

# 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 ( $\text{Hg}^{2+}$ ) and methyl mercury ( $\text{CH}_3\text{Hg}^+$ ) in various waters (ground, lake and sea waters). Preliminary experiments (batch) with powdered PANI for the quantitative removal of both  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$  showed that the retention of  $\text{Hg}^{2+}$  was almost independent of pH while a pH dependent trend from pH 1 to 12 was seen for  $\text{CH}_3\text{Hg}^+$  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  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$ , 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  $\text{CH}_3\text{Hg}^+$  and 0.3% HCl–0.02% thiourea for  $\text{Hg}^{2+}$ . 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  $\text{Hg}^{2+}$ /g and 2.5 mg  $\text{CH}_3\text{Hg}^+$ /g. This method allows both preconcentration and speciation of mercury with preconcentration factors around 120 and 60 for  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$ , respectively. The interfering effects of various foreign substances on the retention of mercury were investigated.

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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 ( $\text{Hg}^{2+}$ ) and methyl mercury ( $\text{CH}_3\text{Hg}^+$ ) [5]. In non-contaminated areas, mercury is usually present in natural waters at trace levels rang-

ing 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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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 radoruthenium 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  $\text{Hg}^{2+}$  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  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$  followed by selective separation has been reported.

In this work, the applicability of polyaniline in conjunction with (i) UV irradiation for degradation of  $\text{CH}_3\text{Hg}^+$  to  $\text{Hg}^{2+}$  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  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$  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  $\text{Hg}^{2+}$  or  $\text{CH}_3\text{Hg}^+$ . Once the procedure was optimized, mixtures of  $\text{Hg}^{2+}$  and  $\text{CH}_3\text{Hg}^+$  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-gauge 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  $\text{HNO}_3$  were prepared in our laboratory by sub-boiling distillation in quartz stills. Ultra-pure water with  $>18 \text{ M}\Omega \text{ cm}$  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%  $\text{HNO}_3$  and cleaned thoroughly with high purity water prior to use.

Tin(II) chloride ( $\text{SnCl}_2$ ) (5%, w/v) used as reducing agent was prepared by dissolving the appropriate amount of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (Merck, India) in HCl and diluting with water. Sodiumborohydride ( $\text{NaBH}_4$ ) (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 ( $\text{NH}_2\text{CSNH}_2$ ) (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 ( $\text{Hg}^{2+}$ ) stock standard solution (1000 mg/l) was prepared from mercuric chloride (Merck). A methyl mercury ( $\text{CH}_3\text{Hg}^+$ ) stock standard (100 mg/l, Hg as  $\text{CH}_3\text{Hg}^+$ ) 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.

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