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Determination of ultra-trace amount mercury (II) ion in Tap water and River water samples with the barium di phenyl amine sulfonate by the chlorate ion in sulfuric acid with kinetic method

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ABACTRACT

A new kinetic spectrophotometic method for the determination of trace amount mercury(II) in Tap water and River water samples has been described based on it s the catalytic effect on the oxidations of barium die phenyl aminosulfunate, by potassium chlorate in sulfuric acid. The reaction is followed spec- trophotometrically by measuring the decrease in the absorbance at 469 nm. Under the optimum conditions of 0.2 molL^{-1} sulfuric acid, 1.0 × 10^{-4} mol L^{-1}, barium die phenyl aminosulfunate, 0.01 mol L^{-1} potassium chlorate at 35^{oC}, calibration graph in the rang of 0.001-0.06 ng L^{-1} mercury(II). Concentration was obtained with detection limit of 0.2303 g mL^{-1} by the fixed-time method of 4.5 min. The relative standard deviation for 0.05 ng L^{-1} mercury(II) is %90. No serious interference was identified. The applicability of the method was demonstrated by the determination of the mercury (II) in Tap water and River water samples.

Keywords: mercury (II); Kinetic barium die phenyl aminosulfunate; Determination; Spectrophotometic.

INTRODUCTION

is an essential micro element for the human body. In normal conditions it plays an important role in bone and tissue formation (normal growth), normal reproductive functions, and carbohydrate and lipid metabolism. The diet is the basic source of the metal. A daily dietary intake of 2 to 5 mg is estimated to be adequate for adults. mercury deficiency in humans is related to delayed blood coagulation and hyper cholesterolaemia. The metal may be considered toxic when dietary in take is significantly higher [1]. Hence, sensitive and selective methods for determination of mercury in foodstuffs, drinking waters and drinks are of great interes. There have been numerous spectrophotometric methods for the determination of mercury. The oxidation of mercury to permanganate and a measurement of the absorption of the charge-transfe band of permanganate at 528 nm has long been used as a standard method for mercury determination; 1, 2 how ever, this method suffers from low sensitivity.Spectrophotometric methods based on complex formation with chromogenic reagents provide good sensitivity, but have showed serious interferences from many cations and anions despite the high detection limit of 0.05 ng mL^{-1}[2,3]. Numerous kinetic methods have been reported based on the catalytic effect of Hg^{2+} on the oxidation of organic compounds with suitable oxidants. Although these methods have shown good sensitivity, they are time consuming and irreproducible, since it is difficult to control the timing of the reaction, which is variable from one experiment to another [4 – 9], The sophisticated techniques, such as inductively coupled plasma- mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), electrochemical analysis, spectrophotometry, neutron activation analysis and atomic absorption spectrophotometry (AAS), been adopted for sensitive assays for both oxidation states of mercury. These methods have disadvantage of cost and instruments used in regular analysis. AAS often has low sensitivity due to the matrix effect of samples such as salinity[10,11]. environmental samples at low levels and has matrix effects with detection limit of lead[12]. Some recent enhancements of the method using a flow injection tech- nique have been reported [13 – 15], However, if the reaction time is longer than the flow rate, the method will not be efficient and still irreproducible. Several efforts in crease the reaction rate by temperature have been reported; however, either the sample degrades or airbubbles will develop that hinder the flow rate [16-20]. The barium die phenyl aminosulfunate is a well-known metallochromic indicator for the quantitative and qualitative determination of variety of metal ions. BDAS has many characteristics required an ionophore. This ionophore reacts highly colored complexes. The complexes can be reversed to form again the ionophore over a large number of repetitions [21]. In this work, the catalytic effect of mercury (II) on the oxidation of barium die phenyl aminosulfunate , with potassium chlorate in the presence of barium die phenyl aminosulfunate, was investigated. A catalytic kinetic Spectrophotometric method for the determination of mercury (II) was developed. The proposed method is extremely sensitive, with higher selectivity and is a simpler procedure than the three methods mentioned above. The method was applied successfully to the determination of total mercury (II) in Tap water and River water samples.

MATERIALS AND METHODS

2.1. Apparatus

All the determinations of the analytes were carried out using a Sens AA GBC double beam atomic absorption spectrometer (AAS) equipped with deuterium background corrector. Hollow cathode lamps were used as radiation sources and the operational conditions of the equipment were established according to the manufacturer’s recommendations for each element. An adjustable capillary nebulizer and supplies of acetylene and air were used for the generation of aerosols and atomizations. The UV/Vis spectra were obtained from a Perkin-Elmer, model Lambda 2 spectrophotometer. A Genway model 3510 pH/Ion meter with a combined glass electrode was used for pH measurements. Laboratory glassware was kept overnight in 10% nitric acid solution. A NBE ultrathermostat (VEB Prufgerate – WerkMedingen, Germany) was used to control the temperature.

2.2. Reagents and materials

All chemicals, except barium die phenyl aminosulfunate, were prepared of the analytical grade purchased from Merck Company, solution (Merck, Darmstadt, Germany). The solutions were prepared with doubly distilled water. The concentrations of the stock solutions were as follows: barium die phenyl aminosulfunate, 1.0×10^{-4} mol L^{-1}, potassium chlorate, 0.1 mol L^{-1} sulfuric acid, 0.2 mol L^{-1} mercury (II) chloride.

2.3. Pretreatment of real samples

Water samples

Analysis of water samples for determination of Hg(II) ion content was performed as following: 200 mL of sample was poured in a beaker and 8 ml concentrated HNO_3 and 3 ml of H_2O_2 of (30%) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tenth volume. After adjustment of samples pH to desired value the were performed according to general described procedure[22].

2.4. Procedure

A typical kinetic Spectrophotometric method experiment required the following steps: 1 ml of manganese solution equated to 0.01 ml grams was added to the 10 ml volumetric flask. Than 1 ml gram of potassium chlorate (0.1 mol L^{-1}) and 1 ml of sulfuric acid solution (0.2 mol L^{-1}) was added. By adding the first drop of 1 ml barium die phenyl aminosulfunate 1.0×10^{-4} mol L^{-1}, to the volumetric flask, the time of the reaction beginning is recorded, after 5 sec the solution is mixed for 30 sec, and then it is volume by adding the distilled water, a sufficient amount of the solution was added to a 1 cm cell, the difference between the quantities of the absorption in a wavelength equal to 469 nm in a time interval equalto 1-4.5 min was measured by mean of spectrophotometer (A As). All these steps would be repeated for a non catalytic reaction without the presence of mercury as the catalyst element (AAb), finally (AA)AAblank-AAsample is calculated. barium die phenyl aminosulfunate, oxidation is traced in the acidic medium by potassium chlorate, which its wavelength is 469 nm. The absorption spectra in an aqueous solution are shown in figures 1 and 2.

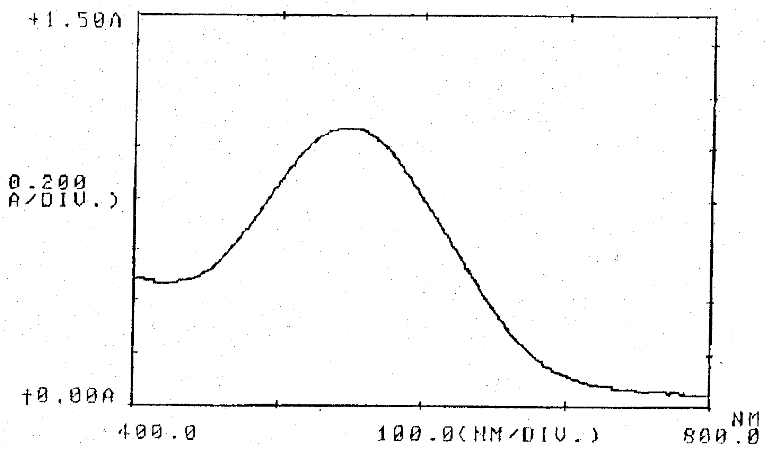

Figure 1: The absorption spectra oxidation of product barium die phenyl aminosulfunate

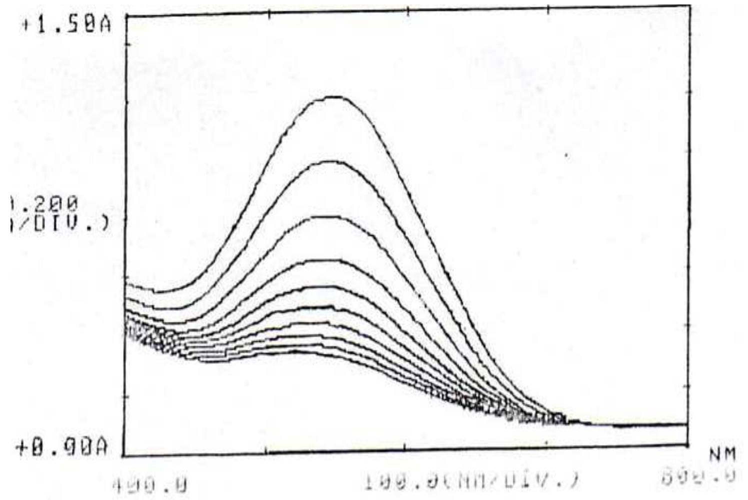

Figure 2: The absorption spectra oxidation of product barium die phenyl aminosulfunate, 20min mg L^{-1}

RESULTS AND DISCUSSION

3.1. Investigation of ligand complexation with metal ions

The complexation studies between the ligand and Hg(II) ion were carried out to determine the stoichiometry of the metals - ligand reactions as well as the formation constants and the molar absorptivities of these complexes. The stoichiometry between the ligand and each of the metal ions were determined from the absorbance-mole ratio data. The plots at 469 nm (Figure 3), clearly show a 1:1 (ligand to metal) stoichiometry for all the metal complexes. The formation constants, K_f, and the molar absorptivities, ε_{ML}, of the resulting complexes were then evaluated from the absorbance-mole ratio data and with the aid of a nonlinear curve fitting of the theoretical absorbance, A_{Theo}, to the experimental absorbance, A_{Exp},using Microsoft Excel program[23]. When known concentrations of metal, C_M, is mixed with a constant concentration of ligand and ML complexes are formed, the following equations can be written;

$L + M \leftrightarrow ML \qquad Kf = [ML] / [L] [M]$

$[L] = C_L - C_M + x \qquad [M] = x [ML] = C_M - x$

$K_f\ x^2 + (K_f C_L - K_f C_M + 1)\ x - C_M = 0$

$A_{Theo} = A_L + A_{ML} = (A_0 / C_L)[L]$

$+ \varepsilon_{ML} K_f C_M [L] / (1+K_f [L])$ (2)

where A_0 is the initial absorbance of the ligand with concentration of C_L before any metal ions addition. Also, x is a reversed amount of ligand or metal reproduced from decomposition of ML at equilibrium which is equal to [M] value under $C_M \geq C_L$ condition. The procedure actually consists of two mutual steps. First, by initial guessing for K_f and solving Equation (1), x value is obtained which yields [L] parameter from $[L] = C_L - C_M + x$ then A_{Theo} is calculated by the substitution of [L] in Equation (2) (C_L, C_M and A_0 are known parameters). In the second step, for fitting the curve of A_{Theo} to that of A_{Exp}, minimization of SSR, sum of squared of residual, is performed by the Excel Solver program and two adjustable parameters K_f and ε_{ML} are found. The results, which are summarized in (Table 1), show the values of formation constants for the considered metal complexes.

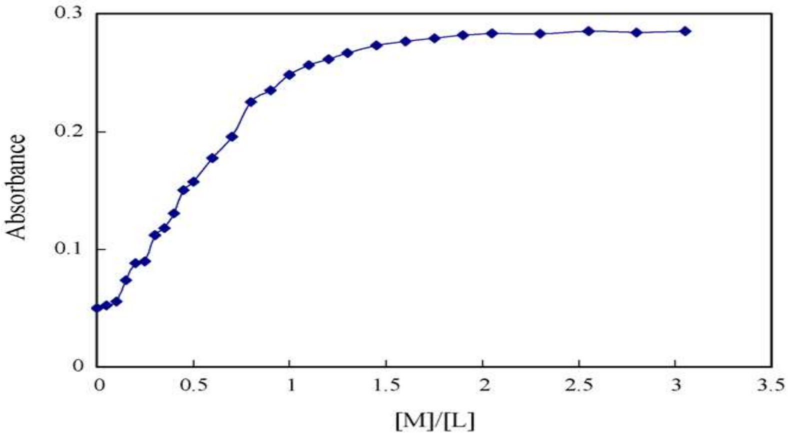

Figure3. Absorbance-mole ratio plot for Hg- barium die phenyl aminosulfunate, complexes at [M] = 469 nm, [BDAS] = 1.0 × 10^{-4} mol/L in Methanol

Table 1. Formation constants and molar absorptivities of the metal complexes

Type of complex	K_f	ε_{ML}	SSR[a]
Hg - BDAS	1.02×10^{-4}	2.71×10^{-3}	1.22×10^{-3}

[a] SSR = $\sum$ ($A_{Exp} - A_{Theo}$)2

3.2. Effect of time on the reaction rate

As it was expressed in the method, to obtain optimum time of the reaction, 1 ml Hg(II) 0.01 mg L^{-1} solution, 1 ml potassium chlorate 0.1 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml barium die phenyl aminosulfunate, 1.0×10^{-4} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of so lutions was measured in the 0-11 min interval of time. The above mentioned operation was repeated for bank solution (the solution without Hg(II). Changes in absorption based on the time at 30 centigrade degrees temperature are shown in figure 4 . 4.5 min was selected as the optimum time.

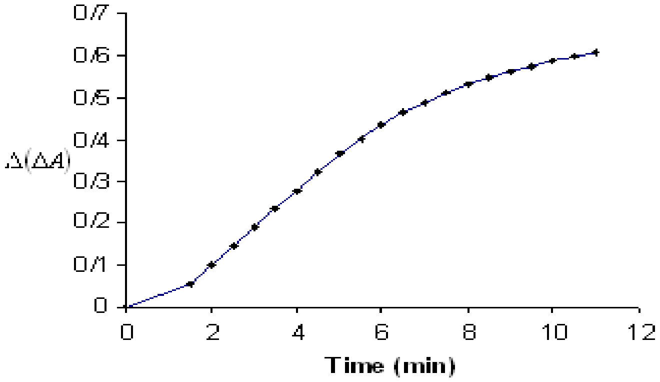

Figure 4: The effect of time on the reaction rate

3.3. Effect of sulfuric acid concentration on the rate of reaction

As it was expressed in the method, to obtain optimum sulfuric acid concentration of the reaction, 1 ml Hg(II) mgL^{-1} solution, 1 ml potassium chlorate 0.2 mol L^{-1}, 1 ml sulfuric acid solution 0.1 to 10 mol L^{-1} and 1 ml, barium die phenyl aminosulfunate , 1.0 × 10^{-4} mol L^{-1}are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. The above mentioned operation was repeated for blank solution (the solution without Hg(II)). As it is shown in figure 5, the o.2 molar concentration of sulfuric acid has the most changes in the absorption, so that, it was selected as the optimum concentration of the acid.

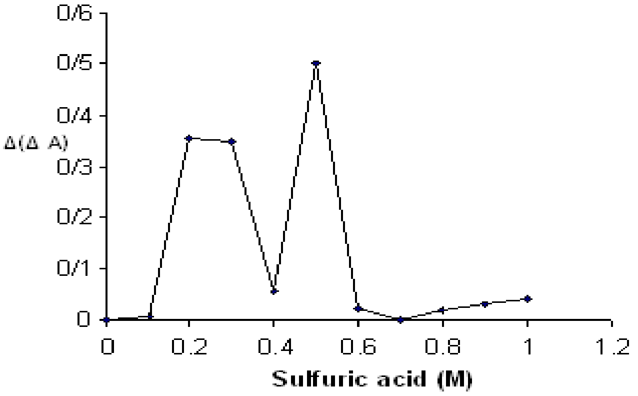

Figure 5: The effect of sulfuric acid concentration on the rate of reaction

3.4. Effect of barium die phenyl aminosulfunate on the reaction rate

To inspecting The effect of barium die phenyl aminosulfunate, on the reaction rate, 1 ml Hg(II) 0.01 mg L^{-1} solution, 1 ml potassium chlorate 0.1 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml barium die phenyl aminosulfunate, 1.56× 10^{-5} to 2.5 × 10^{-3} mol L^{-1} are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. The above mentioned operation was repeated for blank solution (the solution without Hg(II)). The results are shown in and figure 5, based on those results 1.0 × 10^{-4} mol L^{-1} was selected as the desired concentration.

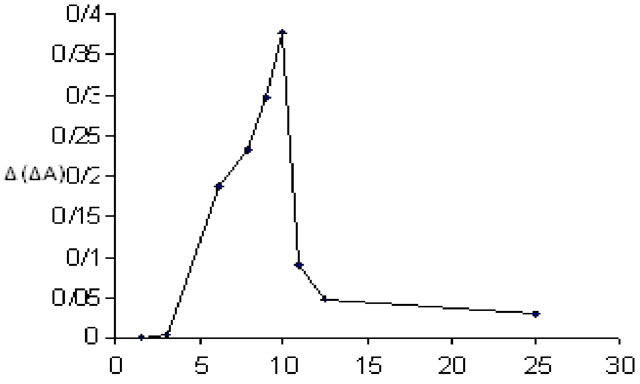

Figure 5: The effect of barium die phenyl aminosulfunate, on the reaction rate

3.5. Effect of potassium chlorate concentration on the reaction rate

To inspecting the effect of potassium chlorate concentration, 1 ml Hg(II) 0.01 mg L^{-1} solution, 1 ml potassium chlorate at different concentration 0.05 to 0.3 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml barium die phenyl aminosulfunate , 1.0 × 10^{-4} mol L^{-1}are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. The above mentioned operation was repeated for blank solution (the solution without Hg(II). Results are shown in figure 6, based on that results, potassium chlorate at a concentration of 0.011 mol L^{-1} was selected as the desired concentration.

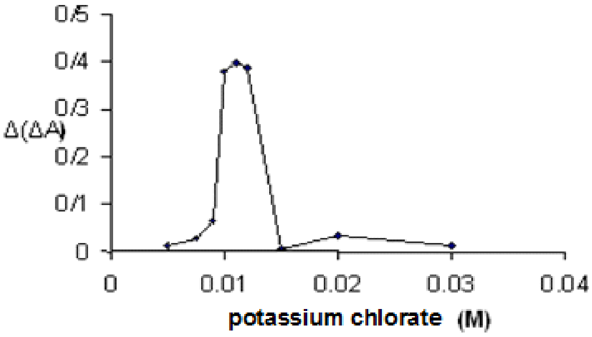

Figure 6: The effect of potassium chlorate, on the reaction rate

3.6. Effect of temperature on the reaction rate

At first put the cells including: Hg(II), potassium chlorate, barium die phenyl aminosulfunate, distilled water and volumetric 10 ml flasks in the thermostat to reach to the desired temperature. After they go to the equilibrium temperature, 1 ml Hg(II) 0.01 mg L^{-1} solution, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml barium die phenyl aminosulfunate, 1.0×10^{-4} mol $L^{-1}$are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. The above mentioned operation was repeated for blank solution (the solution without Hg(II)). As it is shown in figure 7, 35 centigrade degree was selected as the desired temperature.

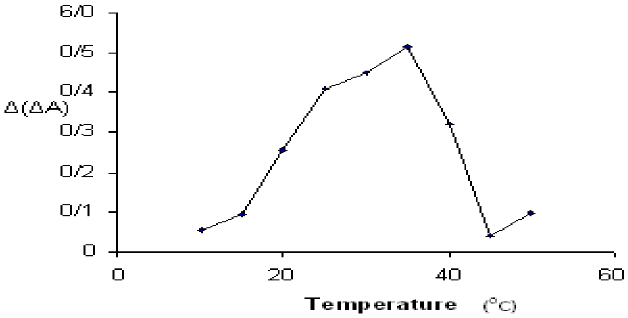

Figure 7:The effect of temperature on the reaction rate

3.7. Effect of ionic power of the medium was also

inspected; potassium chlorate and potassium nitrate were used for this purpose. 1 ml Hg(II) 0.01 mg l-1 solution, 1 ml potassium chlorate 0.1 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml barium die phenyl aminosulfunate, 1.0×10^{-4} mol $L^{-1}$are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. as we can see in figure 8 results show that the effect of ionic power on the reaction rate is neglectible, and can be ignored.

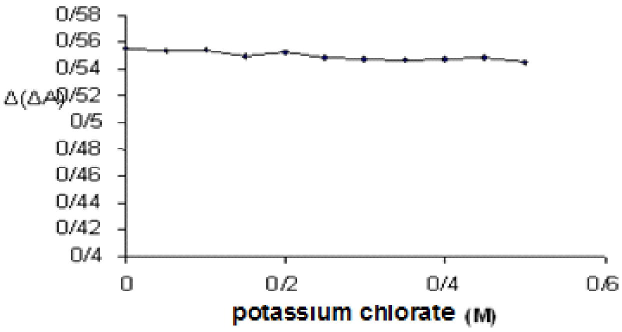

Figure 8: The effect of Ionic power on the reaction rate

3.8. Calibration graph and reproducibility

Reaching to the standard curve of Hg(II) in the reaction, the system went into the desired condition. So different volumes of Hg(II) (100 ng mL^{-1}), 1 ml potassium chlorate 0.1 mol L^{-1}, 1 ml sulfuric acid solution 0.2 mol L^{-1} and 1 ml barium die phenyl aminosulfunate, 1.0×10^{-4} mol $L^{-1}$are added to the volumetric flask 10 ml and by adding distilled water. Absorption of solution was measured after 4.5 min. the above mentioned operation was repeated for blank solutions. The examination/test was done at 35 centigrade degrees. Results are shown figure 9.

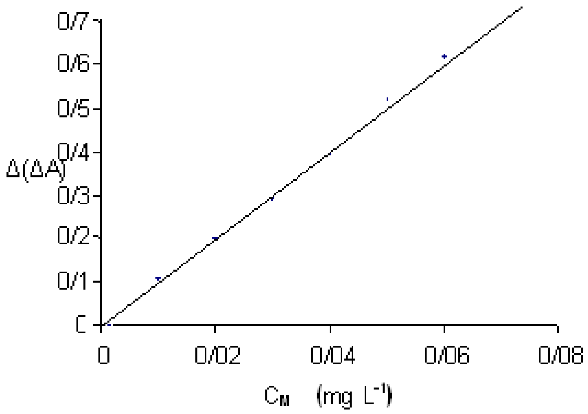

Figure 9: Calibration graph for Hg(II)

3.9. Effect of foreign ions

The accuracy and reliability of this method was evaluated by comparing the results obtained for the same samples by an AAS method. The results estimated by AAS and spectrophotometry are shown in Table 4. The results estimated by spectrophotometry are much less as compare to results obtain by AAS. It may be attributed to the interference of foreign ions in the determination of mercury. The interfering ions. These ions may interfere with mercury (II). In order to assess the potential analytical applications of the proposed kinetic reaction, the influence of foregn ions on the determination of mercury (II) was investigated [24-26]. The tolerated limits for the ions assayed are shown in Table2, (was relative errors less than 5%). As can be seen, the proposed method is highly selective.

Table 2. Effects of the matrix ions on the recoveries of the examined mercury (II) ion (N=6)

Ion	Added As	Tolerance Limit, mg L^{-1}
Cl^-, K^+, Na^+	KCl, NaCl	1000
Mg^{2+},Ca^{2+}	chloride salts	800
Cu^{2+}	Nitrate salts	700
HCO_3^-	$NaHCO_3$	1000
SCN^-	KSCN	1000
PO_4^{3-}	Na_3PO_4	400
Fe^{3+}	Nitrate salts	300
CO_3^{2-}	Na_2CO_3	500
Cr^{3+}	Nitrate salts	150
Mn^{2+}	Nitrate salts	250

3.10. Application

To assess the applicability of the method to real samples with different matrices, containing various amounts of diverse ions were used. For accuracy and reliability of proposed method, spiking experiments and independent analysis were used. The proposed method was applied to the determination of total mercury (II) in Tap water and River water samples. In Table3 the results obtained are shown, and compared with those obtained by atomic absorption spectrophotometry. The level of the analyte ions were found below the detection limit of related element. The results of replicate three analyses of each sample show that the ions recoveries are almost quantitative with a low RSD. The recovery of spiked samples is satisfactory reasonable and was confirmed using standard addition method, which indicate the capability of the proposed method for the determination of trace amounts of these elements in different samples.

Table 3. Recovery of trace mercury (II) from Tap water and River water samples after application of presented procedure (N=6)

Sample	Added (ng L^{-1})	Founded (ng L^{-1})	RSD %	Recovery %
Tap water	0	103.3	1.1	---
	100	161.9	1.8	103
River water	0	61.8	1.1	---
	100	164.3	1.3	95.3

CONCLUSION

The proposed method is very simple, highly selective, sensivite and reproducible for the determination of mercury (II). The method also exploits low–cost instrumentation and overcomes the problems associated with previously reported spectrophotometric method for the determination of mercury [27-30]. The method is simple, accurate can be applied for the determination of analytes in environmental samples [31,32].

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