



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



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## 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  $\text{Hg}^{2+}$  ion was 1.36%.

The proposed method was successfully applied to quantitative determination of  $\text{Hg}^{2+}$  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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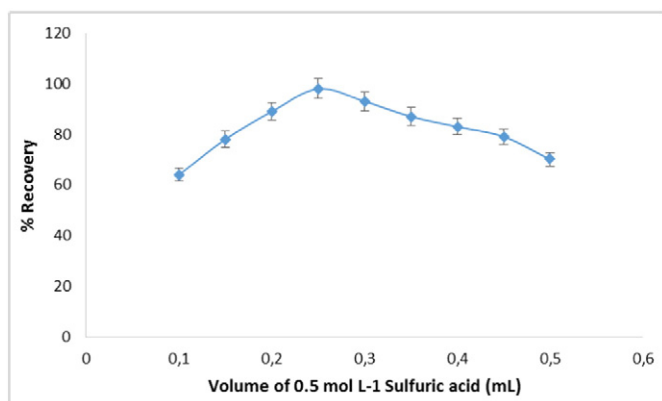


Fig. 1. Effect of volume of 0.5 mol L<sup>-1</sup> sulfuric acid on Hg<sup>2+</sup> recovery. The error bars indicate the standard deviations of three experiments.

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<sup>-1</sup> of Hg<sup>2+</sup> 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<sup>-1</sup> solution. A working solution 0.5 mg L<sup>-1</sup> 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<sup>-1</sup> 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 H<sub>2</sub>SO<sub>4</sub> 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<sup>-1</sup>. 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<sup>-1</sup> 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<sup>-1</sup> 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 Hg<sup>2+</sup> concentration of 280 μg L<sup>-1</sup> 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%).

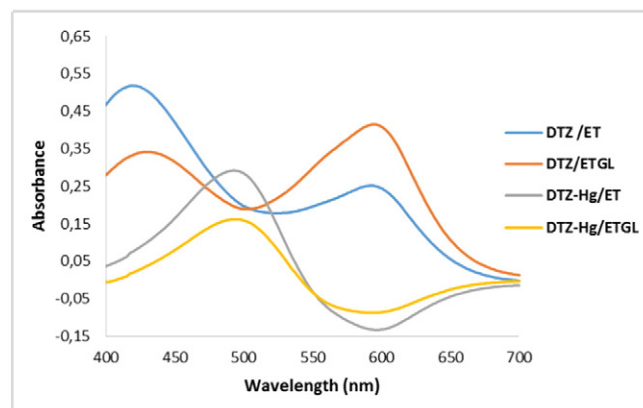


Fig. 2. Comparison of spectra obtained for dithizone–mercury complex (DTZ–Hg with 280 μg L<sup>-1</sup> of Hg<sup>2+</sup>) after elution with ethanol (ET) and poly ethylene glycol (PEG).

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