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Analysis of total dissolved mercury in waters after on-line preconcentration on an active gold column

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ABSTRACT

A reagent-free fully automated flow injection analysis (FIA) system coupled to atomic fluorescence spectrometry (AFS) for mercury (Hg) quantification is reported, using active nano-structured gold collectors for direct preconcentration of dissolved mercury species from natural waters. Recently we had shown the potential of such an approach for Hg analysis in seawater. This paper now describes the optimisation and validation of the proposed method including the investigation of possible limitations arising with matrix constituents, such as dissolved organic carbon (DOC). A broad variety of water matrices (seawater, river water, moorland water, effluent from wastewater treatment plant) were investigated in order to check the feasibility of the proposed method for total dissolved Hg determination in natural waters. All FIA parameters were optimised by checking Hg recovery in real water samples. Figures of merit of the proposed method – working range, carry over effects, detection limit, reproducibility, etc. – were determined. The method provides a high sensitivity (detection limit: 0.2 pg Hg) and very good reproducibility (RSD 1.1%, [Hg] = 5 ng L^{-1}, n = 10). It offers several advantages because no reagents are needed for species conversion, preconcentration, or desorption and therefore the risk of contamination and blank values are lowered, reagent and time consumption are minimized. The system was successfully validated by measurement of a series of recoveries in real waters (all >96%) and in the certified standard reference material BCR 579 (mercury in coastal sea water, recovery 100.5%). Furthermore, the proposed method was applied to 15 real water samples for Hg ultra trace analysis.

1. Introduction

Environmental mercury (Hg) monitoring is very important due to its high toxicity. Mercury is released to the environment through natural and anthropogenic processes and is distributed globally [1]. Nowadays, mercury levels of the land, atmosphere and ocean have increased by a factor of 3–5 due to human activities [2] and approximately one third of the total atmospheric mercury emission is of direct anthropogenic origin [3]. Bioaccumulation in the aquatic food chain has been well documented and factors of 10^6 from water to predatory fish are reached [4–6]. Furthermore, the portion of the most toxic mercury species – methyl mercury – of the total mercury content increases with the trophic level from a value of approximately 5% in water to over 95% in fish tissue [4,7]. Therefore, fish consumption is the most important exposure risk for human and wildlife posing a serious risk to health and enormous costs to public health systems [8]. Consequently, the determination of mercury in the hydrosphere is mandatory in the European Water Framework Directive, where mercury and its compounds are classified as one of the 20 priority hazardous substances.

Among the techniques that have been developed for mercury analysis during the past decades only few are sufficient for mercury determination in the sub ng L^{-1} range, as required for the analysis of natural water samples. Comprehensive reviews on mercury ultra trace analysis techniques are given by e.g. Clevenger et al. [9] and Leopold et al. [10]. Highly sensitive detection methods combined with preconcentration and matrix separation techniques are useful for this purpose. Commonly applied sensitive detection techniques are atomic fluorescence spectrometry (AFS) [11,12] or inductively coupled plasma-mass spectrometry (ICP-MS) [13,14]. For matrix separation and preconcentration cold vapour (CV) generation and subsequent Hg vapour trapping on precious metal traps [11–16] or solid phase microextraction (SPME) techniques in combination with species derivatisation [17–21] are often used prior to Hg detection. The combination of CV generation and AFS detection provides a high sensitivity and is therefore recommended for Hg analysis in natural waters by several standard methods, such as the European Standard (EN) and International Organization for Standardization (ISO) method 17852:2006 and the United States Environment Protection Agency (US EPA) method 1631. However,

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the practical detection limit in mercury ultra trace analysis is often restricted by mercury blank values that arise with contamination of the applied reagents. CV generation technique requires the addition of several reagents for decomposition and subsequent reduction of dissolved mercury species to Hg^0, whereas SPME techniques often use reagents for species derivatisation and/or complexation. Therefore, these techniques require elaborative and time-consuming cleaning procedures for the applied reagents and often the remaining Hg blank still lowers the sensitivity and accuracy of the proposed analytical method. Furthermore, the use of harmful and/or toxic reagents (that are often used for sample digestion) is a drawback, especially for *in situ* mercury monitoring e.g. on shipboard. Several approaches have been reported to overcome these limitations in mercury ultra trace analysis leading to green analytical chemistry [22], lower reagent consumption [23–25], the use of flow injection systems [26,27] and *in situ* preconcentration [28].

Recently, we have reported that nano-structured gold surfaces retain dissolved mercury species (Hg^0, Hg^{2+} and $MeHg^+$) with comparable adsorption rates directly from aqueous phases [29]. Hence such collectors have a high potential for the preconcentration of dissolved mercury species from natural water samples without the need for any reagents.

Therefore the aim of this work was to set-up an optimised FIA system for direct preconcentration of total dissolved Hg species from natural waters onto active nano-gold microcolumns. The fully automated system is coupled to AFS for highly sensitive mercury quantification. The main focus of this work was to optimise and validate the method, show its robustness and investigate possible limitations. For this purpose the influence of different water ingredients, such as dissolved organic carbon (DOC) and salinity, was tested. The system was validated by measurement of a series of recoveries in real water matrices and in the certified standard reference material BCR 579 (mercury in coastal sea water) [30]. The feasibility of the proposed method for dissolved Hg analysis in different natural waters was investigated by application to 15 real water samples.

2. Materials and methods

2.1. Instrumentation

The analysis of mercury in the lower to sub-ng L^{-1} range requires rigorous clean working conditions to minimize contamination from the ambient environment. Therefore, all instrumentation for mercury determination was set-up in a class 100 clean room where all experiments were performed. In order not to contaminate the clean room, only solutions containing <5 μg Hg L^{-1} were handled in there.

An atomic fluorescence spectrometer (AFS, mercur, Analytik Jena AG, Jena, Germany) was used for mercury resonance fluorescence detection at 253.7 nm. The system offers both, direct detection and the possibility of mercury vapour preconcentration on an integrated gold trap. The atomic fluorescence spectrometer was coupled to the developed FIA system for direct preconcentration of dissolved mercury species from aqueous samples on an active gold collector.

Fig. 1A shows the FIA manifold that consists of peristaltic pumps (HS 60, Analytik Jena AG) a heatable collector, magnetic valves and a gas–liquid separator. The FIA was interfaced to a personal computer and controlled by special software developed by Analytic Jena AG. Pharmed® tubing was used for the transport of solutions with peristaltic pumps and methoxyfluoroalkyl (MFA, I.D. = 1 mm) was used for all other tubing.

UV digestion of natural waters was performed using 50 mL quartz glass flasks that were placed in front of a UV lamp (254 nm, 8 W, Camag, Muttenz, Switzerland) inside a box lined with aluminium foil. For a more homogeneous irradiation, the flasks were rotated every hour. After digestion the samples were cooled to room temperature and analysed for Hg without any further transfer in order to avoid potential losses of UV generated Hg^0.

Dissolved organic carbon (DOC) in real water samples and stock DOC solution was measured as non-particular organic carbon (NPOC) with a total organic carbon analyser (High TOC II, Elementar Analysensysteme, Hanau, Germany) using the EN 1484 DEV H3

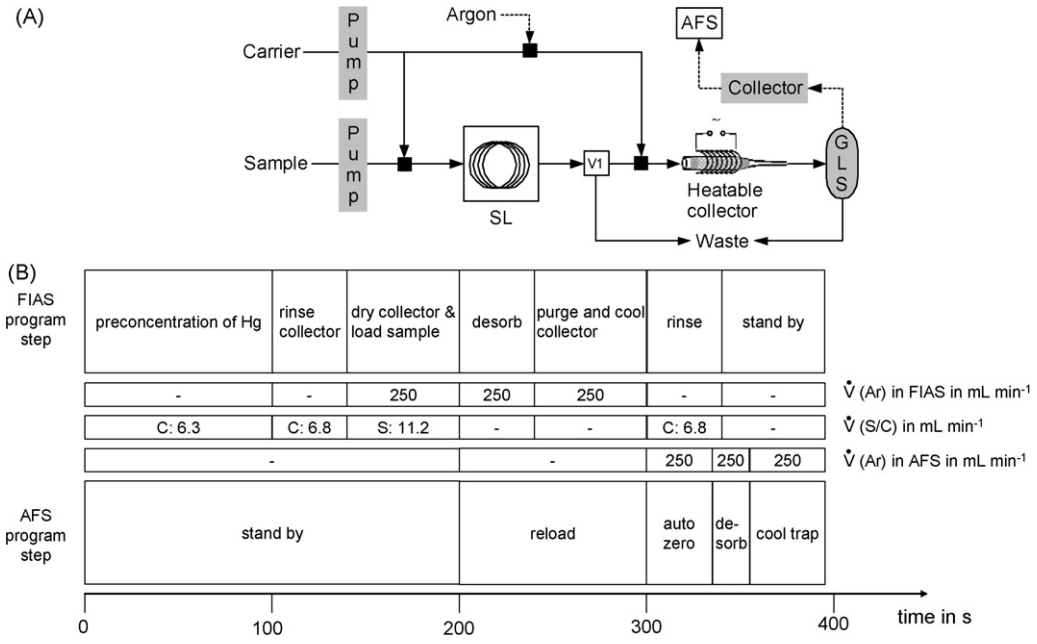

Fig. 1. (A) Flow injection manifold for direct preconcentration of dissolved Hg species onto a nano-gold collector. (B) Time line of the procedural steps for flow injection atomic fluorescence measurement. Abbreviations: SL, sample loop (2.5 mL); V, magnetic valve; GLS, gas–liquid separator; AFS, atomic fluorescence spectrometer; ■ T-joint; —, liquids; - - -, gases; FIAS, flow injection analysis system; S, sample and C, carrier.

method. This method provides a detection limit of 1.0 mg L^{-1} and a relative standard deviation (RSD) <10%.

The gold surfaces were examined using a scanning electron microscope (SEM, JEOL JSM 5900 LV, JEOL Ltd., Tokyo, Japan) equipped with a RÖNTEC system for energy dispersive X-ray spectroscopy (EDX).

2.2. Flow injection analysis procedure

In the following the general procedure for preconcentration and desorption of Hg in the flow injection analysis (FIA) system is described. First, preconcentration of dissolved mercury species onto the active gold collector is performed. A sample volume of 2.5 mL, which is defined by the length of the sample loop, is transported through the FIA system by the carrier solution (0.5%, v/v HCl). Then the collector is rinsed with carrier solution and dried in an argon stream (250 mL min^{-1}). Meanwhile the sample loop is loaded for the next measurement. The adsorbed mercury is released from the collector by heating (700 °C) and an argon gas stream transports the Hg vapour to an in-build gold trap for mercury reload by amalgamation. On the way to the in-build gold trap the gas stream passes a gas–liquid separator (GLS) and a water-permeable membrane tube for the removal of remaining water. The hot active gold collector is purged and cooled in an Ar gas stream. As a last step the collector is rinsed with carrier solution to ensure the complete cooling of the gold collector to room temperature. The optimised timeline and flow rates for the FIA procedure coupled to AFS are summarised in Fig. 1B.

2.3. Chemicals and cleaning procedures

Ultra pure water (UPW) with a resistivity of 18.2 MΩ cm was obtained from a Milli-Q-Gradient system (Millipore, Billerica, USA) and was used for preparation of all aqueous solutions. Mercury stock standard solutions of 10 mg Hg L^{-1} as Hg^{2+} or $MeHg^{+}$ were prepared weekly from commercially available standard solutions (mercury(II)nitrate, 1000 mg L^{-1}, Merck, Darmstadt, Germany; methylmercury chloride, 1000 mg L^{-1}, Alfa Aesar, Karlsruhe, Germany) by dilution in 0.5% (v/v) hydrochloric acid (HCl) and were stored in the dark at 4 °C. Solutions with mercury contents lower than 10 mg Hg L^{-1} were prepared daily prior to analysis by adequate dilution of 10 mg Hg L^{-1} stock mercury solution in 0.5% (v/v) HCl.

Elemental mercury standard solutions were prepared freshly before each experiment by purging Hg^0 vapour with a nitrogen carrier stream (50 mL min^{-1}) into 0.5% (v/v) hydrochloric acid for 5 min at room temperature. The resulting stock solutions were investigated for their Hg^0 concentration by AFS and standard solutions were prepared by diluting with 0.5% (v/v) hydrochloric acid.

All chemicals were purchased in the highest available purity and/or purified by the following procedures. Hydrochloric acid (p.a. max 0.001 mg Hg L^{-1}, Merck, Darmstadt, Germany) – used for acidification of samples, standard and carrier solution (0.5%, v/v HCl) – was efficiently reduced in Hg contamination by adding 0.1 g of $NaBH_4$ (p.a., Merck, Darmstadt, Germany) to 400 mL of hydrochloric acid and purging the solution for 12 h with nitrogen (120 mL min^{-1}). The nitrogen was purified by passing it over a homemade activated carbon/sulphur column (activated carbon: granular, 2.5 mm, Merck, Darmstadt, Germany; sulphur: elemental sulphur for external pharmaceutical application, Merck). The glass column (length 180 mm; I.D. 55 mm) was filled with 500 mL of the carbon/sulphur mixture (sulphur content 3%, m/m) and had a sintered-glass filter.

NaCl (p.a., Merck, Darmstadt, Germany), Na_2SO_4 (p.a., Merck), $CaCl_2$ (technical, VWR BDH Prolabo, Darmstadt, Germany) and KCl (p.a., Merck) were heated in a drying oven at 260 °C for at least 24 h and KBr and $KBrO_3$ (both p.a., Merck) are pre-treated at 220 °C for 48 h to reduce mercury contamination by evaporation. $MgCl_2{\cdot}6H_2O$ (p.a., Merck, Darmstadt, Germany), $NaHCO_3$ (p.a., Merck, Darmstadt, Germany) and H_3BO_3 (p.a., Merck, Darmstadt, Germany) were used as purchased without further purification. Most salts were required for the preparation of the artificial seawater according to DIN EN ISO 10253 with a salinity of 33 practical salinity units (psu). Model solutions with lower salinity were prepared by appropriate dilution of this stock standard in UPW.

Dissolved organic carbon (DOC) stock solution was prepared by dissolving 110 mg of the sodium salt of humic acid (Roth, Karlsruhe, Germany) in 100 mL UPW. For this DOC stock solution a carbon concentration of 342 mg L^{-1} was determined. DOC model solutions were obtained by dilution of adequate amounts of the stock solution in 0.5% HCl (v/v).

For ethylene diamine tetraacetic acid (EDTA) interference test a Titriplex® III-Solution ($c(Na_2\text{-EDTA}{\cdot}2H_2O) = 0.1$ mol L^{-1}, Merck, Darmstadt, Germany) was added to mercury standard solutions.

Blank values in model solutions caused by the addition of matrix substances were carefully investigated and given results were corrected when necessary.

For the preparation of bromine chloride (BrCl) stock solution, 4.32 g of KBr were dissolved in 400 mL of hydrochloric acid. In a fume hood, 6.08 g of $KBrO_3$ were then added slowly under constant stirring. This process generates free halogens (Cl_2, Br_2, BrCl), which are released from the bottle. Therefore, the solution was stirred for another hour in a loosely capped bottle before the lid was tightened. Warning: because of the release of free halogens it is strongly recommended to work in an appropriate fume hood. The resulting saturated BrCl solution was used as a stock solution for the preparation of oxidant solution in the application of EPA method 1631 and as reagent for cleaning procedures (dilutions are further given as % (v/v) of the saturated stock solution). The stock solution was stored for a maximum of 1 week.

The gold collectors used for the direct mercury preconcentration consisted of a rolled up gold gauze (purity 99.99%; gauze size 20 mm × 30 mm; diameter of the wires 0.06 mm; 1024 meshes cm^{-2}, Heraeus, Hanau, Germany) placed in a quartz glass tube (length 70 mm; inner diameter 3 mm; wall thickness 0.5 mm) that was reduced in diameter at the flow outlet (inner diameter 0.5 mm). The rolled up gold gauze was fixed in the tube with quartz wool wads (4–12 μm, VWR, Darmstadt, Germany). Purification of the collectors was achieved by heating to 700 °C for at least 60 min. A detailed description of the activation procedure can be found in [29].

The cleaning of vessels was adapted according to the Hg concentrations to be handled. For the handling of solutions with mercury contents higher than 5 μg L^{-1}, glass vessels were used and cleaned with nitric acid steam in a steaming apparatus (quartz glass steaming apparatus, H. Kuerner Analysetechnik, Rosenheim, Germany) for at least 6 h, rinsed three times with ultra pure water and then kept under a laminar stream of particle-free air. For Hg concentrations lower than 5 μg L^{-1}, the vessels were treated with a BrCl solution (1%, v/v) for at least 24 h. After removing the BrCl solution, the vessels were rinsed with UPW three times and the whole procedure was then repeated. Polytetrafluoroethylene (PTFE) vessels were then put in plastic bags and kept in sealed plastic boxes in the clean room until use, whereas glass vessels were heated to 260 °C for at least 12 h in a drying oven. After cooling to room temperature, the vessels were put in plastic bags and kept in sealed plastic boxes in the clean room until use. Polyethylene (PET) containers for water sampling (VWR, Darmstadt, Germany) were used only once without previous cleaning. Mercury blank values of the PET bottles were examined for each acquired batch of bottles confirming absence of Hg contamination.

All pre-cleaned chemicals, collectors and containers were stored in the clean room.

2.4. Sampling and storage

Seawater samples from the North Sea were collected by the German federal office for maritime navigation and hydrography (Bundesamt für Seeschifffahrt und Hydrographie, Hamburg, Germany) and the Institute for Chemistry and Biology of the Marine Environment–Terramare (ICBM, Wilhelmshaven, Germany). Seawaters from 4 different sampling sites, namely a station off the coast (NGW8), two coastal stations (AMRU1, ELBE1) near Amrum and near Elbe esturary, respectively, and a shore water station near Wilhelmshaven (Groedendamm) were investigated. The sampling of North Sea water was performed with PTFE polymer containers with automated sealing controlled by a shipboard crane. A Black Sea water sample was taken manually at Varna harbour (Bulgaria) in a distance of 10 m to the shore in PET bottles. All seawater samples were determined without the use of UV digestion.

River, brook and lake water samples were collected manually in Bavaria in South-Eastern Germany in PET bottles. 2 samples were taken from the river Isar (near Munich) in 100 m and 5000 m distance to the outlet of the wastewater treatment plant (WWTP) Gut Grosslappen. Furthermore, a sample from the effluent of the WWTP itself was taken. Brook water samples from the Leuschnitz (near Wallenfels) were taken at 4 different sampling sites, namely the spring and in 3 distances from the spring of approximately 2000 m, 4000 m and 6000 m downstream. The first three sampling sites were located in the forest, whereas the last sample was taken in an inhabited area beside a street. The four lake water samples were collected in the surrounding area of Munich at the Starnberger See at Possenhofen, at the Ammersee in Herrsching, at the Wesslinger See in Wessling and at the Feringasee near Unterföhring/Munich.

The sampling procedure always included a 3-fold rinsing of the container with the water sample before it was filled up until no headspace remained. Samples were collected in depths of 20–30 cm underneath the water surface. All samples were filtered through 0.45 μm filters (either polyethersulfone or polycarbonate filters, VWR, Darmstadt, Germany; or cellulose membrane filter Sartorius, Goettingen, Germany) and acidified (by addition of HCl (0.5%, v/v) immediately after collection. The filters were pre-cleaned with 0.5% (v/v) HCl solution and mercury blank values were checked. Each filter was conditioned with 20 mL of the sample solution before the filtered water was collected in a bottle for storage and analysis. All water samples were stored in the dark at 4 °C until analysis.

The certified reference material BCR 579 (mercury in coastal sea water) was purchased from the Institute for Reference Materials and Measurements of the European Commission (IRMM, Geel, Belgium) and handled according to the recommendations given in the certificate.

3. Results and discussion

3.1. Optimisation of the flow injection analysis procedure

The most crucial points that had to be assured within the FIA procedure are:

- Reproducible and equivalent adsorption of all dissolved mercury species,
- Quantitative desorption of Hg from the gold collector,
- Complete removal of water for interference-free mercury AFS detection,
- Minimization of memory effects within the FIA system.

For the purpose of checking reproducible adsorption rate of mercury species onto the active gold collector model solutions of Hg^0, Hg^{2+}, $MeHg^+$ and Me_2Hg were passed over the collector and mercury was measured in the flowing through. Thereby, an adsorption rate of 83 ± 4% (for all Hg species) up to a concentration of at least 100 ng Hg L^{-1} was obtained at a sample flow rate of 6.3 mL min^{-1}. Higher flow rates lead to lower adsorption rates due to reduced residence time. However, more important in this regard is the composition of the sample solutions which can strongly affect the adsorption rate. Therefore, a systematic study on the impact of different matrix constituents is given in the next section.

Different heating temperatures of the gold collector were applied to assure quantitative release of Hg from the collector. A temperature of 700 °C for 40 s ensures complete thermal desorption.

Interference-free mercury detection by AFS requires the complete removal of water and water vapour from the collector and the tubing to the AFS cell, because water vapour in the fluorescence cell causes signal quenching and condensed water drops result in irreproducible values. In cold vapour generation technique a gas–liquid separator (GLS) is usually sufficient for this purpose. In the proposed method a more sophisticated procedure is necessary because, remaining water drops in the collector are evaporated during the heating step. Hence, not only water droplets have to be separated from the gas stream, but also water vapour has to be removed. For this purpose, beside a GLS for separation of condensed water droplets a water-permeable membrane tube that connects the GLS with an in-build gold trap assures removal of water vapour.

With these optimal adsorption/desorption conditions several recovery experiments with different Hg species in a concentration range from 0.4 to 5.5 ng L^{-1} were performed. In Fig. 2A the results of these measurements are presented as a recovery function reveal-

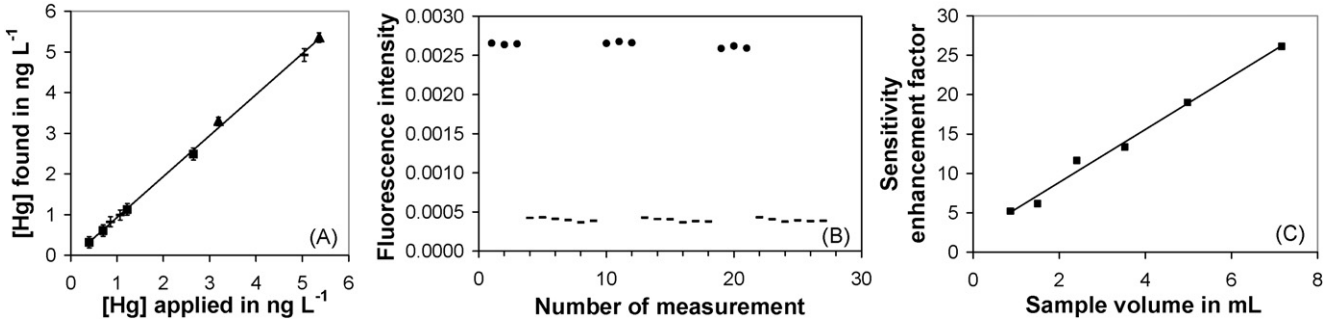

Fig. 2. (A) Mercury recovery from different model solutions containing (▲) Hg^0; (■) Hg^{2+}; and (-) $MeHg^+$ (recovery function: $y = 1.007x + 0.079$; regression coefficient $R^2 = 0.9985$, $n = 27$; error bars represent ± one standard deviation, $n = 3$); (B) Investigation of carry over effects: alternating measurement of (●) 10 ng Hg L^{-1} standard solution (as Hg^{2+}) and (-) blank solution (0.5% (v/v) HCl); (C) enhancement of sensitivity with increasing sample volumes given as a factor calculated from the slope of a calibration ([Hg] = 1–10 ng L^{-1}) obtained by the proposed method compared to cold vapour AFS measurement.

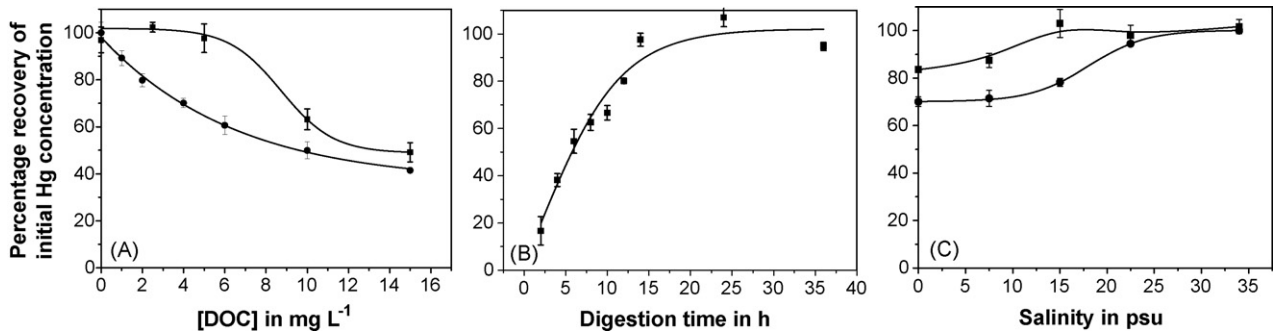

Fig. 3. Percentage of Hg recovery dependent on (A) DOC content in a model solution containing 5 ng Hg L^{-1} as a mixture of Hg^{2+} and $MeHg^{+}$ (1:1) (●) without UV digestion and (■) after 7 h of UV digestion, respectively, (B) digestion time in a natural moorland water sample with [DOC] = 14.5 mg L^{-1} and (C) salinity in a model solution containing 5 ng Hg L^{-1} as a mixture of Hg^{2+} and $MeHg^{+}$ (1:1) and with (■) [DOC] = 0.5 mg L^{-1} or (●) [DOC] = 5 mg L^{-1}, respectively.

ing excellent accuracy and precision ($y = 1.01x + 0.08$; $R^2 = 0.9985$; $n = 27$). Furthermore, this experiment proves that accurate and precise Hg detection with the proposed method is independent from the Hg species.

Moreover, the used tubing material and optimised measurement conditions allow mercury determination without any memory effects as shown in Fig. 2B. Finally, the enrichment factor of the optimised procedure was determined at different sample volumes by comparison of the slopes of a calibration function of this method and CV-AFS measurement [11]. As expected, the enrichment factor increases linear with the sample volume (Fig. 2C) and for a sample volume of only 2.5 mL (which was used in all further experiments) the sensitivity is enhanced by a factor of 10 in comparison to CV-AFS measurement. Higher sample volumes offer the possibility to further increase the sensitivity of the proposed method for the detection of extremely low mercury levels.

3.2. Investigation of possible interferences from matrix constituents

Several natural and anthropogenic water constituents may affect mercury determination with the proposed method. In particular substances that form complexes with Hg species (and hinder thereby its adsorption onto the gold collector) and substances that may cause fouling of the active gold surface have to be considered.

Ionic mercury species have high affinity to dissolved organic carbon (DOC). In marine waters DOC content is usually less than 0.5 mg L^{-1}, whereas the DOC content in fresh waters can be 10 mg L^{-1} or even more (e.g. in marsh waters). Hence in fresh waters 94–99% of inorganic mercury and 72–97% of methyl mercury are complexed by DOC [31]. In seawater the proportion of mercury bound to humic matter is very low due to high chloride ion concentration (~19 g L^{-1}), which stabilises Hg species by ionic interactions. In ocean waters the dominant complexes are $HgCl_4^{2-}$, $HgCl_3^{-}$ and CH_3HgCl [32]. Besides these natural ligands, anthropogenic complexing agents can occur in contaminated natural waters. Ethylene diamine tetraacetic acid (EDTA) is nowadays a commonly used complexing agent in many sectors of industry and can be found in a concentration range from 1 to 100 μg L^{-1} in contaminated surface waters [33]. Therefore, in a series of experiments the influence of DOC, chloride and EDTA content of the sample on mercury recovery with the proposed method was investigated. Thereby, model solutions of the different potential interfering agents were spiked with 5 ng Hg L^{-1} as a mixture of $MeHg^{+}$ and Hg^{2+} (1:1).

Fig. 3A shows the percentage of mercury recovery with increasing DOC revealing that even low DOC contents affect quantitative recovery. At a DOC concentration of 15 mg L^{-1} Hg recovery of only 41% was achieved. Hence, the strong bonding between DOC and mercury inhibits the preconcentration of mercury on the gold collector. Therefore, the Hg–DOC complexes have to be cracked in order to achieve quantitative Hg adsorption. In a first attempt digestion of the model sample solution by UV radiation was performed for 7 h. The resulting recoveries are also given in Fig. 3A. With this pre-treatment procedure the maximum tolerable DOC content is 5 mg L^{-1}. Water samples with higher DOC require longer digestion times. Fig. 3B shows the increase of the mercury recovery rate in a natural water sample from the Deininger marsh with a DOC content of 14.5 mg L^{-1} with increasing UV digestion duration. Complete mercury recovery was obtained after 14 h for this sample.

Another approach to enhance recovery in DOC containing samples is to increase the ionic strength of the sample solution in order to shift the chemical equilibrium of bound mercury [34,35]. Fig. 3C shows the obtained Hg recoveries from model solutions containing 0.5 mg L^{-1} or 5 mg L^{-1} DOC, respectively dependent on the salinity of the solution. Sample salinity of at least 20 psu ensures quantitative Hg recovery without the need for UV radiation. Furthermore, the results indicate that accurate analysis of seawater samples should be possible. As expected, no interferences from chloride (up to 21 g L^{-1}) and sulphate (up to 3 g L^{-1}) were observed in recovery experiments.

The investigation of EDTA containing model solutions up to a concentration of 200 μg L^{-1} revealed no detectable influence on Hg recovery.

Table 1
Results of mercury recovery experiments in different water samples spiked with mercury as a mixture of Hg^{2+} and $MeHg^{+}$ (1:1).

Samples	Origin	[Hg] spikes (ng L^{-1})	Recovery rate (%)	[DOC][a] (mg L^{-1})
Artificial seawater	DIN EN ISO 10253	0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	102.4 ± 6.4	<1
Natural seawater	North Sea, ELBE1	0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0	97.0 ± 6.8	2.3
River water	Isar, Garching, Germany	0.0, 0.5, 1.0, 1.5, 2.0	96.0 ± 7.8[b]	3.9
Moorland water	Deininger Moor, Deining, Germany	5.0	97.6 ± 2.7[c]	14.5

[a] DOC values measured by EN 1484 DEV H3 method.
[b] After 7 h UV digestion.
[c] After 14 h UV digestion.

Table 2
Analytical figures of merit.

Linear working range	0.08–100 ng Hg L^{-1}
Typical calibration range	0.1–5 ng Hg L^{-1}
Regression coefficient R^2 (n = 12)	0.9997
Detection limit as derived from calibration function [41]	80 pg Hg L^{-1}
Blank value as fluorescence intensity	$0.40 \times 10^{-3} \pm 0.02 \times 10^{-3}$
Relative standard deviation	
With [Hg] = 5 ng L^{-1} and n = 10	1.1%
With [Hg] = 1 ng L^{-1} and n = 7	2.1%
With [Hg] = 0.2 ng L^{-1} and n = 8	3.3%
Sample volume	2.5 mL
Sample consumption for 3-fold measurement	25 mL
Analysis time for 3-fold measurement	20 min
Lifetime of collector	>5000 cycles

Furthermore, a wide range of cations was tested in regard to fouling of the collector's surface. For this purpose a Hg model solution was spiked with 23 metal ions (namely Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl and Zn) of a multielement standard solution to a concentration of 10 μg L^{-1} of each metal. Thereby, no decrease in the fluorescence intensity of Hg was detected. However at element concentrations >100 μg L^{-1} a considerable interference in the fluorescence signal was observed. This signal decrease was reversible, i.e. after rinsing of the collector with carrier solution quantitative Hg recovery was regained. Hence a permanent fouling of the gold surface can be excluded. This was also confirmed by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) of the gold collector's surface revealing no adsorption of elements on the rinsed collector.

In conclusion, these investigations indicate a high robustness of the used gold collector towards matrix constituents in natural waters.

3.3. Validation and analytical figures of merit

The proposed method was validated by a series of Hg recovery experiments in different spiked real matrices, i.e. seawater, freshwater and moorland water, confirming accurate Hg determination. The recovery rates calculated from the recovery functions in the investigated Hg concentration interval range from 96 to 102% and are summarised in Table 1.

Moreover, the total dissolved mercury concentrations of 11 unspiked real waters obtained by means of the proposed method were compared to the values achieved by performing standard EPA method 1631. The results are shown as a recovery function in Fig. 4 revealing a recovery rate of 99.7 ± 17.4%.

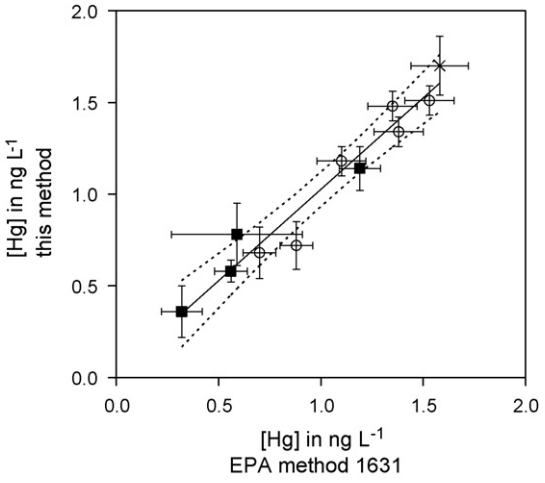

Fig. 4. Mercury recovery function resulting from a comparison of data obtained by applying the proposed method and EPA method 1631 to several unspiked natural water matrices: (x) effluent of a waste water treatment plant, (■) seawaters, (o) river waters (recovery function: $y = 0.997x + 0.0295$, regression coefficient, $R^2 = 0.9492$ with $n = 44$, error bars represent ± one standard deviation with $n = 4$ and (- - -) confidence interval with $P = 95\%$).

Further validation of the method was performed by investigation of the standard reference material BCR 579. This sample with a certified mercury value of 1.9 ± 0.5 ng Hg L^{-1} is a non-spiked acidified coastal seawater sample from the North Sea (Marsdiep). It was analysed on three different days with the proposed method (n = 4) and a mean value of 1.91 ± 0.17 ng Hg L^{-1} was obtained. The difference between the mean measured value and the certified value (Δ_m = 0.01 ng L^{-1}) is by far smaller than the expanded uncertainty (U_Δ = 0.51 ng L^{-1}) [36]. Hence, there is no significant difference between the mercury concentration measured with the proposed method and the certified mercury value, i.e. the accuracy and precision of the method was confirmed by this experiment. In Table 2 the analytical figures of merit of the proposed method are summarised.

3.4. Application to real water samples

The proposed method was applied to quantify total dissolved mercury in 14 natural waters and one effluent of a wastewater

Table 3
Mercury concentrations in different natural waters obtained by the proposed method.

Samples	Origin	[Hg] (ng L^{-1})	[DOC][a] (mg L^{-1})
Effluent of WWTP	Gut Großlappen	1.70 ± 0.14[b]	2.68
River water	Isar, 100 m	0.72 ± 0.08[b]	3.10
	Isar, 5000 m	0.68 ± 0.08[b]	2.78
	Leuschnitz 1 near spring	1.18 ± 0.12[b]	1.6
	Leuschnitz 2–2000 m downstream	1.34 ± 0.12[b]	1.4
	Leuschnitz 3–4000 m downstream	1.48 ± 0.12[b]	1.7
	Leuschnitz 4–6000 m downstream	1.51 ± 0.12[b]	1.9
Lake water	Starnberger See, in Possenhofen	0.38 ± 0.06[b]	3.9
	Ammersee, in Herrsching	0.41 ± 0.06[b]	3.5
	Feringasee, near Unterföhring	0.39 ± 0.06[b]	3.2
	Wesslinger See, in Wessling	0.20 ± 0.07[b]	4.3
Sea water	North Sea, NGW 8	0.36 ± 0.10	n.a.
	North Sea, AMRU 1	1.14 ± 0.10	n.a.
	North Sea at Grodendamm	0.78 ± 0.32	2.3
	Black Sea at Varna	0.58 ± 0.08	3.1

[a] DOC values measured by EN 1484 DEV H3 method.
[b] After 7 h UV digestion.

treatment plant (WWTP). Table 3 summarises the found mercury and DOC concentrations.

The highest mercury concentration found was in the effluent of the WWTP "Grosslappen" in Munich, Germany (1.70 ± 0.14 ng Hg L^{-1}). However, this value is lower than others reported from outlets of WWTPs that range from 3.5 to 39 ng Hg L^{-1} [28,37,38]. The samples taken 100 m and 5000 m downstream of the inlet of the WWTP in the river Isar are significantly lower ($\sim$0.7 ng Hg L^{-1}). The series of samples collected in the river Leuschnitz show increasing Hg concentrations with increasing distance from the spring. Natural leaching from ore rich soil and sediment in this former mining area most probably causes this increase. The obtained mercury levels of the rivers Isar and Leuschnitz are in an expected concentration range for Bavarian rivers (usually <5 to maximum 41 ng L^{-1}) [39]. The same applies to the dissolved mercury concentrations found in the lakes [12]. Low Hg concentrations were found at the off shore sampling position in the North Sea (0.36 ± 0.10 ng Hg L^{-1}). The 3 coastal seawaters showed mercury concentrations in an expected range [40].

The very good agreement of the obtained Hg values with the values determined by EPA method 1631 (see Fig. 4) confirms the feasibility of Hg analysis in natural waters with the proposed method.

4. Conclusions

The applicability of direct preconcentration of dissolved Hg species onto active gold collectors for reagent-free total Hg analysis in natural waters has been clearly demonstrated in this work. High sensitivity with a detection limit of 0.08 ng Hg L^{-1} (derived from the calibration function [41]) was achieved with a sample volume as low as 2.5 mL, corresponding to an absolute detection limit of 0.2 pg Hg. However, the large linear working range allows for analysis not only of pristine waters. The low blank value and detection limit as well as the high precision and reproducibility are a consequence of the reagent-free procedure where only hydrochloric acid as carrier solution and for sample acidification is used. Furthermore, the applied gold collector shows a high tolerance towards matrix constituents as well as a high robustness with a lifetime of at least 5000 measuring cycles without any measureable loss of activity. Saline waters can be analysed with the proposed method without any pre-treatment, whereas DOC containing fresh water samples should be digested by UV radiation prior to analysis.

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