



Spectrophotometric determination of dithizone–mercury complex by solid phase microextraction in micropipette tip syringe packed with activated carbon xerogel



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ARTICLE INFO

Article history:

Received 14 March 2016

Received in revised form 13 April 2016

Accepted 13 April 2016

Available online 14 April 2016

Keywords:

Mercury

Dithizone

Activated carbon xerogel

Solid phase microextraction

Visible spectrophotometry

ABSTRACT

A new simple miniaturized solid phase microextraction system in a syringe was developed for mercury (Hg) preconcentration of in water samples based on the adsorption of its dithizone complex on a microcolumn. The syringe system contains a micropipette tip packed with activated carbon xerogel. The influence of acidity, eluting agents, amount of adsorbent, complex stability and interfering ions was studied in detail. The complex retained on activated carbon xerogel in the micropipette tip–syringe system could be eluted using ethanol and the concentration was determined by visible spectrophotometry.

The method showed good linearity in the range of 30–280 $\mu\text{g L}^{-1}$, with a limit of detection of 7.6 $\mu\text{g L}^{-1}$. The relative standard deviation (RSD%) for six replicate measurements of 280 $\mu\text{g L}^{-1}$ of Hg^{2+} ion was 1.36%.

The proposed method was successfully applied to quantitative determination of Hg^{2+} in ground water and mineral water with satisfactory results.

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1. Introduction

Heavy metals determination in water samples is a task frequently asked to analytical chemists by environmentalist, for the evaluation and phenomenon interpretation of ecosystems. However, in many cases the available analytical instrumentation does not show enough sensibility compatible with Hg concentration in environmental samples. As such, a previous preconcentration step results necessary, and it is for this reason many enrichment procedures have been proposed [1].

Mercury (Hg) is one of the most critical contaminants in the environment and it is present in water, soils, sediments and air usually at trace levels [2]. However, anthropogenic sources like mining, industry, coal-fired power plants and sludge dumping have increased the natural concentration of Hg and led to severely contaminated environments [3, 4]. Thus, monitoring the environment in view of mercury pollution is very important.

Development of high sensitive detection methods is really important for determination of extremely low Hg concentration [5]. Consequently, considerable effort and progress have been made to develop the techniques in which the determination of Hg in the contaminated samples is carried out rapidly [6].

Solid phase extraction (SPE) is a rapid, simple, economical and environmentally friendly preconcentration step, compared to traditional liquid–liquid extraction. SPE followed by electrothermal atomic absorption spectrometry (ET-AAS), inductively coupled plasma atomic emission (ICP-AES) or ICP-mass spectrometry are suitable for analysis of metal traces [7–10]. However, these instruments are very expensive and costly for the maintenance.

Different absorbents such as alumina, silica and cellulose offered advantages in terms of mechanical and chemical stability under different experimental conditions [11,12].

Carbon gels are porous carbon materials that have found applications in adsorption, catalysis and electrochemical energy [13]. Carbon gels are obtained after carbonizing organic gels obtained in the sol–gel process by polycondensation of multifunctional organic monomers in alcohol solutions [14]. Adsorption is one of the most important xerogel application. Because of high surface area and easiness of pore size distribution control, these materials should be perfect sorbents [15].

In this work, retention of Hg–dithizone complex on activated carbon xerogel is proposed for subsequent quantification by spectrometry UV–

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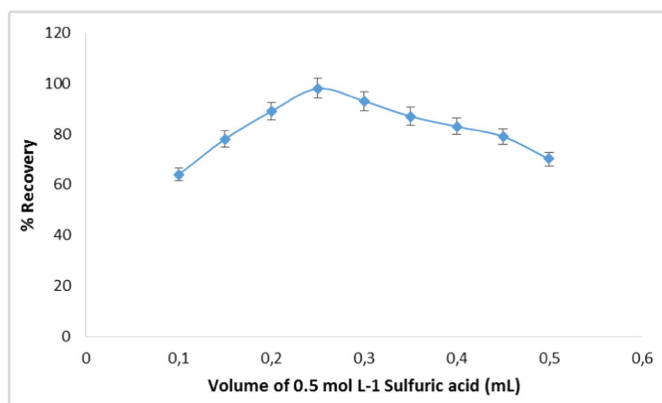


Fig. 1. Effect of volume of 0.5 mol L⁻¹ sulfuric acid on Hg²⁺ recovery. The error bars indicate the standard deviations of three experiments.

visible in water samples. Dithizone has been long recognized as a highly sensitive colorimetric reagent for mercury and other heavy metal ions, forming intensely colored stable complexes due to the presence of a thiol group. [16–18].

The study was carried out analyzing the different factors which the influence of acidity, eluting agents, amount of adsorbent, complex stability and interfering ions.

2. Experimental

2.1. Apparatus

A Shimadzu UV–vis spectrophotometer model 1800 double beam UV–vis spectrophotometer fitted with tungsten lamp as the source was used for absorbance measurements. 1 cm matched quartz cells were used for absorbance measurements.

2.2. Reagents

Reagents of analytical grade were used. Triple distilled water was used for preparation of solutions. A stock solution of 1000 mg L⁻¹ of Hg²⁺ was prepared dissolving 0.1354 g of mercury (II) chloride (99.5% Sigma-Aldrich) in water and diluting to 100 mL in a volumetric flask. A 0.2 mL volume of this solution was diluted to 50 mL in another volumetric flask, to get 4 mg L⁻¹ solution. A working solution 0.5 mg L⁻¹ was prepared by dilution. 0.01 g of Dithizone (Merck) was dissolved in 100 mL of acetone/ethanol (3:7) (Sintorgan, Argentina). Ethanol (Sintorgan, Argentina) was used as the desorbing agent. Sulfuric acid (Anedra, Switzerland) 0.5 mol L⁻¹ was prepared by dissolving 27.6 mL of sulfuric acid in 1 L of deionized water.

2.3. Preparation of carbon xerogel

Carbon xerogel was obtained by polycondensation of resorcinol (R) and formaldehyde (F) in aqueous solution using sodium carbonate as catalyst. Resorcinol 3 g and sodium carbonate 53 mg were first dissolved in 6 mL deionized water under stirring. After, 4.5 mL formaldehyde solution was added. The final mixture was placed in a thermostatic bath at 70 °C as gelation temperature.

After 24 h organic gel was dried at 80 °C to constant weight. Dried gel was carbonized at 600 °C for 1 h. The carbon xerogel was washed with triple distilled water and dried to constant weight.

2.4. Chemical activation of carbon xerogel

For the chemical activation, carbon xerogel and potassium hydroxide were mixing in 1:1 mass ratio in 50 mL of water. The mixture was continually stirred at 85 °C until all water was removed. Dried Carbon

Xerogel activated was carbonized at 550 °C for 1 h. Then the sample obtained after activation was washed by distilled water and mixed with 5% HCl solution and placed in the ultrasonic bath at 50 °C. Next, the obtained deposit was washed by distilled water until the pH of the solution reached 6. Finally the sample was dried at 100 °C for 24 h.

2.5. Design of M-SPμE in-syringe system procedure

5 mL of each standard were taken into polypropylene vials (15 mL capacity). Then 0.25 mL H₂SO₄ 0.5 M to adjust to pH and 80 μL dithizone solution was added as complexing agent. The proposed M-SPμE in-syringe system set up was quite simple; a micropipette tip (1 mL polypropylene) was washed with triple distilled water and ethanol and then dried at room temperature. Glass wool was placed at the bottom of the column for the Carbon Xerogel to settle properly. 50 mg of carbon xerogel was packed into the micropipette tip by simple inserted with needle and directly connected with syringe system. Before the extraction, carbon xerogel in the micropipette tip was washed with ethanol and water sequentially to remove impurities from the extraction system. The sample solution was loaded on to syringe system maintaining a flow rate of 0.3 mL min⁻¹. Finally, complex retained were eluted with 1 mL of ethanol.

3. Results and discussion

3.1. Effect of acidity

The effect of acidity is an important parameter in preconcentration studies. Since, the Hg–dithizone complex is known to be stable in acid medium. The volume of 0.5 mol L⁻¹ sulfuric acid was varied from 0.1 to 0.5 mL in 5 mL sample. Recovery 97% was obtained for 0.25 mL of 0.5 mol L⁻¹ sulfuric acid. The results are showed in Fig. 1.

3.2. Choice of the eluent and volume of elution

Other important factor that affect the extraction is the elution solvent used for complex removal from Carbon Xerogel column. These studies were carried out maintaining Hg²⁺ concentration of 280 μg L⁻¹ in 5 mL sample volume. The eluents tried were acetone, methanol, ethanol and polyethylene glycol (PEG). The desorbed fractions with acetone and methanol showed turbidity. The elution was quantitative with PEG and ethanol (Fig. 2) showing quantitative recovery (>97%) with 1 mL of ethanol. Volumes lower than 1 mL show a reduction in the percentage of complex eluted (<85%) with ethanol. Volumes higher than 1 mL of ethanol shows the same percentage of complex eluted (>97%).

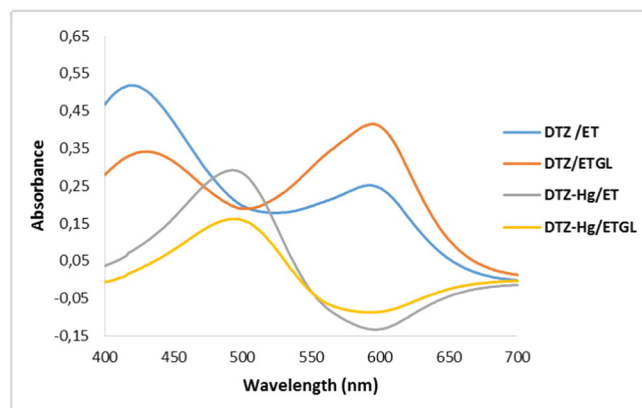


Fig. 2. Comparison of spectra obtained for dithizone–mercury complex (DTZ–Hg with 280 μg L⁻¹ of Hg²⁺) after elution with ethanol (ET) and poly ethylene glycol (PEG).

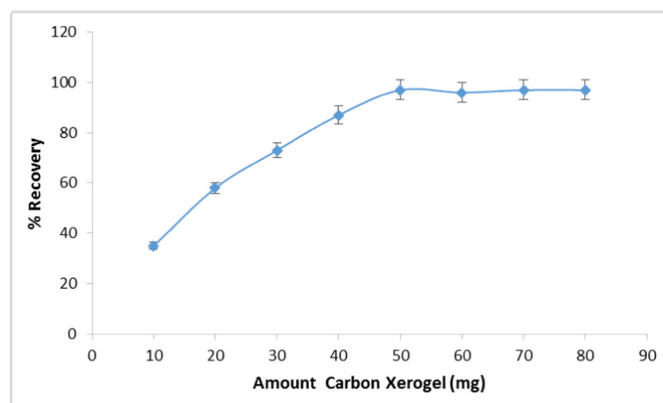


Fig. 3. Effect of the amount of carbon xerogel on the recovery of Hg^{2+} . The error bars indicate the standard deviations of three experiments.

3.3. Effect of flow rate

The flow rate for adsorption and elution process was determined. Flow rates higher than 0.4 mL min^{-1} shows a reduction in the percentage of mercury adsorption. This due to the insufficient contact time between the complex solution and carbon xerogel. For the same reason, flow rates higher than 0.3 mL min^{-1} show a reduction in the percentage of complex eluted. Flow rates of 0.3 mL min^{-1} and 0.2 mL min^{-1} were maintained for adsorption and elution respectively.

3.4. Effect of mass of adsorbent

In order to establish the optimum adsorbent quantity, different amounts of carbon xerogel were used in the range of 10–70 mg for the preconcentration of Hg^{2+} . The result shown in Fig. 3 indicate that quantitative recovery of Hg^{2+} could be obtained in the range 40–70 mg of carbon xerogel. In this procedure 50 mg of carbon xerogel was selected as the optimum amount of adsorbent.

3.5. Stability of the microcolumn

The stability of Carbon Xerogel microcolumn was tested using $280 \mu\text{g L}^{-1} \text{ Hg (II)}$ maintaining a sample volume of 5 mL. The column could be used with good precision and quantitative recovery (>95%) for 15 cycles. Beyond 15 cycles, there was a reduction in the mercury recovery.

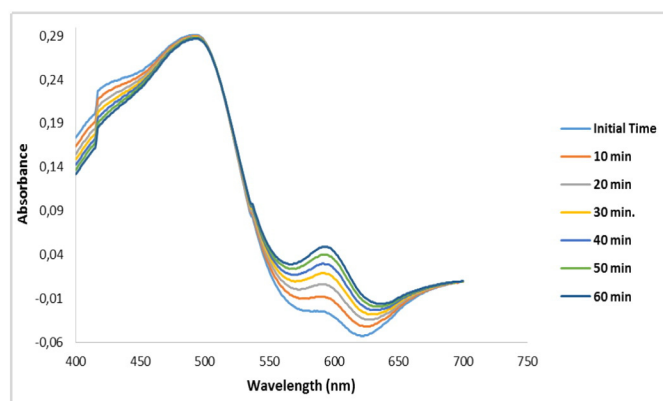


Fig. 4. Stability of dithizone–mercury complex ($280 \mu\text{g L}^{-1} \text{ Hg}^{2+}$) after elution with 1 mL ethanol.

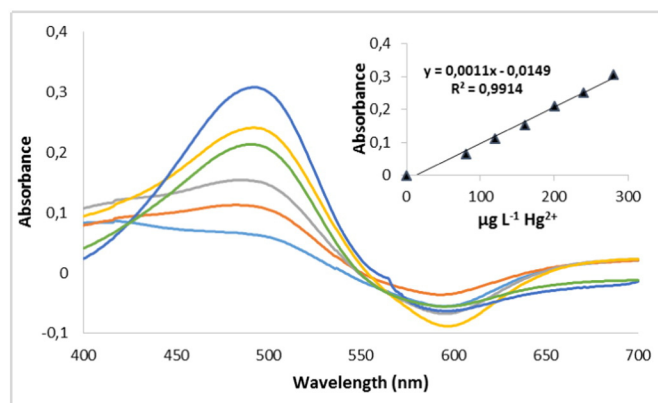


Fig. 5. UV–visible absorption spectra complex dithizone–mercury after elution with ethanol 1 mL from 50 mg carbon xerogel column at different concentrations and the corresponding calibration curve.

3.6. Stability of the complex

The complex stability was evaluated for 1 hs. Absorbance measures was determined every 10 min. The results in Fig. 4 show the high stability for the complex Hg^{2+} –dithizone after elution with ethanol.

3.7. Analytical performance

The analytical characteristics of the developed procedure were evaluated. The absorbance was measured at $\lambda = 490 \text{ nm}$ by UV–visible spectrophotometer and a blank solution was also run under same conditions without adding any Hg^{2+} ion. The calibration curve was linear in the range of $30\text{--}280 \mu\text{g L}^{-1}$ of Hg^{2+} with a correlation coefficient (r) of 0.9914. The equation of the line for Hg^{2+} was $A = 0.0011 C - 0.0149$ where A is the absorbance and C is the concentration of Hg^{2+} in $\mu\text{g L}^{-1}$ in the initial solution. The UV– visible absorption spectra of Hg –dithizone after the elution from Carbon Xerogel at different concentrations and the corresponding calibration curve are shown in Fig. 5. The limit of detection (LOD) calculated based on the signal at intercept and three times the standard deviation about regression of the calibration curve was $7.8 \mu\text{g L}^{-1}$ and the relative standard deviation (RSD%) for six replicate measurements of $280 \mu\text{g L}^{-1}$ of Hg^{2+} ion was 1.36%. Enrichment factor was calculated as the ratio of the slopes of calibration graphs with and without preconcentration of Hg was found to be 25.

A comparison of the developed method with some of the previously reported methods for Hg^{2+} by different preconcentration procedures is shown in Table 1. As can be seen from the table, it is evident that the limit of detection obtained with this method is comparable or even better than previous works. Other significant advantage of the propose method is the sample volume which is less than previous works.

3.8. Interferences studies

The effect of other ions on the intensity signal were studies under optimum experimental conditions. The study was performed at a

Table 1
Comparison with others analytical methods for Hg preconcentration.

Analytical method	LOD ($\mu\text{g L}^{-1}$) ^a	RSD %	Sample volume (mL)	Ref.
Spectrophotometry	0.83	0.27	10	[19]
Spectrophotometry	2	3.5	100	[11]
Spectrophotometry	4	2.5	100	[12]
Spectrophotometry	6.01	–	–	[20]
Spectrophotometry	26	1.3	10	[21]
Spectrophotometry	7.8	1.36	5	Present work

^a LOD = Limit of detection.

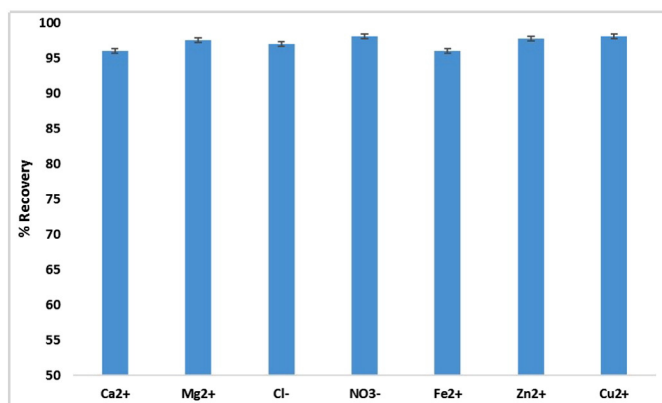


Fig. 6. % recovery of Hg²⁺ in the presence of different ions. The concentration of Hg²⁺ was 280 µg L⁻¹. The concentration of Ca²⁺, Mg²⁺, Cl⁻ and NO₃⁻ was 10 mg L⁻¹. The concentration of other metal ions was 2.5 mg L⁻¹. The error bars indicate the standard deviations of three experiments.

constant concentration of Hg²⁺ (280 µg L⁻¹) and measuring the absorbance before and after adding each ion. The results in Fig. 6 show that the interference is not quantitative in the concentration range studied for each metal ion. The ions selected are commonly present in water samples. This results match with previous works [22,23].

3.9. Validation and application

The accuracy of the methodology was performed using the standard addition method. The reproducibility was evaluated repeating the proposed approach 6 times for each sample. The recoveries of Hg²⁺ in two samples of water (ground water and mineral water), based on the average of replicate measurements, are illustrated in Table 2; the obtained results show that the proposed method is suitable for determination of Hg²⁺ in such samples, for the entire range of studied concentrations.

4. Conclusions

In this work a novel and sensitive analytical methodology for mercury preconcentration and determination in water samples by solid phase microextraction in micropipette tip syringe packed with activated carbon xerogel has been presented. The developed method reduces the risk of contamination or sample loss becoming a low cost technique compared to on-line methods. The proposed method requires only a conventional glass syringe as extraction unit. M-SPµE in-syringe system was successfully applied for determination of Hg in real water samples (mineral water and ground water). The analytical characteristics obtained for the proposed preconcentration method encouraged to propose this methodology as a worthy tool in Hg trace analysis.

Table 2
Recuperation study. Hg²⁺ determination in groundwater and mineral water (San Juan, Argentina).

Sample	Hg ²⁺ added (µg L ⁻¹)	Hg ²⁺ found ± SD (µg L ⁻¹) ^a	% Recovery (n = 6)
Ground water	0	30.8 ± 0.5	–
	40	69 ± 0.8	97.45
	120	152.3 ± 1.8	101
	240	260.2 ± 4.1	96.08
Mineral water	0	<LOD	–
	40	41 ± 0.5	102.5
	120	121.8 ± 1.2	101.7
	240	229.1 ± 3.7	95.46

^a SD = Standard deviation.

Acknowledgements

The authors wish to thank the Instituto de Ciencias Básicas and CICITCA – Universidad Nacional de San Juan (Project F/1008) for the financial support.

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