L^{-1} were not tested in order not to contaminate the experimental setup.

accumulation procedure followed by reagent-free Hg quantification after thermal desorption significantly minimize the contamination risk and analyte loss during sampling, transportation, and sample pretreatment. Moreover, it shortens sampling procedure because rinsing of sampling containers, filtration of the sample, and addition of stabilizing reagents are omitted. First validation experiments performed in both, seawater and SGD natural waters confirmed the accurate determination of Hg traces. Further in situ investigations will have to show the robustness of the method in the field. Before this, however, optimization of the material and/or the procedure is planned in order to prolong the lifetime of the sampler and lower the detection limit for its application to open ocean seawater.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b03303.

> Parameters of the mass calibration, and recovery of Hg(II) spike in seawater (PDF).

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Notes

The authors declare no competing financial interest.

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