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Determination of Hg in water by CVAAS using 2-aminothiazole modified silica

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Abstract: This paper discusses a rapid and sensitive method developed to determine trace levels of mercury in natural water samples by cold vapor atomic absorption spectrometry using a preconcentration system composed by mini-column packed with 100 mg of 2-aminothiazol modified silica gel (SiAT) coupled on-line with the spectrometer's cold vapor generator system. The optimum preconcentration conditions are also described here. The preconcentrated Hg(II) ions were eluted directly from the column to the spectrometer's cold vapor generator system using 100 μL of 2 mol L^{-1} hydrochloric acid and the retention efficiency achieved exceeded 95%. The enrichment factors determined were 29, 38 and 46 using 3, 4 and 5 mL of preconcentrated aqueous solutions containing 400 ng L^{-1} of Hg. The detection limit calculated was 5 ng L^{-1}. The preconcentration procedure was applied to determine trace level mercury in spiked river water samples.

Keywords: mercury; flow-injection analysis; CVAAS; modified silica; preconcentration.

Introduction

Heavy metals (e.g., Hg) at trace levels are provenly toxic elements and can cause human health disorders [1-3]. Since the main sources of mercury for humans are water and food, the monitoring of mercury content in natural waters is of paramount importance [4-6].

Mercury contamination in environmental samples is usually caused by less than 1 mg L^{-1} of this element, thus requiring highly sensitive techniques to determine and quantify its presence. Several analytical techniques exist to determine mercury at trace levels [7-20]. One of these techniques is cold vapor atomic absorption spectrometry (CVAAS), which is suitable due to its high sensitivity for accurate determinations of mercury [11, 14, 18]. However, CVAAS technique's selectivity and sensitivity to environmental samples is strongly dependent on the matrix components [19]. Preconcentration steps based on amalgamation onto a gold trap have been used to enhance the sensitivity in mercury determinations by atomic absorption spectrometry [7-10, 15, 16]. The flow injection preconcentration technique is useful for application in determining mercury by CVAAS, providing improved performance by enhancing the sensitivity, separating the analyte from the matrix, and decreasing of the risk of contamination [13, 18, 20].

In recent years, studies have focused on the use of chemically modified silica gel matrices

with various groups to chelate organofunctional groups designed for the adsorption and preconcentration of metal ions in aqueous media [21-27]. The literature contains descriptions of columns packed with chemically modified silica gel with groups attached having a selective affinity for mercury ions [22-26]. A manual procedure with this sorbent packed column has been proposed for pre-concentrating mercury [25, 26]. However, the routine applicability of this procedure is limited by the time-consuming analysis it involves (100 min for each determination).

This paper describes the analytical performance of a flow injection system with on-line preconcentration in a sorbent mini-column packed with 2-aminothiazole modified silica (SiAT) gel for determining mercury in a series of spiked river water samples. The system proposed here was tested initially on a synthetic aqueous solution containing trace levels of mercury, and was subsequently applied to spiked river water samples.

Materials and methods

Reagents, analytical solutions and samples

All the solutions were prepared with high purity chemicals and distilled-deionized water (Milli-Q system, Millipore). The hydrochloric and nitric acids used were Suprapur (Merck).

A solution of 10% m/v $SnCl_2$ in 6 mol L^{-1} HCl was prepared daily by dissolving the appropriate amount of the salt (Merck) in about 50 mL of concentrated hydrochloric acid and diluting it in up to 100 mL of water.

Standard mercury solutions (80 – 800 ng L^{-1}) were prepared by stepwise dilution from 1000 mg L^{-1} stock solution (Merck – Titrisol) with Milli-Q water, acidified with nitric acid to pH 2.

The 2-aminothiazole modified silica (SiAT) was prepared as described by Alcântara et al. [28]. The column (a 5 cm long glass tube with 3 mm i.d.) was dry-packed with 100 mg of SiAT.

Samples collected from natural water (Tietê, Parapanema and Paraná rivers, SP, Brazil) were immediately filtered through a 0.45 µm membrane. After acidification (pH < 2.0) with 6.0 mol L^{-1} HNO_3 solution, the samples were stored in highly purified PE containers. A volume of 50 mL water sample and 30 µL of 1000 µg L^{-1} Hg(II) were added to a 100 mL volumetric flask and the resulting solution diluted to the final volume with water. The river water samples spiked with 300 ng L^{-1} Hg(II) were digested by photocatalysis in the presence of 100 mg of TiO_2 and 0.01 mol L^{-1} potassium persulfate.

Mineralization of river water samples spiked with Hg(II)

The mineralization of river water samples spiked with 300 ng L^{-1} Hg(II) were performed in a Quimis cylindrical photoreactor thermostatted at 25°C (298K) with luminous intensity of 3.81mW/cm^2. Nitrogen was bubbled into the sample before conducting the experiment to remove excess oxygen. A BECKMAN model PMA 2100 radiometer was used to measure the luminous intensity. A mass of 100 mg of TiO_2 and 2,70 g $K_2S_2O_8$ were suspended in 100 mL of samples and stirred for 60 min under mechanical agitation. The photocatalytic reaction was conducted with the reactor open to the air. After the period of time, the TiO_2 was separated of solution by fitration using 0.22µm Millipore filters and the organic carbon concentration was determined using Total Organic Carbon Analizer SHIMADZU/TOC-V_{CPH}.

Apparatus

A SHIMADZU model AA-6800 atomic absorption spectrometer equipped with a hollow mercury cathode lamp and a deuterium lamp for background correction, and a homemade T-shaped acrylic flow cell with quartz windows (190 x 4 mm) were used. The spectrometer's monochromator was adjusted to 253.7 nm (the resonance line corresponding to a wavelength of great sensitivity for mercury) and the spectral-resolution to 0.5 nm. The atomic signal was measured in peak height mode.

An Ismatec model IPC-8 peristaltic pump equipped with Tygon pumping tubes (i.d. 0.5 mm) and a homemade Perspex injector-commutator were used in the flow injection system.

Preconcentration system

Figure 1 shows the flow diagram of the SiAT-packed mini-column system, which consisted of a peristaltic pump (1), an injection valve-1 (2), a mini-column packed with SiAT (4), a Loop-L_R (5), a reaction cell (6) coupled to the AAS flow cell (10),

and a N_2 line (9) crossing the injection valve 3 (8). Standard solutions or water samples in the 80 – 800 ng L^{-1} Hg(II) concentration range were passed through the column at 0.5 mL min^{-1} for 4 min. to sorb the Hg(II) in the column with the opening valve-1 (2). The mercury was eluted with 100 µL of 2.0 mol L^{-1} HCl solution and added through the injection valve-1 (2) at 1 mL min^{-1}. The eluted Hg(II) ions were transported to the reaction cell (250 x 10 mm) through the opening of loop-L_R (5). After valve-1 and Loop-L_R were switched, the injection valve-2 (7) was opened and a volume of 500 µL of 10% m/v $SnCl_2$ in 6.0 mol L^{-1} HCl solution was added to reduce the Hg(II) ions to mercury vapor. The mercury vapor generated was carried out with a nitrogen flow by opening the injection valve-3 (8) towards the flow cell of the spectrometer (10), and the signal was recorded in peak height mode.

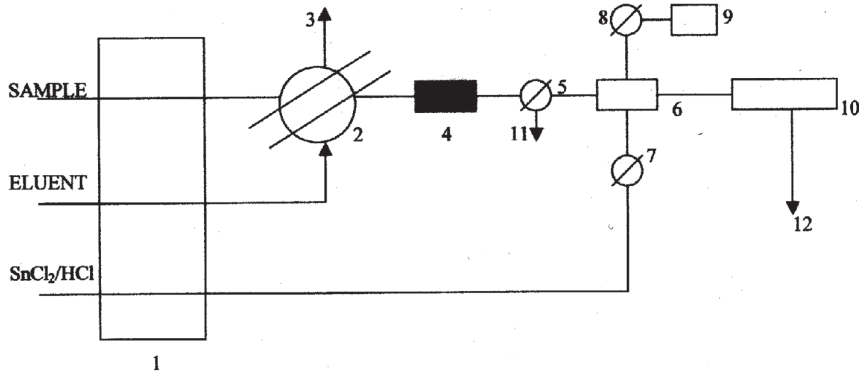

Figure 1. Flow Injection System for mercury preconcentration by cold vapor atomic absorption spectrometry: 1 – peristaltic pump; 2 – injection valve-1; 3 – aqueous discharge; 4 – mini-column; 5 – loop-L_R; 6 – reaction cell; 7 – injection valve-2; 8 – injection valve-3; 9 – N_2 flow; 10 – AAS flow cell; 11 – aqueous discharge; 12 –mercury vapor discharge in 0.50 mol L^{-1} $KMnO_4/H_2SO_4$ 4 mol L^{-1} solution.

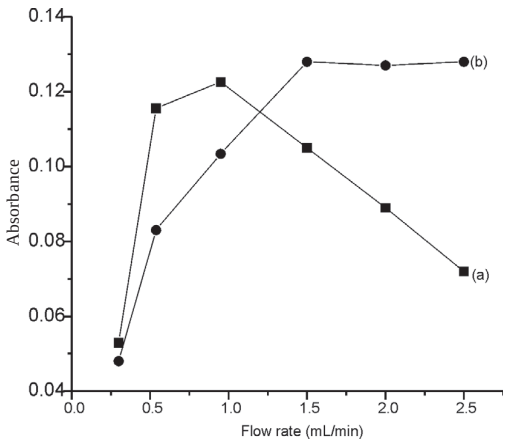

Figure 2. Effect of flow rate on peak absorbance: a – preconcentration flow rate; b – elution flow rate.

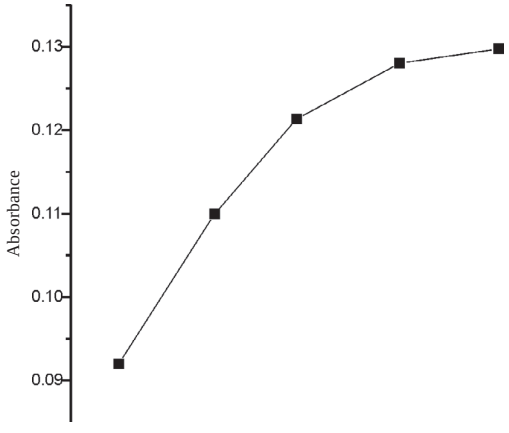

Figure 3. Effect of pH on mercury preconcentration in the mini-column packed with 100 mg of SiAT.

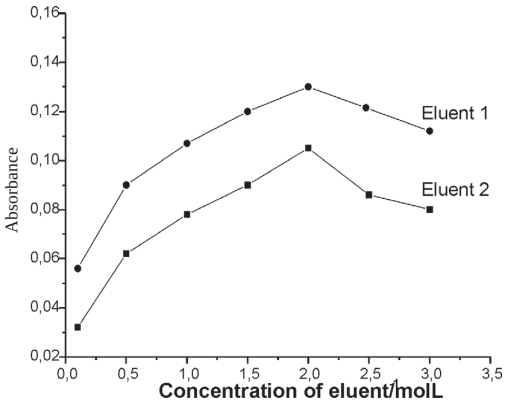

Figure 4. Influence of eluent concentration on peak absorbance: eluent –1, HCl; eluent-2, HNO_3.

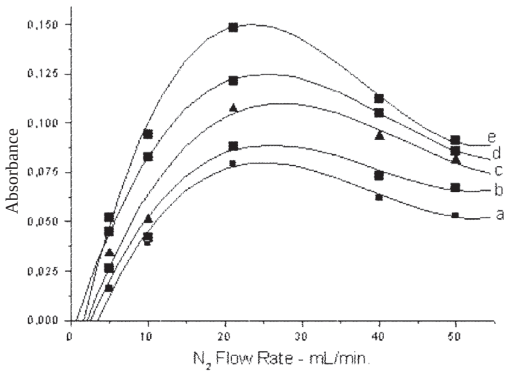

Figure 5. Influence of N_2 flow rate in the Hg carrier stream on the peak absorbance. Reducer volume ($SnCl_2$): a – 50 µL; b – 100 µL; c – 250 µL; d – 1000 µL; e – 500 µL.

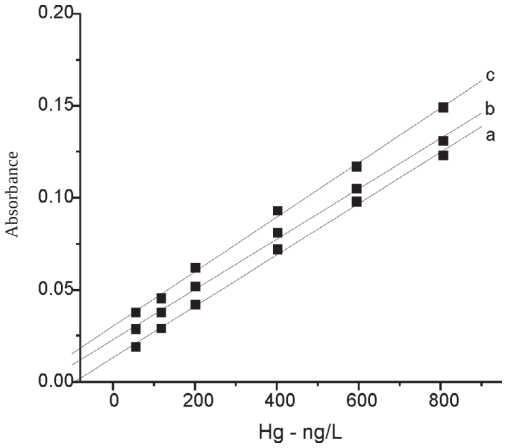

Figure 6. Influence of HCl and $SnCl_2$ concentrations on the formation and generation of Hg vapor (experimental conditions: Hg(II) = 600 ng L^{-1}; pH = 5.0; 500 µL of 10% m/v $SnCl_2$; Hg carrier stream – 20 mL N_2 min^{-1}): a – 6 mol L^{-1} HCl; b – 3 mol L^{-1} HCl; c – 1 mol L^{-1} HCl.

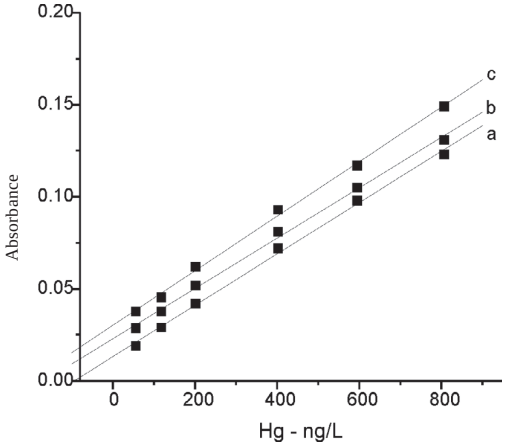

Figure 7. Calibration graphs for different sampling times (experimental conditions: pH = 5.0, 2 mol L^{-1} HCl with eluant, eluant flow rate – 1.5 mL min^{-1}; 500 µL of 10% m/v $SnCl_2$ and Hg carrier stream – 20 mL N_2 min^{-1}): a – 3 min, b – 4 min, and c – 5 min at a flow rate of 1.0 mL min^{-1}.

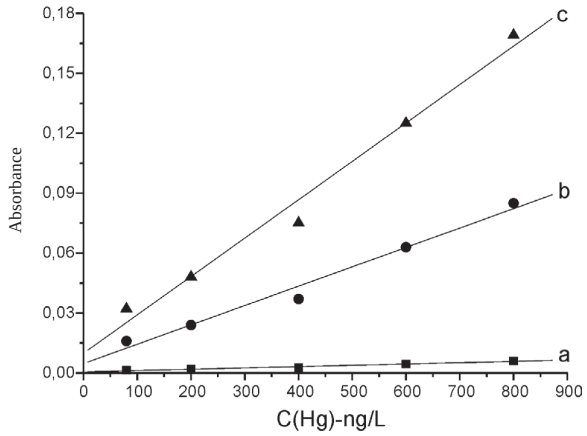

Figure 8. Calibration graphs: a – without preconcentration; b – with preconcentration in a gold minicolumn; c – with preconcentration in a SiAT minicolumn (experimental conditions: pH = 5.0, 2 mol L^{-1} HCl as eluant, eluant flow rate of – 1.5 mL min^{-1}; 500 µL of 10% m/v $SnCl_2$ and Hg carrier stream – 20 mL N_2 min^{-1}, sampling time = 5 min at a flow rate of 1.0 mL min^{-1}).

Table 1. Enrichment factor and efficiency of mercury preconcentration minicolumn (Mercury Concentration = 400 ng L^{-1}; Eluent – 100 mL of 2 mol L^{-1} HCl solution; Flow Rate – 1.5 mL min^{-1})

Sampling Time (min)	Experimental preconcentration factor	Theoretical preconcentration factor[a]	Efficiency
3	29.4	30	98
4	38	40	95
5	46	50	92

[a]Volume added/volume eluted

Table 2. Tolerance limits of interfering ions (400 ng L^{-1} of Hg(II), 5 min sampling time)

Ion – (500 μg L^{-1})	% mercury recovery
Cu(II)	96±4
Ni(II)	97±3
Fe(III)/Fe(II)	95±3
Pb(II)	94±2
Zn(II)	98±2
Mn(II)	97±3
Cd(II)	97±5
Cl^-	58±6
NO_3^-	99±3
SO_4^{2-}	94±3
PO_4^{3-}	94±3

Samples from: 1 – Tietê River; 2 – Parapanema River; 3 – Paraná River
UV-P: Digest samples by oxidizing with UV-Photocatalysis

Table 3. Determination of mercury in different water samples (spiked with 300 ng L^{-1} Hg(II)) by CVAAS with on-line preconcentration in a SiAT-packed minicolumn, with and without digestion by UV-photolysis.

Samples	SiAT-CVAAS	SiAT-CVAAS/UV-P
1	218 ± 8	288 ± 9
2	214 ± 4	294 ± 3
3	216 ± 64	290 ± 7

Results and discussion

Effect of physical and chemical parameters

In order to adjust the physical and chemical variables for mercury preconcentration and elution, the following parameters were tested.

The preconcentration and elution flow rates were varied from 0.5 to 3 mL min^{-1} while the amount of injected mercury was kept constant at 600 ng L^{-1}. As shown in Fig. 2 (graph a), optimum signal absorbance was obtained at a flow rate of about 1.0 mL min^{-1}. The sensitivity increased with increasing elution flow rate (Fig. 2, graph b.), remaining constant at 1.5 mL min^{-1}. As a compromise between the sampling rate and sensitivity, the preconcentration and elution flow rates selected were 1.0 and 1.5 mL min^{-1}, respectively. Various column lengths and inner diameters were tested, resulting in the selection of 4 cm and 2 mm diameters, respectively, as a compromise between loading capacities and eluant volumes.

The effect of pH on mercury sorption in the column's reactive phase was evaluated by varying the pH in the 1 - 5 range [19] with a constant injection of 600 ng L^{-1} of mercury solution and 3 min. sampling time. Figure 3 shows that the sorption of Hg(II) ions decreased with the solution's acidity and pH 5.0 was optimal for the sorption of Hg(II) ions. A pH of 5.0 was chosen for further experiments, using 5.10^{-3} mol L^{-1} of acetate buffer.

The elution efficiency of Hg(II) ions was investigated using HNO_3 and HCl in different concentrations. Fig. 4 depicts the influence of eluant concentrations, indicating that the HCl solutions proved the most favorable for eluting Hg(II) ions. However, the elution efficiency improved as the HCl concentration was increased up to 2 mol L^{-1}. Therefore, the 2 mol L^{-1} HCl solution was chosen as eluant.

The formation and generation of mercury vapor were investigated by varying the concentrations of reducing agent (5 - 20% m/v $SnCl_2$), the concentrations of hydrochloric acid (1 - 10 mol L^{-1}), the volume of $SnCl_2$ (50 - 1000 µL) and the Hg carrier stream (10 - 50 mL min^{-1} N_2). The results obtained in these experiments, which are illustrated in Fig. 5 and Fig. 6, indicate that, when the N_2 flow rate was increased from 10 to 50 mL min^{-1}, the highest absorbance peak for the solution containing 600 ng L^{-1} Hg(II) was reached with a N_2 flow rate of 20 mL min^{-1} and a 10% m/v $SnCl_2$ volume (in 6 mol L^{-1} HCl solution) of 500 µL.

Analytical Performance

A linear calibration curves were obtained for the 80 – 800 ng L^{-1} range of Hg(II) preconcentrated for 3, 4, and 5 min (volumes injected in triplicate at a flow rate of 0.5 mL min^{-1}). The results obtained are illustrated in Figure 7, which indicates that the calibration slopes increased, though not in proportion with the increasing preconcentration time; hence, the retention efficiency was not constant.

The experimental preconcentration factor, calculated as the ratio of slopes in the calibration graphs obtained from preconcentrations in the minicolumn packed with SiAT ($A= 9.83 \times 10^{-3} + 1.92 \times 10^{-4}[Hg^{2+}]$), the preconcentration in the gold minicolumn ($A= 4.66 \times 10^{-3} + 9.70 \times 10^{-5}[Hg^{2+}]$) and no preconcentration ($A= 5.145 \times 10^{-4} + 6.60 \times 10^{-6}[Hg^{2+}]$), was evaluated under the same conditions as described previously. Figure 8 shows the aforementioned calibration graphs. The preconcentration factor, calculated by comparing the calibration graph with preconcentrations (Figure 8, graph c) against the calibration graphs without preconcentrations (Figure 8, graph a) and with the preconcentration in the gold minicolumn (Fig.8, graph b), was 29 and 2, respectively. Differences between the preconcentration factor and the added and eluted volumes may occur due to loss of efficiency with increasing sample volumes. As it can be seen in Table 1, the preconcentration efficiency declined from 98% to 92% when the sample volumes passed through the column increased from 3 to 5 mL. The preconcentration factor under these conditions increased from 29 to 46. The precision, expressed as RSD for twelve independent determinations, was 4% for 200 ng L^{-1} Hg(II) solutions. The detection limit (LOD) calculated on the basis of 3 SD/b, were b is the slope of the calibration curve c illustrated in Figure 8 and SD the standard deviation of 10 consecutive measurements of blank solution, was 5 ng L^{-1}.

The repeatability of column preconcentrations, expressed as SD and tested by sampling a 400 ng L^{-1} Hg(II) solution for 5 min through 12 independently prepared minicolumns, was approximately 95 ± 6.

The influence of dissolved salts on the preconcentration of Hg(II) was evaluated by adding 500 µg L^{-1} of Cu(II), Ni(II), Fe(III)/Fe(II), Pb(II), Zn(II), Mn(II), Cd(II), Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}. The interference study (Table 2) showed that

the proposed method is fairly selective for Hg(II) and that Cl^- caused most of the interference. This was attributed to the formation of chlorocomplexes of mercury ($HgCl_4^{2-}$). However, the interference of this anion in water samples can be eliminated by using the digestion procedure proposed in this work. In this procedure the Cl^- ions are convert to Cl_2 by oxidizing photocatalysis in the presence of 100 mg of TiO_2 and 0.01 mol L^{-1} potassium persulfate. In this conditons the Hg(II) ions to remain stable in the solutions.

Determination of mercury in river water samples

The proposed method was successfully applied in mercury recovery tests using river water samples containing 20 -25 mg L^{-1} of dissolved organic carbon. The results achieved through the proposed method are illustrated in Table 3, which shows recoveries of up to 97% were attained in predigested samples and 70% in undigested samples. This difference between the recovery results, was attributed to the formation of inert complexes of mercury with aquatic humic substances (HS), which are less accessible for the functional groups of the collector [25]. After digestion (by oxidizing with photocatalysis in the presence of 100 mg of TiO_2 and 0.01 mol L^{-1} potassium persulfate), Hg(II) ions previously bound to HS as inert complexes can react quantitatively with functional groups of SiAT, due the total mineralization of organic matter in the process of digestion by photocatalysis.

Conclusions

The proposed method offers a good alternative for determining mercury in ultratrace levels in an aqueous medium. The high stability of the mini-column packed with SiAT was evidenced by lifetimes of at least one year when unused and at least two month when used 4 h per day (aproximately 800 analysis). The proposed method allows mercury to be determined on-line by CVAAS in natural water samples, but requires predigestion of the sample, e.g., by oxidizing with photocatalysis in the presence of 0.01 mol L^{-1} potassium persulfate, which is necessary to eliminate the interference of Cl^- ions and to inhibit the reduction of Hg(II) by UV radiation during the digestion phase.

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F. A. Silva, P. S. Roldan, I. L. Alcântara, C. C. F. Padilha, A. B. Araújo, J. P. S. Valente, A.O. Florentino, P. M. Padilha. Determinação de mercúrio em águas por CVAAS empregando sílica modificada por 2-aminotiazol.

Resumo: O presente trabalho descreve o desenvolvimento de um método rápido e sensível para determinar traços de mercúrio em amostras de águas naturais por espectrometria de absorção atômica com geração de vapor a frio, utilizando-se um sistema de preconcentração composto por uma mini-coluna empacotada com 100 mg de sílica gel modificada com o ligante 2-aminotiazol e acoplado em linha com o sistema de geração de vapor a frio do espectrômetro de absorção atômica. As condições ótimas de preconcentração são descritas. Os íons Hg(II) preconcentrados foram eluídos diretamente da mini-coluna para o sistema de geração de vapor a frio utilizando-se 100 µL de solução 2 mol L^{-1} de ácido clorídrico, com uma eficiência de 95%. Os fatores de enriquecimento determinados foram 29, 38 e 46 percolando-se 3, 4 e 5 mL de solução aquosa contendo 400 ng L^{-1} de Hg(II). O limite de detecção calculado foi de 5 ng L^{-1}. O procedimento de preconcentração foi aplicado na determinação de traços de mercúrio adicionados em amostras de águas de rio.

Palavras-chave: mercúrio; análise por injeção em fluxo; CVAAS; sílica modificada; preconcentração.

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