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SCIENCE DIRECT®

Talanta 68 (2005) 329–335

Talanta

www.elsevier.com/locate/talanta

Preconcentration and speciation of inorganic and methyl mercury in waters using polyaniline and gold trap-CVAAS

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Abstract

Applicability of polyaniline (PANI) has been investigated for the preconcentration and speciation of inorganic mercury (Hg^{2+}) and methyl mercury (CH_3Hg^+) in various waters (ground, lake and sea waters). Preliminary experiments (batch) with powdered PANI for the quantitative removal of both Hg^{2+} and CH_3Hg^+ showed that the retention of Hg^{2+} was almost independent of pH while a pH dependent trend from pH 1 to 12 was seen for CH_3Hg^+ with maximum retention at $pH > 5$. Time dependence batch studies showed that a contact time of 10 min was sufficient to reach equilibrium. The K_d values were found to be $\sim 8 \times 10^4$ and $\sim 7 \times 10^3$ for Hg^{2+} and CH_3Hg^+, respectively.

Subsequently column experiments were carried out with PANI and the separation of the species was carried out by selective and sequential elution with 0.3% HCl for CH_3Hg^+ and 0.3% HCl–0.02% thiourea for Hg^{2+}. This was then followed by further pre-concentration of mercury on a gold trap and its determination by CVAAS. The uptake efficiency studies showed that the PANI column was able to accumulate up to 100 mg Hg^{2+}/g and 2.5 mg CH_3Hg^+/g. This method allows both preconcentration and speciation of mercury with preconcentration factors around 120 and 60 for Hg^{2+} and CH_3Hg^+, respectively. The interfering effects of various foreign substances on the retention of mercury were investigated.

Keywords: Polyaniline; Mercury; Speciation; Pre-concentration; CVAAS

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1. Introduction

Despite low crustal abundance, mercury and its compounds are considered to be ubiquitous global pollutants [1]. A large quantum of the anthropogenic input of mercury to the environment comes from coal fired thermal power plants and the manufacture of sodium hydroxide and chlorine by the electrolysis of brine [2]. Mercury toxicity is well known to be highly dependent of its chemical forms [3]. Chemical information about mercury species in various environmental samples is thus more relevant, for toxicological, biogeochemical and transportation studies.

Water is probably the most studied environmental sample and in fact the major part of speciation studies has been carried out in waters [4]. For mercury in natural waters, the main species to be identified and quantified are inorganic mercury (Hg^{2+}) and methyl mercury (CH_3Hg^+) [5]. In non-contaminated areas, mercury is usually present in natural waters at trace levels ranging from 0.2 to 100 ng/l while methyl mercury levels are much lower, around 0.05 ng/l or below detection limits of most analytical methods which leads to the need for very large sample volumes to be processed [6]. The World Health Organization (WHO) recommends a limit of 1 ng/ml of Hg in drinking water. Due to the very low concentration levels of mercury and its organic compounds in water samples, a preconcentration step should be included prior to the analysis in order to achieve a final concentration level matching the detection limits accessible with the technique selected. In order to improve the limits of detection, several approaches such as co-precipitation [7], noble metal amalgamation [8–11], solvent extraction [12–14], solid phase extraction [15–20], chelating sorbents [21,22] and various bio-sorbents [23–25] have been proposed for the preconcentration of mercury from natural waters.

A variety of analytical methods [26–31] have been applied for the speciation of mercury gas chromatography (GC) and high performance liquid chromatography (HPLC) with detection by atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS). Although these methods have

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doi:10.1016/j.talanta.2005.08.066

very high sensitivities, their high instrumental and running costs make it difficult to use these methods for detection with GC or HPLC.

Owing to its simplicity, high sensitivity, relative freedom from interferences, low operation costs, speed and ready acceptance of liquid samples, cold vapour atomic absorption spectrometry (CVAAS) has generally been used for the determination of mercury in various samples [32]. In conjunction with a pre-concentration based on amalgamation of the generated mercury vapour on gold trap provides further enhancement in the detection limits [33,34]. Various chromatographic and non-chromatographic speciation schemes employing CVAAS have been reported for the speciation of mercury compounds. HPLC–CVAAS has been reported for the speciation of mercury compounds [35,36]. Without any prior decomposition procedure, inorganic mercury is selectively determined, subsequently total mercury is determined after the transformation of organic mercury to inorganic mercury. Subtraction of inorganic fraction from total mercury is a common indirect approach to arrive at organic fraction for speciation which is usually found in the literature.

Polyaniline (PANI) has been one of the most intensely investigated conducting polymers during the last 15 years because of its good combination of properties, stability, price, ease of synthesis, treatment, etc. [37]. PANI exists in various oxidation states: leucoemeraldine, emeraldine and pernigraniline which are characterized by the extent of oxidation. In the leucoemeraldine state all the nitrogen is in the form of amines, whereas in pernigraniline the nitrogen atoms are imines. The amine/imine ratio in emeraldine is $\sim$1. Moreover, emeraldine can be in its base or salt form, depending on the pH.

Various studies on the applicability of PANI have been reported in the literature [38,39]. PANI has been used for the separation of noble metals Pt, Pd, Ir and Au prior to their determination in meteorite and rock samples [40]. Polyaniline has been used as base material for the preparation of mercury standard for use in neutron activation analysis [41]. The capability of polyaniline for the determination of Cd, Cu, Pb and Sb in the KI medium in biological matrices was also studied [42]. In our earlier studies, PANI was successfully used for the removal of radioruthenium from actual low-level radioactive waste solutions [43]. Gupta et al. have employed PANI for sorption of inorganic mercury from aqueous solutions [44]. Here it was shown that the sorption capacity of PANI for Hg^{2+} is not affected by irradiation. Despite the extensive literature on various applications of PANI, no information on the application of PANI for preconcentration of both Hg^{2+} and CH_3Hg^+ followed by selective separation has been reported.

In this work, the applicability of polyaniline in conjunction with (i) UV irradiation for degradation of CH_3Hg^+ to Hg^{2+} and (ii) a gold trap for enhancing the sensitivity has been investigated, to the best of authors knowledge, for the first time, for the preconcentration and speciation of Hg^{2+} and CH_3Hg^+ in various waters such as bottled waters, ground waters, lake waters and sea-waters samples. Column experiments were carried out with polyaniline loaded in home made mini-column followed by determination of mercury with gold trap-CVAAS. The effects of various experimental conditions such as pH and flow rate of loading solution were initially studied and conditions were optimized using separate solutions containing Hg^{2+} or CH_3Hg^+. Once the procedure was optimized, mixtures of Hg^{2+} and CH_3Hg^+ of different ratios were passed through PANI column prior to their selective elution.

2. Experimental

2.1. Instrumentation

Mercury content in all samples was analyzed by cold vapour atomic absorption spectrometry (CVAAS) using a mercury analyzer (Model MA 5840E, Electronics Corporation of India Ltd., Hyderabad, India). Matrix matched standards were used for quantification of mercury.

A homemade gold trap was introduced to further enhance the sensitivity of determination of mercury. The gold trap was constructed using a 0.2 g of 0.3 mm diameter gold wire, which was wound on a platinum mesh. This was inserted into a quartz tube (4 mm i.d.). Ar gas freed from any traces of mercury impurity by passing through a second gold trap was used to flush mercury vapors from the reaction cell on to the gold trap. Then the concentrator trap was removed and connected to the mercury analyzer. The trap was inserted into a 22-guage nichrome wire coil which was rapidly heated to 750 °C to release the mercury for analysis by CVAAS.

2.1.1. Reagents and standards

All chemicals were of analytical grade unless otherwise stated. Sub-boiled HCl and HNO_3 were prepared in our laboratory by sub-boiling distillation in quartz stills. Ultra-pure water with >18 MΩ cm resistivity, obtained using a Milli-Q high purity water system, located in class 200 area, was used through out this work. All containers were soaked in 20% HNO_3 and cleaned thoroughly with high purity water prior to use.

Tin(II) chloride ($SnCl_2$) (5%, w/v) used as reducing agent was prepared by dissolving the appropriate amount of $SnCl_2\cdot 2H_2O$ (Merck, India) in HCl and diluting with water. Sodiumborohydride ($NaBH_4$) (Merck, Darmstadt, Germany) (0.5%, w/v) was prepared fresh daily by dissolving the solid in 0.1% (w/v) NaOH solution. A 10% (v/v) HCl was used as carrier. Thiourea (NH_2CSNH_2) (Merck, Darmstadt, Germany) which has widely been used for the preparation of resins for binding of mercury as well as an eluent for stripping of mercury [45], was used in the elution studies.

Inorganic mercury (Hg^{2+}) stock standard solution (1000 mg/l) was prepared from mercuric chloride (Merck). A methyl mercury (CH_3Hg^+) stock standard (100 mg/l, Hg as CH_3Hg^+) was prepared from methyl mercury chloride (Merck) by dissolving appropriate amount of the solid in acetone and making up to volume with high purity water. All the stock standards were stored in a refrigerator at 4 °C and protected from light. Working standards were prepared just before use by appropriate dilution of the stock standard solutions.

2.2. Preparation of polyaniline

PANI was synthesized in our laboratory following the procedure given by Syed and Dinesan [38,39]. Doubly distilled aniline, 15.35 g (0.33 mol/l) was initially dissolved in 500 ml of 1 mol/l HCl. To this 36.5 g (0.32 mol/l) of ammonium peroxydisulfate was slowly added while stirring. The reaction was allowed to continue for 1.5 h at room temperature. The insoluble black precipitate of polyaniline thus formed was filtered, washed thoroughly with Millipore water then by acetonitrile (in order to remove soluble species), and again with water and dried. The resultant material was ground in a ceramic mortar and sieved to get 100–150 mesh.

2.3. Batch experiments with PANI

Preliminary batch experiments were performed to determine the optimal binding pH and exposure time. The pH of the solution was adjusted by addition of a very dilute solution of HCl/NaOH at the beginning of the experiment. The pH of the solution was recorded using a digital pH meter with ±0.1 unit accuracy. To determine optimal binding pH for the quantitative retention of both Hg^{2+} and CH_3Hg^+ by PANI, 20 ml of high purity water spiked with known amount of Hg^{2+} and CH_3Hg^+ separately as well as together, was adjusted to desired pH (in the range of 1–12) and 50 mg of PANI was added. Then the mixture was equilibrated on a mechanical shaker for about 30 min. Separate sample aliquots were used for each of optimization experiments.

All the experiments were conducted simultaneously at different pH levels. At each respective pH, after equilibration followed by centrifugation, residual mercury was determined in the solution. Removal percentage (R) of Hg^{2+}/CH_3Hg^+ from spiked sample solution:

$$R(\%) = \frac{C_\mathrm{i} - C_\mathrm{e}}{C_\mathrm{i}} \times 100$$

where C_i is the initial concentration of Hg^{2+}/CH_3Hg^+ in solution and C_e is the final concentration of Hg^{2+}/CH_3Hg^+ after equilibration.

The kinetic studies in batch mode were performed using a procedure similar to that of pH experiments but at a constant pH of ∼5. The time dependence studies were carried out from 1 to 60 min. From the initial concentration and the concentration measured in the supernatants after the appropriate time interval, the percentage removal of mercury was calculated. The reproducibility of the mercury removal was found to be ±5–10% on repetition of experiments.

2.4. Column experiments with PANI

To investigate the efficacy of PANI for the preconcentration of both Hg^{2+} and CH_3Hg^+ species from various aqueous media, a home made PTFE mini-column (30 mm × 2.0 mm i.d.) with end caps was used. Fifty milligrams of PANI was weighed and packed in the PTFE mini-column plugged with glass wool at both the ends. Prior to an experiment, the column was conditioned to the desired pH. Separate sample solutions containing Hg^{2+} or/and CH_3Hg^+ were passed through the column at a constant flow rate with the help of a peristaltic pump. The effect of the flow rate of the sample solution was investigated by varying flow rate. About 100 ml of sample solutions (pH ∼ 5) spiked with 100 ng of each of Hg^{2+} and CH_3Hg^+, were passed through the column at different flow rates. The flow rates were varied in the range of 0.5–4 ml/min.

Once the procedure was optimized, solutions containing both Hg^{2+} and CH_3Hg^+ at different ratios were passed. One hundred milliliters of high purity water spiked with known amount of Hg^{2+} and CH_3Hg^+ separately or together, was adjusted to an optimized pH ∼ 5 and then passed through a column loaded with PANI at a constant flow rate of 2 ml/min. The column effluent was analysed for residual mercury. The retained mercury species (Hg^{2+} or/and CH_3Hg^+) from the column was selectively eluted with an optimized concentration of 0.3% HCl and 0.3% HCl–0.02% thiourea, respectively. The total volume of the Hg^{2+} fraction of the eluent was taken in the reaction cell, and using $SnCl_2/NaBH_4$ as reducing agent the resulting mercury vapour was flushed onto a gold trap. This was released on heating and was measured by CVAAS. CH_3Hg^+ content was measured similarly after UV irradiation as described elsewhere [46].

3. Results and discussion

The effects of various parameters such as pH and rate of adsorption (batch experiments), flow rate and sample volume (column experiments), affecting the speciation of mercury in waters by PANI were investigated and discussed.

3.1. Effect of pH on the removal of Hg^{2+} and CH_3Hg^+

The influence of the pH on the retention of Hg^{2+} and CH_3Hg^+ on PANI was studied by equilibrating the mercury solutions containing one of the species at a time. Fig. 1 shows the retention behaviour of both Hg^{2+} and CH_3Hg^+ on PANI as a function of pH. As can be seen from Fig. 1, the retention of Hg^{2+} on PANI is independent of sample pH, in conformity with the observations of Gupta et al. [44] who studied the sorption of Hg^{2+} in the

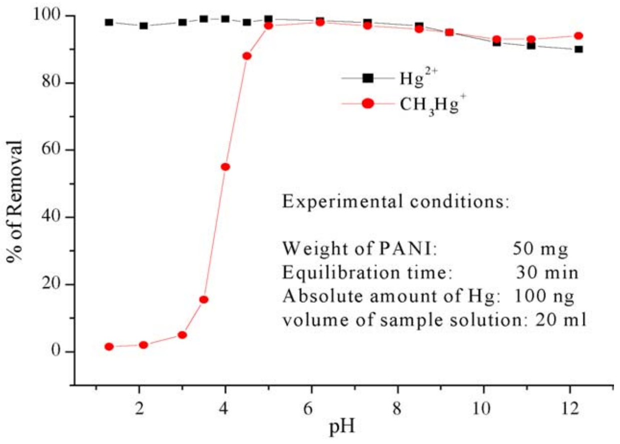

Fig. 1. Effect of pH on the removal of Hg^{2+} and CH_3Hg^{2+} by PANI.

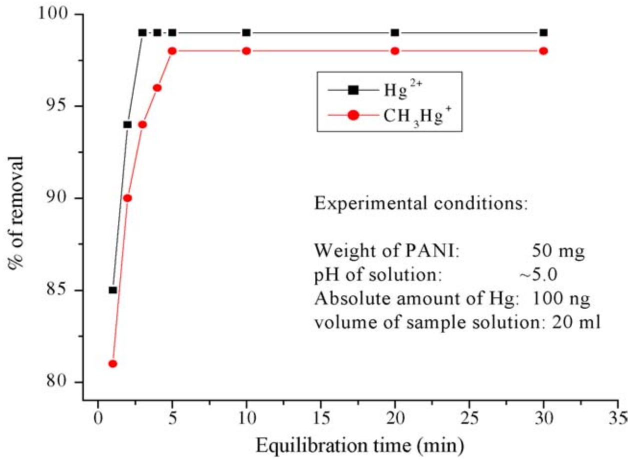

Fig. 2. Effect of equilibration time on the removal of Hg^{2+} and CH_3Hg^+ by PANI.

pH range 3–10. However, the retention of CH_3Hg^+ is highly pH dependent. The uptake of CH_3Hg^+ by PANI was <2% of initial concentration at pH 1 and increases to >95% when pH of solution increases to 5 and remains constant thereon. However, at a $pH > 8$, the retention of Hg^{2+} decreased to about 92%, possibly due to the formation of various hydroxides of mercury whereas this decrease was less predominant for CH_3Hg^+. These studies showed that both Hg^{2+} and CH_3Hg^+ species were retained quantitatively on PANI in the pH range of 5–8. Though quantitative separation of Hg^{2+} and CH_3Hg^+ can be achieved at pH 1, with the aim of simultaneous preconcentration of both species from various aqueous media, a pH of ∼5 was used for all subsequent experiments.

The distribution coefficients (K_d) of the amount of Hg^{2+}/CH_3Hg^+ per gram of resin to the amount per ml of the solution were found to be $\sim 8 \times 10^4$ for Hg^{2+} and $\sim 7 \times 10^3$ for CH_3Hg^+ (when 50 mg of PANI is equilibrated with 20 ml of solution containing 20 μg of Hg^{2+}/CH_3Hg^+ as absolute amount).

3.2. Effect of equilibration time

The effect of equilibration time on removal of Hg^{2+} and CH_3Hg^+ by PANI is presented in Fig. 2. These studies clearly indicate that the removal of both species from aqueous solutions by PANI is quite rapid and more than 85% is taken up in the first min, the plateau (>99%) is reached after a contact period of 5 min. The increase of contact time from 5 to 60 min has no significant effect on retention of both IM and MM. Therefore, a contact time of 10 min was used for all subsequent experiments.

3.3. Effect of flow rate of loading solution

The flow rate of sample solution is another important parameter that influences the sorption of the analyte. Therefore, the effect of the flow rate of sample solution was examined using the general procedure under the optimum conditions such as pH, amount of mercury and volume of sample solution.

Table 1
Effect of flow rate of sample solution on the removal of Hg^{2+} and CH_3Hg^+ by PANI column ($n = 3$)

Flow rate of sample solution (ml/min)	Removal (%)	
	Hg^{2+}	CH_3Hg^+
0.5	100	98
1.0	100	98
1.5	100	98
2	100	97
2.5	99	93
3	99	89
3.5	99	84
4.0	98	78

Volume of sample solution 100 ml, pH of sample solution ∼5, amount of Hg^{2+} and $CH_3Hg^+ = 100$ ng.

The results of these studies are presented in Table 1. As may be seen from Table 1, quantitative retention (>95%) of Hg^{2+} occurs even at a flow rate of 4 ml/min whereas for CH_3Hg^+, the optimum flow rate is about 2 ml/min. At higher flow rates (>2 ml/min), retention of CH_3Hg^+ decreases gradually due to a possible decrease in the adsorption kinetics at higher flow rates. Hence, a flow rate of 2 ml/min was used in all the subsequent experiments.

3.4. Selective elution of CH_3Hg^+ and Hg^{2+}

The pH profile experiments of Hg^{2+} and CH_3Hg^+ suggested that both mercury species could be selectively stripped from the PANI column by using a relatively low acidic media without damaging the PANI enabling regeneration of the column for its reuse. The strength of acid solution used for stripping of mercury from loaded column must be as low as possible while the volume of the eluent solution decides the pre-concentration that can be achieved. The volume of eluent mixture (10 ml) was kept constant in all cases.

Among the acids employed as eluents, HCl has been reported to have an enhanced performance due to its complexing properties with mercury. To check the influence of HCl concentration on the elution of Hg^{2+} and CH_3Hg^+, elution studies were performed with HCl in the range of 0.1–0.5% at an optimized flow rate of 1 ml/min. As shown in Fig. 3, the quantitative elution of CH_3Hg^+ from the column could be achieved with 0.3% HCl where as the recovery of Hg^{2+} was almost insignificant. The quantitative elution of Hg^{2+} could not be achieved even with 30% HCl.

It is known that PANI has alternating arrangement of quinoid and benzene rings [48] and the mercury is sorbed by attaching to the nitrogen atoms in the chain [44]. Thus, the large size of the CH_3Hg^+ may prevent the ion from diffusing inside to reach the functional groups. This may probably account for the lower capacity of PANI for CH_3Hg^+. As the ion may thus sorb preferentially on the surface its elution occurs with a low strength eluent. The elution behaviour of CH_3Hg^+ suggests that the retention mechanism on PANI seems to be a simple adsorption/desorption process.

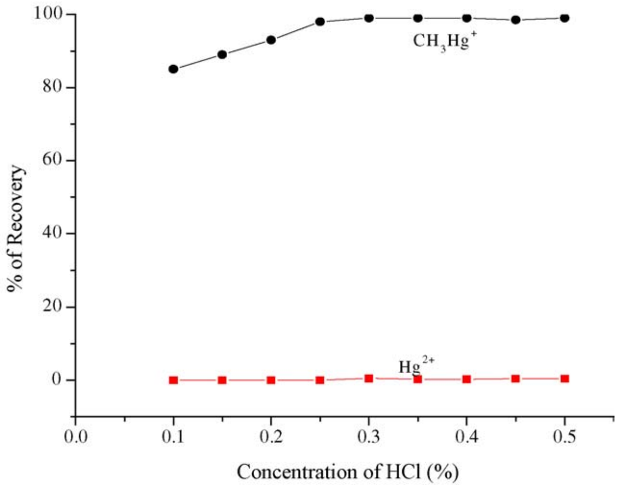

Fig. 3. Effect of HCl concentration on the recovery of Hg^{2+} and CH_3Hg^+ from PANI column.

Earlier Gupta et al. [44] had reported similar observations, when Hg^{2+} was sorbed onto PANI; when it was suspended in 0.1N HNO_3, only 47% and in the presence of complexing agent diphenylthiocarbazone, about 72% of the sorbed mercury could be recovered. Hg is known to preferentially bind to sulfur containing ligands and thiourea has often been used for elution of mercury [45].

To achieve quantitative elution of Hg^{2+} avoiding high acid concentrations, the complexing agent thiourea was added to HCl solutions. In order to optimize the concentrations of HCl and thiourea, a factorial (two factors, three level) experimental design approach was applied and the recovery of Hg^{2+} at each level of the treatment was estimated. Based on the results obtained from various preliminary experiments, the base level was chosen as 0.3% HCl and 0.02% thiourea and the upper and lower levels were obtained using a difference of ±0.1% for HCl and ±0.01% for thiourea from the base level. Fig. 4 shows the effect of passing 0.3% HCl + 0.02% thiourea through the column of PANI (after reversing the column) which contained bound Hg^{2+}. Quantitative recovery (>98%) of the bound Hg^{2+} was achieved after passing 10 ml of 0.3% HCl–0.02% thiourea.

The recoveries of the species from spiked water samples were investigated using optimized conditions. The recoveries obtained are Table 2. As may be seen from Table 2, quantitative recoveries (>96%) were obtained for both the species in all the cases.

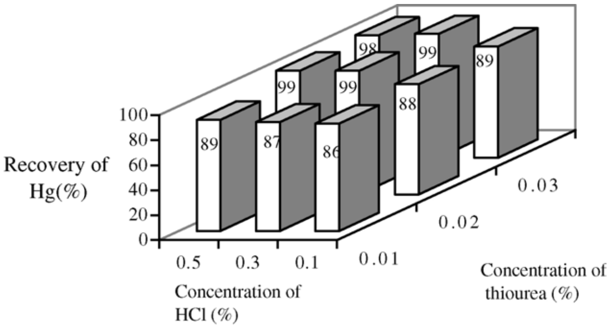

Fig. 4. Optimization of eluent concentration for the recovery of Hg^{2+} from PANI column (volume of sample solution = 100 ml, amount of Hg^{2+} loaded = 100 ng, volume of eluent passed at a flow rate of 1 ml/min = 10 ml).

Table 2
Recovery of Hg^{2+} and CH_3Hg^+ from synthetic water samples after passing through the PANI column

Added[a] (ng)		Found[b] (ng)		Recovery (%)	
Hg^{2+}	CH_3Hg^+	Hg^{2+}	CH_3Hg^+	Hg^{2+}	CH_3Hg^+
100	–	102	–	102 ± 2	–
–	100	–	98	–	98 ± 3
50	50	49	49	98 ± 3	98 ± 4
100	50	99	48	99 ± 2	96 ± 3
50	100	49	97	98 ± 1	97 ± 2
100	100	99	98	99 ± 1	98 ± 2
50	25	48	24	98 ± 3	96 ± 4

[a] Sample volume 100 ml, pH ∼ 5, flow rate 2 ml/min, ±S.D. ($n = 3$).
[b] After eluting from the column.

3.5. *Determination of retention capacities for Hg^{2+} and CH_3Hg^+*

The maximum amounts of Hg^{2+} and CH_3Hg^+ retained by PANI were evaluated using breakthrough (BT) capacity curves. A feed solution of Hg^{2+}/CH_3Hg^+ (5 μg/ml) was passed through PANI column at an optimized flow rate of 2 ml/min. The process was continued till 100% breakthrough occurred. The pH of the solution was adjusted to ∼5. The column effluents were analyzed periodically for residual Hg^{2+}/CH_3Hg^+. The elution of CH_3Hg^+ was carried out using 10 ml of 0.3% HCl and that of Hg^{2+} with 10 ml of mixture of 0.3% HCl and 0.02% thiourea. The maximum amounts of Hg^{2+} and $MeHg^+$ retained in the column obtained using breakthrough curves were 100 mg Hg^{2+}/g and 2.5 mg CH_3Hg^+/g. The efficacy of the PANI used in the column remained relatively constant even after 5 cycles of retention and elution.

3.6. *Effect of volume/concentration of sample solution*

To determine the pre-concentration factor of mercury from very dilute analyte solutions, the maximum applicable volume of sample that could be passed through the column loaded with PANI was determined. To study this effect, a series of solutions spiked with a constant total amount 100 ng each of Hg^{2+} and CH_3Hg^+ with increasing sample volumes 200, 400, 600, 800, 1000 and 1200 ml of sample solutions were passed through the column under the optimum conditions such as pH (∼5) and flow rate (2 ml/min). The general procedure described previously was followed. The retained mercury species from the column was eluted with 10 ml of 0.3% HCl for CH_3Hg^+ whereas 10 ml of mixture of 0.3% HCl and 0.02% thiourea was used as eluent for Hg^{2+}.

Fig. 5 shows effect of sample volume on Hg^{2+} and CH_3Hg^+ retention, where it is evident that, for a given column, quantitative recoveries (>95%) of Hg^{2+} and CH_3Hg^+ could be achieved up to 1200 and 600 ml of sample solutions, respectively. As shown in Fig. 5, a slow reduction in the retention occurred after passing 600 ml of CH_3Hg^+ and 1200 ml of Hg^{2+} spiked

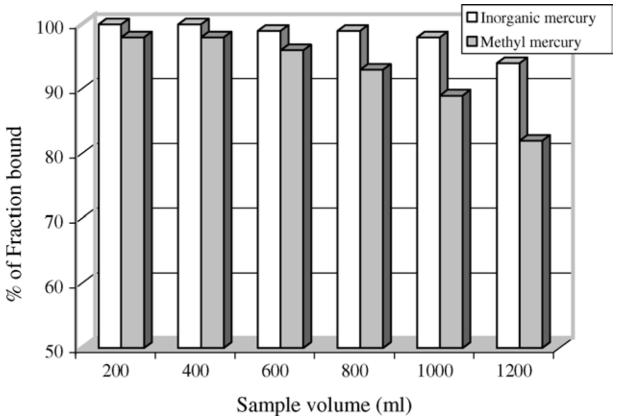

Fig. 5. Effect of sample volume on the uptake of Hg^{2+} and $MeHg^{+}$ by PANI column (amount of Hg^{2+}/CH_3Hg^{+} = 100 ng, flow rate = 2 ml/min).

the sample solutions. Reduction of recoveries with increasing volumes, i.e. sample solutions containing very low contents of mercury, was also noticed by Perez-Corona et al. [23]. In the case of Hg^{2+}, the maximum admissible volume was 1200 ml with a recovery of >98% whereas for CH_3Hg^{+}, the admissible volume was about 600 ml with a recovery of >95%. The recovery was evaluated by comparing the signal with that of signal obtained with corresponding matrix matched mercury standard solution. With 10 ml eluent volumes, the preconcentration factors were found to be about 120 and 60 for Hg^{2+} and CH_3Hg^{+}, respectively, when spiked water samples were introduced into the column.

3.7. *Limit of detection*

The LOD of the gold trap-CVAAS, calculated on the basis of three times the standard deviation of the blank was 0.05 ng/l for Hg^{2+} when 500 ml of water was taken.

3.8. *Effect of foreign substances*

In waters, mercury species coexist with various other metal ions. Hence, the presence of those metals gives rise to interactive effects that could influence the removal of the desired contaminant. The effect of various cations such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{2+}, Pb^{2+} and anions Cl^{-}, SO_4^{2-} and NO_3^{-} which are commonly encountered in various waters, on the retention of Hg^{2+} and CH_3Hg^{+} on PANI column, was evaluated to assess the selectivity of the method. Solutions containing 100 ng of Hg^{2+} and/or $MeHg^{+}$ and different salts in the range 10–200 μg/ml were passed throughout columns filled with PANI to asses the effect of the presence of different ions in solution on pre-concentration. Results demonstrated that the presence of the aforementioned substances did not cause any interference in the pre-concentration of Hg^{2+} and/or $MeHg^{+}$, at least at the levels reported in the present work.

4. Application to water samples

The proposed preconcentration and speciation procedure was applied to the determination of Hg^{2+} and CH_3Hg^{+} in bottled water, lake water, ground water and sea water samples. Immediately after sampling, the samples were passed through the PANI column without adjusting the pH where as some part of the sample were spiked with known amount of Hg^{2+} and CH_3Hg^{+} and the pH was adjusted to ∼5. The reliability of the proposed preconcentration method was checked by recovery experiments. Recovery values were found to be >95% in all the cases (Table 3) except in lake water samples.

However, when water from a polluted lake, Hussainsagar, Hyderabad, India which is in an advanced state of eutrophication [47] was used, about 8–10% reduction in recovery of

Table 3
Determination of Hg^{2+} and CH_3Hg^{+} in spiked natural water samples

Sample	Added[a] (ng)		Found[b] (ng)		Recovery[b] (%)	
	Hg^{2+}	CH_3Hg^{+}	Hg^{2+}	CH_3Hg^{+}	Hg^{2+}	CH_3Hg^{+}
Bottled water (mineral)	0	0	25	ND	–	–
	100	100	130	97	104 ± 5	97 ± 2
	50	50	73	48	97 ± 2	96 ± 1
Lake water	0	0	48	ND	–	–
	100	100	135	96	91 ± 2	95 ± 2
	50	50	88	44	90 ± 4	94 ± 3
Ground water 1	0	0	54	ND	–	–
	100	100	151	95	98 ± 1	97 ± 2
	50	50	100	49	96 ± 2	98 ± 1
Ground water 2[c]	0	0	350	ND	–	–
	250	250	583	242	97 ± 3	98 ± 4
	500	500	841	489	99 ± 2	98 ± 3
Sea water	0	0	20	ND	–	–
	100	100	120	95	100 ± 5	95 ± 2
	50	50	67	48	95 ± 2	96 ± 1

[a] Sample volume 100 ml, pH ∼ 5, flow rate = 2 ml/min, ±S.D. (n = 3).
[b] After eluting from the column, ND: not detected.
[c] Collected near battery making factory.

mercury was obtained. This may probably due to the ligand-bound mercury not being available. Hence, an additional step may be necessary to free the bound mercury [33] for it to be held by the PANI column.

5. Conclusions

It has been demonstrated that PANI in conjunction with (i) UV irradiation for degradation of CH_3Hg^+ to Hg^{2+} and (ii) a gold trap for enhancing the sensitivity could be effectively used for the preconcentration and speciation of Hg^{2+} and CH_3Hg^+ in bottled waters, lake waters and seawaters. Furthermore, this method allows not only retention of mercury species but also selective elution from the PANI column Hg^{2+} and CH_3Hg^+ can be sequentially eluted with 10 ml of 0.3% HCl and a mixture of 0.3% HCl and 0.02% thiourea, respectively. The preconcentration factors were 60 and 120, respectively. The proposed method is very simple and is suitable for routine speciation analysis of Hg^{2+} and CH_3Hg^+ in various waters.

PANI has the additional benefit of being a more robust sorbent that is resistant to attack by acids and insoluble in many organic solvents. It has also been reported to be stable under irradiation and retain its sorption characteristics [44].

Acknowledgements

The authors desire to gratefully acknowledge the immense help rendered by the anonymous referees in improving the language and quality of the manuscript with their invaluable suggestions.

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