

Determination of Hg in Water and Wastewater Samples by CV-AAS Following On-Line Preconcentration with Silver Trap¹

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Abstract—An online mercury preconcentration and determination system consisting of cold vapor atomic absorption spectrometry (CV-AAS) coupled to a flow injection (FI) method was studied. The method was developed involving the determination of ng/L levels of mercury retained on the silver wool solid sorbent. Experimental conditions such as sample volume, flow rate, stability of the column and effect of foreign ions on the determination of trace amounts of mercury were optimized. The detection limit is 3 ng/L and dynamic range 10–250 ng/L of analysis requires only 50 mL of sample. The relative standard deviations (RSD) of the determinations are below 4%. The presence of common metal ions, such as K⁺, Na⁺, Cu²⁺, Pb²⁺, Fe³⁺, Ni²⁺ and Mn²⁺, does not interfere with the measurement of mercury by this method. The method was successfully applied to the determination of mercury in water and wastewater samples.

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The determination of trace amounts of mercury, which is highly toxic, is of considerable importance in connection with the growing environmental problems. It is included in all lists of priority pollutants, and different regulations and guidelines have been developed for limiting its level in water and sediments [1]. During the past decades, concentration of mercury in air, soil, and water has been increasing because of greater utilization of fossil fuels and expanded use of this element in industry and agriculture. Accurate and sensitive determination of mercury is now a challenging problem. Because of extremely low levels of mercury in various matrices, high sensitivity and sophistication in the analytical procedures are required for its determination. The most commonly used methods are cold vapor atomic absorption spectrometry (CV-AAS) [2–5], cold vapor atomic fluorescence spectrometry (CV-AFS) [6–12], inductively coupled plasma optical emission spectrometry (ICP-OES) [13, 14], and inductively coupled plasma mass spectrometry (ICP-MS) [15–17].

Determination at trace amounts requires a preliminary preconcentration step in order to achieve quantifiable levels. The solid phase extraction (SPE) and liquid–liquid extraction are widely applied for the separation and preconcentration of metals among a variety of methods. The first presents some advantages over the other, such as, lesser waste generation, lesser matrix effect, availability and easy recovery of the solid phase, achievement of higher preconcentration factors, easy adaptation of solid phase in a minicolumn coupled to a continuous flow preconcentration sys-

tem; SPE does not generally require the use of toxic solvents [18, 19].

Cold vapor atomic absorption spectrometry (CV-AAS) is the most widely used technique for the determination of mercury because of its high sensitivity, resistance to interferences and operational simplicity. Recently, several separation and preconcentration procedures including preconcentration on gold amalgamator [20, 21], liquid-liquid extraction [22, 23], cloud point extraction [24] and solid phase extraction with appropriate adsorbents such as silver and silver wool [25–28], chelating resins containing dithiocarbamate [29], methylthymol blue [30], mercaptobenzothiazole [31], activated carbon [32], and modified silica C₁₈ [33] have been used prior to measurement by CV-AAS.

In recent years, various online techniques have been proposed for Hg preconcentration or/and separation [34–39] of which mini-column SPE was most commonly used. SPE is being utilized for preconcentration of heavy metals due to its flexibility, economical and environmental friendliness, absence of emulsion, speed and simplicity, feasibility of sampling in the field, safety and ease of automation [40].

In this work, a sensitive and efficient method was developed for flow injection preconcentration and determination of trace amount of mercury in water samples by silver trap- CV-AAS. The effect of various experimental parameters such as sample volume, flow rate, stability of the column, effect of diverse ions, stability of column and detection limit were studied in detail. The developed method has been successfully

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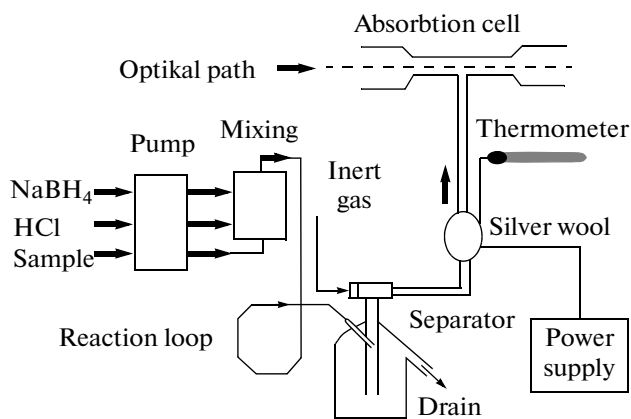


Fig. 1. Scheme of flow injection system for online preconcentration.

used to determine mercury in tap water, seawater and wastewater samples.

EXPERIMENTAL

Reagent. Hg-free reagents provided by Merck (Darmstadt, Germany) were employed in all experiments and Ultra-pure quality water produced by a Milli-Q system (Millipore, Bedford, USA) was used throughout. Inorganic mercury (Hg^{2+}) stock standard solution (1000 mg/L) was prepared from mercury chloride (Merck); working standards were prepared just before use by appropriate dilution of the stock standard solutions. Sodium borohydride solution was prepared daily by dissolving an appropriate amount of NaBH_4 salt (Merck) in 0.01% sodium hydroxide solution. Nitric acid (65%, Merck) and hydrochloric acid extra pure (32%, Merck) and argon 99.999% were used.

Apparatus. A GBC flow injection mercury system Model AAS-P176932 equipped with a deuterium background corrector and an auto-sampler was used for all mercury determinations. The absorbance wavelength was set at 253.7 nm (resonance line) and the spectral bandwidth at 0.5 nm. A Jenway model 3020 pH meter with a combined glass electrode was used. A homemade silver trap was introduced to further enhance the sensitivity of determination of mercury. The silver trap was constructed using a 0.1 g of silver wool. This was inserted into a glass tube (2 cm long 5 mm i.d.). The trap was inserted into a nichrome wire coil which was rapidly heated to 400°C to release the mercury for analysis by CV-AAS.

Operational Procedure. For all measurements a GBC flow-injection cold vapor atomic absorption spectrometer was used. Argon gas was employed to carry the mercury vapor into the absorption cell. The sample solution (at 8 mL/min flow rate), the hydrochloric acid 5% (at 5 mL/min flow rate) and the reducing agent solution at 3 mL/min are introduced

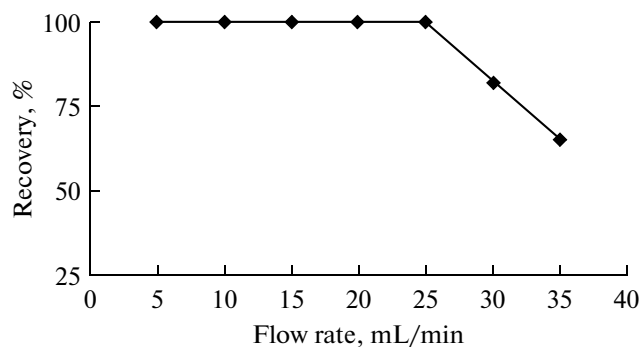


Fig. 2. The effect of argon flow rate on the recovery of 25 ng/L Hg^{2+} .

separately through tubing's with the aid of a peristaltic pump. The flows are regulated by magnetic valves, which are switched under computer control. The modified experimental set-up is schematically shown in Fig. 1. In set-up the elemental Hg is generated in the reaction loop and goes into the gas phase. In the gas-liquid separator the gases are separated from the waste solution. The gases at room temperature are lead through a drying tube for the removal of water vapor and optionally to the silver wool trap. Here, mercury is preconcentrated by amalgamation and afterwards thermally released by resistance heating. Finally, the Hg vapors are transferred to the absorption cell (quartz, 180 mm, i.d. 8 mm) electrically heated to 400°C and after 25 sec the absorbance of the 253.7 nm line is measured. As primary radiation source a low pressure Hg lamp is used and the radiation is led through the absorption cell onto the detector consisting of an interference filter ($\lambda = 254$ nm, bandwidth, 0.5 nm) and a photomultiplier. Peak area measurements were performed with the aid of the software of the GBC spectrophotometer.

RESULTS AND DISCUSSION

Influence of argon flow rate. The influence of argon flow rate on the mercury response obtained by the CV-AAS system was investigated. Low argon gas flow rate means a long analysis run, while high flow rate may lead to incomplete Hg adsorption. When flow rate is 25 mL/min, the efficiency is around 100%. However, high back-pressure on the column was observed at flow rates higher than 30 mL/min. In addition, high flow rates lead to decrease in the adsorption in the column. Therefore, 25 mL/min was used as the optimal sample flow rate (Fig. 2).

Column optimization. The column dimensions were carefully optimized. Very little retention is achieved with a short column (less than 1 cm); maximum efficiency was obtained with a 2 cm column. Lengths greater than 2 cm are unnecessary for the proposed system. Also, the effect of the column internal diameter and amount of silver wool on the recovery

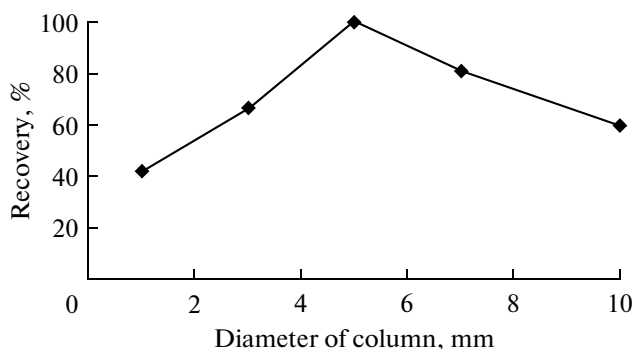


Fig. 3. Influence of column diameter on the recovery of 25 ng/L Hg^{2+} .

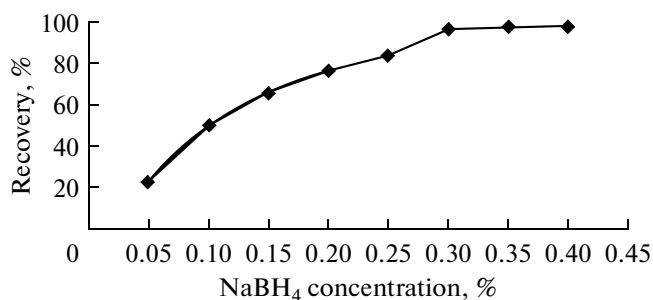


Fig. 4. Influence of NaBH_4 concentration on the recovery of 25 ng/L Hg^{2+} .

was studied and 5 mm was considered as an acceptable column i.d. Hence, a glass tube column (2 cm \times 5 mm i.d.) with 0.1 g of silver wool to a height of 2 cm was selected for this study (Fig. 3).

Stability of the column. The stability of the silver wool column was tested using 50 ng/L $\text{Hg}(\text{II})$ maintaining sample volume at 50 mL. The column could be used with good precision and quantitative recovery (>95%) for 350 cycles. Beyond 350 cycles, there was a reduction in the recovery of mercury.

Reductant concentration. Important parameters of the hydride generation system for cold vapor generation that should be optimized included the flow rate of the argon carrier and the flow rate and concentration of the reductant agents. The use of SnCl_2 as a reductant was also investigated, but it was found to be a weaker reductant compared to NaBH_4 . Figure 4 shows that the sensitivity of the mercury response obtained with the proposed system increased considerably with increasing NaBH_4 concentration up to 0.3% and no further improvement was observed with the addition of more reducing agent. On the other hand, the use of NaBH_4 in concentration over 0.3% did not result in a better improvement in sensitivity.

Interference studies. The effects of representative potential interfering species (at the concentration levels at which they may occur in water samples) were tested for their effect upon retention and determination of mercury under the optimum conditions described above, using standard solution of 50 ng/L $\text{Hg}(\text{II})$. Interferences of various ions on the preconcentration and determination of mercury were examined by comparing the signal intensities of mercury in the presence and absence of interfering ions. As the results show (Table 1), excessive amounts of common cations, anions and common matrix components such as alkali elements generally do not interfere with the determination of trace quantities of mercury. The reported tolerance limit is defined as the ion concentration causing a relative error $<\pm 5\%$.

Determination of mercury in certified reference material. In order to establish the validity of the pro-

posed procedure, the developed method was applied to the determination of the content of Hg^{2+} in certified reference material ORMS-4 of river water. The determined value of 20.7 ± 0.5 ng/L coincides with the certified value of 22 ± 1.6 ng/L.

Figures of merit. Under the previously optimized conditions the analytical figures of merit of the developed procedure were determined. First of all the linear working range was investigated. For this purpose 20 solutions with concentrations of between 10 and 300 ng/L were prepared and analyzed with the procedure developed. The calibration graph was linear in the range of 10–250 ng/L of mercury (comparison to values of similar techniques reported in literature is given in Table 2). The data were analyzed by least squares method and the best straight line was drawn with a correlation coefficient of 0.9996. The limit of detection (LOD) of the proposed method based on three times the standard deviation ($3S_b$) and for 10 replicate measurements of blank solution at optimized conditions was 3 ng/L. The precision of the method for aqueous standards was evaluated by analyzing 8 replicates with Hg^{2+} concentration of 50 ng/L and 75 ng/L, which gave RSD of 2.4 and 3.2%, respectively. To evaluate the precision of the method, a series of independent standard samples was used. The concentration of standard mercury samples varied between 30 and 100 ng/L in CV-AAS. The results showed that the RSD for the determination of different concentrations of

Table 1. Effect of foreign species in the determination of 50 ng/L of $\text{Hg}(\text{II})$

Species	Tolerance ratio, w/w
Na^+ , K^+ , NH_4^+ , Li^+ , Mg^{2+} , Ca^{2+} , Cd^{2+} , Cu^{2+}	50000
Fe^{3+} , Ni^{2+} , Ba^{2+} , Mg^{2+} , Zn^{2+}	20000
Al^{3+} , Mn^{2+} , As^{3+} , Bi^{3+} , Pb^{2+}	5000
PO_4^{3-} , NO_3^- , CO_3^{2-} , SO_4^{2-}	40000

Table 2. Results for the determination of Hg in real and spiked samples

Sample	Mercury concentration, ng/L		Recovery, % ($n = 5$)
	Added	Found*	
Tap water	–	ND	–
	20.0	19.8 ± 1.1	99.0
	40.0	39.4 ± 1.2	98.5
Seawater	–	31.7 ± 2.3	–
	30.0	59.4 ± 3.1	96.30
	100.0	126.5 ± 2.8	96.00
River water	–	28.0 ± 3.3	–
	20.0	47.1 ± 2.2	98.1
	45.0	71.8 ± 1.9	98.3
Khark petrochemical wastewater	–	120.3 ± 3.2	–
	30.0	152.4 ± 2.5	101.4
	50.0	173.6 ± 2.6	102.0
Tehran petrochemical wastewater	–	58.3 ± 2.8	–
	40.0	101.4 ± 2.5	103.1
	60.0	115.8 ± 2.8	97.8

Notes: * Mean of five determinations ± confidence interval ($P = 0.95$); ND: not detected.

Hg(II) was in the range of 2.20–3.12%. The absolute value of the relative error was ≤5%.

Application. The proposed procedure was applied to the determination of mercury in tap water, sea water and wastewater samples. The results are shown in Table 2. All samples were filtered through a 0.45 μm filter (glass fiber) to remove the suspended solids, then acidified to ca. pH 3.5 and stored at 4°C in acid-cleaned polyethylene bottles. When the water samples spiked with Hg(II) standards of different concentrations were treated by the proposed method, the recoveries were all in the range of 97–103% with RSD of 1.0–4.0%.

The determination of concentrations of Hg in water samples are of great environmental importance because the hydrological cycle is one the main pathways of the dispersion of this contaminant in the environment. Moreover, it is responsible for the contamination of aquatic food web. Therefore sensitive and precise analytical methods are required for efficiently monitoring surveys. The main objective of this work was to develop and validate a reliable, easy and fully automated flow injection system method for determination of mercury in water and wastewater samples. The use of silver wool as an adsorbent for Hg preconcentration offered several advantages such as high stability, high preconcentration efficiency, and low interference. Conditions for Hg adsorption and desorption on the SPE column made of silver wool were readily online coupled with CV-AAS, which made the established method concise and suitable for routine analysis. The dynamic linear range of the proposed method

has been compared with other reported methods in literature [41, 42]. In addition, FI on-line separation and preconcentration, with column containing silver wool as an adsorbent, has been a much used method to increase sensitivity and selectivity in the analytical determination of trace mercury. This method offers some very favorable features in relation to batch systems, such as: higher sample throughput, better efficiency and enrichment reproducibility, low reagent and samples consumptions, lesser risk of contamination and simple automated operation. Common metal ions such as Cu, Pb, Zn, Co, Ni, Fe and Mn did not interfere with mercury measurements by this method, which was successfully applied to the determination of mercury in various water samples. In addition this method is sensitive, low cost and applicable when sophisticated techniques such as CV-AFS or ICP-OES are not available.

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