Selective Separation and Trace Determination of Hg(II) From Environmental Samples Using New Modifier

A. M. El-Menshawy & A.A. El-Asmy*

Department of Chemistry, Faculty of Science, Mansoura University, Mansoura, Egypt

Abstract: A preconcentration method based on the sorption of Hg(II) on silica gel coated with 1- isatin-4-phenylthiosemicarbazone(HIPTSC) for its determination spectrophotometrically and/or by cold vapor atomic absorption spectrometry (CVAAS) has been developed. The sorbed Hg(II) was eluted with 0.1 mol l^{-1} HCl. The effect of pH, stirring time and eluent concentration on the recovery of Hg(II) was examined. The influence of some matrices individually or in combination on the recovery of Hg(II) was investigated using the developed method. The results showed that 500 µg ml^{-1} each of K^+, Cl^-, NO_3^- and NH_4^+; 350 µg ml^{-1} each of CH_3COO^- and F^- ; and 200 µg ml^{-1} each of Ca^{2+}, Al^{3+}, Mg^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}, Pb^{2+} and Cd^{2+} did not interfere with the Hg(II) sorption. At the optimum conditions, the recovery of Hg(II) was found > 98 %. The relative standard deviation and detection limit of the method were found to be < 1.0% and 5 ng ml^{-1}, respectively. The adsorption isotherm of Hg(II) was studied and the binding equilibrium constant and adsorption capacity were calculated to be 8.60 l mg^{-1} and 14.005 mg g^{-1}, respectively. The proposed method was successfully applied for the determination of Hg(II) in binary mixtures and environmental water samples.

Key words: Mercury(II); Silica gel; HIPTSC; adsorption isotherm; CVAAS.

Introduction

Mercury and its compounds are hazardous for human, plants and animals due its protoplasmic poisons [1]. The tolerance limit of inorganic mercury in aqueous solution is 1 µg l^{-1}. The major sources of mercury poisoning are due to its mining, recovery, usage, industrial waste and its accumulation in human body *via* food. Mercury has a tendency to absorb and amalgamate to various surfaces. It is capable to form complexes with many ligands [2,3]. The low level of mercury in environmental and biological samples makes necessary to preconcentrate these samples before their actual determination. A number of solid-liquid preconcentration systems have been used for mercury in off-line procedures such as activated carbon [4], metal oxides, ion exchange resins [5,6] and with immobilized reagents such as diethyldithiocarbamate[7], 8-hydroxyquinoline [8] and dithizone [9] onto solid phases.

Recently, the use of solid phase extraction (SPE) for the preconcentration of trace elements is reasonably well understood. Activated carbon, functionalized polymers, and chelating resins have been used at the SPE for the determination of metal ions in water analysis [10-11]. However, extension of this method does not have enough chemical and mechanical stability. The main problem associated with ion-exchange resins are that matrices containing a high concentration of solutes, and particularly a high content of electrolytes, have limited adsorption capacity and selectivity. Silica gel is the most widely used solid support in analytical chemistry due to its thermal, chemical, and mechanical stability [12]. Its surface is characterized by the presence of silanol groups (weak ion exchangers) that bring about the low interaction, binding, and extraction of the target analytes [13]. For this reason, modification of silica-gel surface with certain functional groups has successfully employed to produce a solid phase with certain selectivity indicators [14].

The major objective of immobilized silica gel is to incorporate selectivity to apply as selective solid phase extractor. The size of organic modifier, the length of hydrocarbon chain [15], the activity of the loaded surface groups [16], the nature of the donor atoms [17-19] and the formula of (hard–soft) acid–base [20, 21] are the main factors that may ruled.

* *Corresponding author: aelasmy@yahoo.com*

Sulfur containing compounds (soft bases) and mercury(II) (soft acid) favoring strong and selective binding between these species. This behavior prompted many researchers to immobilize silica gel surface with sulfur containing compounds for selective extraction of these metal ions. The reactivity of sulfur containing compounds towards mercury (II) was reported [22].

This work is devoted to synthesis, characterization and evaluation of the sorption properties of silica gel modified with isatin-4-phenylthiosemicarbazone (IPTSC) with the anticipation of the potential application of this phase as a new selective solid phase extractor for mercury(II) from aqueous natural samples.

Experimental

Reagents

Stock solution of Hg(II) (1000 μgml^{-1}) was prepared by dissolving appropriate amount of $HgCl_2$ (Aldrich) in deionized water. Other reagents (BDH) were of Analytical reagent grade.

Equipment

A perkin-Elmer model 2380 Atomic Absorption Spectrometer (USA) was used. The IR spectra were carried out using Mattson 5000 FTIR Spectrophotometer in the range 4000-200 cm^{-1} in KBr disc. UV–Vis measurements were performed on a Unicam 2001 UV-Vis Spectrophotometer using a 1 cm quartz cell. The pH values were measured using a pH-meter (Hanna Instruments, 8519, Italy) with accuracy of ±0.01 and standardized with 0.05 moll^{-1} potassium hydrogen phthalate (pH 4.01) and standard pH tablet (9.2) at 25°C.

Preparation of the reagent

Isatin-4-phenylthiosemicarbazone (HIPTSC) was synthesized [23] as follows: a hot solution of 4-phenylthiosemicarbazide (0.343g, 2 mmol in ethanol) was added to (0.30g, 2 mmol) isatin dissolved in very small amount of glacial acetic acid. The resulting solution was boiled under reflux for 1h. The yellow crystals of IPTSC were filtered off, washed with ethanol, recrystallized from absolute ethanol and finally dried in a vacuum desiccatore (Fig. 1). The purity was checked by TLC, elemental (C, H and N) analysis, and IR spectra. The product is crystalline (m.p. 241-242 °C). Its stock solution is prepared in acetone.
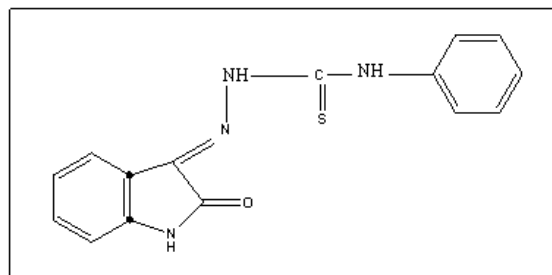
Figure1: Structure of HIPTSC

Preparation of silica gel-isatin-4-phenylthiosemicarbazone

Silica gel was firstly purified with 5% hydrochloric acid and washed with deionized water til no acidity, then dried at 120°C for one day. The cleaned silica gel was mixed with 0.1g HIPTSC, dissolved in 25 mL acetone, and 5 g of previously activated silica. Complete evaporation of acetone allows deposition of HIPTSC on the surface of silica. The amount of IPTSC supported was 0.02 g /g silica gel.

Recommended Batch procedure

A sample solution (100ml) containing 10µg/ml of Hg(II) was transferred to a glass stoppered bottle (250ml). After adjusting the pH to 5.0, 100mg of the modified silica was added; the feed solution was shaken for 30 min. After filtration, the modified silica was washed with deionized water and the sorbed Hg(II) was eluted with 5 ml 0.1 moll^{-1} HCl and the resulting solution was completed to 100 ml and determined using CVAAS or spectrophotometrically using dithizone method [24].

Results and discussion

Characterization

The elemental analysis for HIPTSC, $C_{15}H_{11}N_4SO$, (C, 59.3; H, 3.8; N, 18.96%) shows a good agreement with the calculated values. The IR spectra showed the presence of strong bands at 3125, 1700, 1635, and 780 cm^{-1} assigned to $\upsilon(NH)$, $\upsilon(C=O)$, $\upsilon(C=N)$, and $\upsilon(C=S)$, respectively [25].

A careful comparison of the IR spectrum of [Hg(IPTSC)Cl] with that of HIPTSC showed that, IPTSC acts as a tridentate ligand in the thiol- form coordinating *via* C=N, C=O and C-S with the displacement of the thiol hydrogen atom (Fig. 2).

This mode of chelation is supported by the following evidences: (1) the bands assigned to $\upsilon(C=O)$ and $\upsilon(C=N)$ are slightly shifted with low intensity, (2) the band
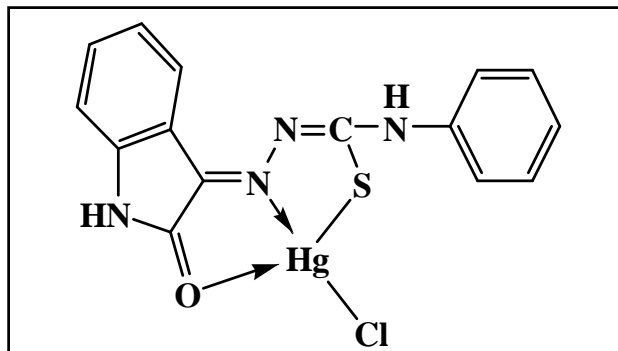
Figure 2: Structure of [Hg(IPTSC)Cl]

assigned to υ(C=S) is disappeared with the appearance of a new band due to υ(C-S) and (3) the appearance of new bands at 420, 400 and 330 cm^{-1} which assigned to υ(M-O), υ(M-N) and υ(M-S), respectively, indicating the coordination *via* oxygen, nitrogen and sulfur atoms(25). The presence of υ(M-Cl) at 270 cm^{-1} confirms its terminal rather than bridged.

Effect of pH

The effect of pH on the ability of HIPTSC-coated silica gel to preconcentrate Hg(II) ions was investigated. For this purpose, the pH values of Hg(II) solutions were adjusted within a range of 1–10 with HNO$_3$ or NaOH. As shown in Fig. 3, the optimum pH of the sample solution was 5 for the studied metal ion. With very strong acidic (pH < 2) or basic (pH > 10) solutions, the Hg(II) is not retained by HIPTSC immobilized on silica gel. Its retention is very low, because the donor functional groups are strongly protonated in acidic solution or the Hg(II) is bound to the medium OH groups [26] in strong basic solution.
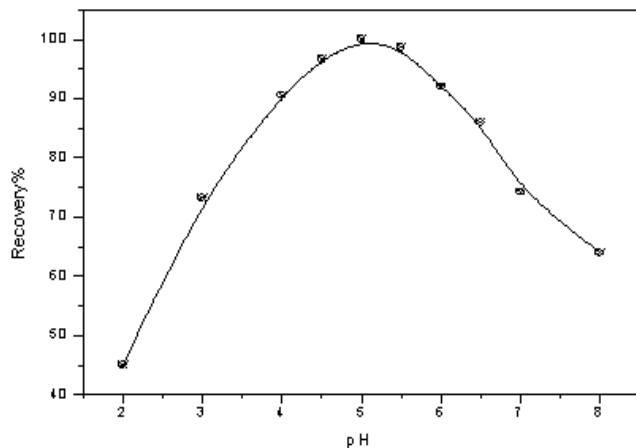
Determination of sorption capacity

The sorption capacity of the modified silica for Hg(II) was determined by shaking excess metal ions with 100mg of the modified silica at pH 5. The maximum sorption capacity for Hg (II) ion with silica-HIPTSC is 0.07 mmol g^{-1}.

Effect of stirring time

To determine the rate of sorption of Hg(II) on the modified silica, batch experiments were elaborated by shaking 100 mg of the modified silica with 100ml of feed solution containing the metal ions at room temperature (25ºC). Aliquots of 1ml solution were taken out for analysis at pre-determined intervals. The concentration of metal ions in the supernatant solution was determined and the amount of sorbed metal ions on silica-HIPTSC was calculated by mass balance.

The sorption half-time ($t_{1/2}$) defined, as the time needed to reach 50% of the total sorption capacity was estimated from Fig. 4. From the data obtained, it was observed that, the maximum sorption of Hg(II) with silica-HIPTSC reached its equilibrium time after 5 min.

Choice of eluent

Choice of the most effective eluent for the quantitative stripping of the retained Hg(II) on silica-HIPTSC is of special interest. The Hg(II) sorbed on the modified silica can be eluted with acid solutions (hydrochloric, nitric and sulphuric acid) into the aqueous phase. Other approach was the use of complexing agent such as EDTA for elution of the sorbed metal ion. Literature survey
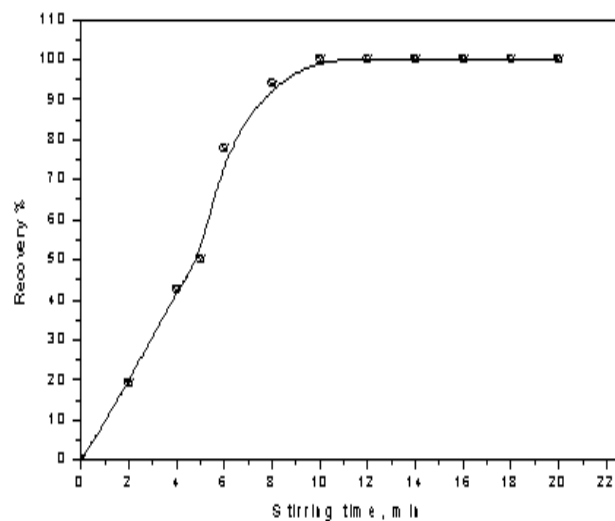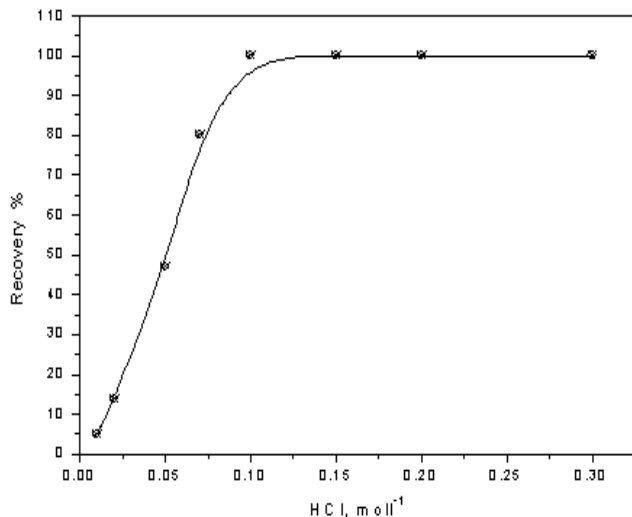

Figure 3: Effect of pH on the recovery % of Hg(II) at 100 mg immobilized silica and stirring time 30min at 25°C

Figure 4: Effect of stirring time on the recovery% of Hg(II) using 100 mg silica-HIPTSC and pH = 5 at 25°C.

showed that, AAS may be handicapped by the presence of a complex organic matrix that causes severe suppression of the analyte signal. So, the use of acid solution is analytically preferred.

The data obtained in Fig. 5 indicated that, 0.1 moll^{-1} of all acids could afford quantitative elution of Hg(II) ion from the modified silica. Subsequent elution of metal ions was carried out with hydrochloric acid taken the advantage that, chloride ion is an acceptable matrix for both AAS and spectrophotometric determinations of metal ions.

Interferences

The influence of several cations and anions on the sorption and determination of Hg(II) is summarized in Table 1. Most of examined cations and anions did not interfere in the extraction and determination of Hg(II). However, some of the species, such as Cd^{2+}, Ni^{2+}, Cu^{2+}, and especially Co^{+2} interfered in the determination of Hg(II). These interferences were eliminated or reduced considerably in the presence of EDTA [27] which forms a stable complex with most metals ions, but doesn't interfere in the reaction between Hg(II) and HIPTSC.

Figure 5: Effect of HCl concentration (5 ml) on the recovery of Hg(II) silica-HIPTSC= 100mg; stirring time= 10 min at 25°C.

Adsorption isotherm

In order to examine the adsorption behaviour of the modified silica gel, the Hg(II) was added to synthetic solution at increasing concentrations (5–300 μg ml^{-1}). After adding the modified silica (1 g), the pH of the solution was adjusted to 5.0. The prepared solution was

Table 1
Influence of some interferences on the recovery % of 20 μg ml^{-1} Hg(II) using 100 mg of Silica-HIPTSC, pH 5.0 at 25°C.

Coexisting ion(s)	Concentration ug ml^{-1}	Hg(II) Recovery (%)
K^+, Cl^-, NO_3^-, NH_4^+,	500	100.0
$CH3COO^-$, F^-	350	100.0
Ca^{2+}, Al^{3+}, Mg^{2+}	200a	99.5
Ni^{2+}	200a	99.0
Mn^{2+}, Co^{2+}	200a	98.9
Cu^{2+}	200a	99.8
Fe^{3+}, Zn^{2+}	200a	99.9
Pb^{2+}	200a	98.8
Cd^{2+}	200a	99.9

^{a} in presence of 2×10^{-3} mol.l^{-1} EDTA .

stirred for 1 hr. Hg(II) in the eluate was determined as usual. The concentration of the adsorbed Hg(II) (n) in milligrams per gram was studied as a function of Hg(II) concentrations (C, in mg l^{-1}) in the initial solution. Figure 6 shows the adsorption isotherm which confirms Langmuir equation®. The adsorption capacity (n_m) of the modified silica gel for Hg(II) was calculated from the Langmuir equation given in the following form:

$$\frac{C}{n} = \frac{1}{n_m k} + \left(\frac{1}{n_m}\right) x C$$
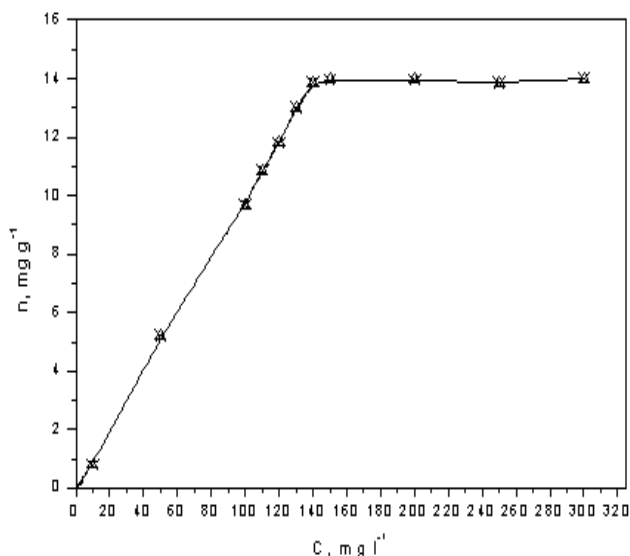

Figure 6: Langmuir Adsorption isotherm of Hg(II) onto silica-IPTSC; Si-IPTSC = 1 g, pH = 5 at 25°C.

The adsorption capacity (n_m) and the binding equilibrium constant (K) were calculated from the slope and the intercept of the least squares regression plot, respectively (Fig. 7). The adsorption capacity of the modified silica gel for Hg(II) was found to be 14.005

mg g^{-1} (0.0698 mmol g^{-1}) and the binding equilibrium constant was found to be 8.60 l mg^{-1}. Higher value for n_m indicates higher affinity of silica-IPTSC for Hg(II) ion and the value of k lies between 1and 10 indicating favorable adsorption.

Effect of sample volume and preconcentration factor

The aqueous solution of 100, 250, 500, 1000, 1250, 1500 ml containing 5 µg of Hg(II) was stirring with the modified silica (1 g) for 2 h, eluted with 5ml of 0.1 moll^{-1} HCl, and determined as usual. It was found that, Hg(II) could be removed quantitatively up to 500 ml of the sample solution. Above such volume, the recovery decreased remarkably.
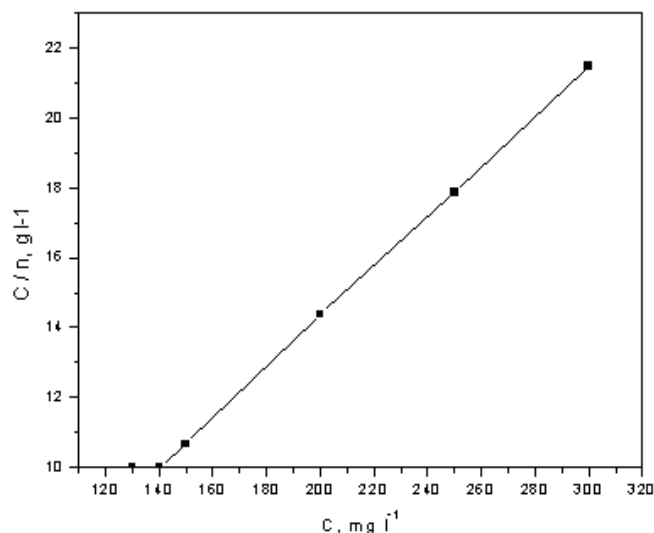
Figure 7: Langmuir plot for Hg(II) adsorption on silica-HIPTSC(= 1 g), pH = 5 at 25°C.

Therefore, using 5ml of 0.1moll^{-1} HCl as eluent, a practical maximum of 100-folds preconcentration factor was obtained.

Lower limit of metal ion detection

The lowest concentration of Hg(II) below which is the quantitative sorption of the metal ion by the modified silica was investigated using Hg(II) ion solution in the concentration range (10^{-4} to 10^{-2} µg ml^{-1}) stirred with the modified silica for 2 h. The limit of detection (LOD) value (5 ng ml^{-1}), shows high sensitivity of the developed silica in preconcentrating trace Hg(II) down to ppb level without any loss.

Analytical application
Selective separation of Hg(II) from binary mixtures

In order to investigate the selective separation and determination of Hg(II) from its binary mixtures with diverse metal ions, an aliquot of aqueous solution (500 ml) containing 1 mg Hg(II) and 25mg of another cation was taken and the recommended procedure was followed. The results are summarized in Table 2. The data show that the Hg(II) ions in the binary mixtures are almost selectively sorbed by the modified silica gel, even up to 25 mg of the diverse ions. It is interesting to note that, no effect on the recovery of the investigated metal ions in the presence of EDTA under the optimum conditions was found on silica-HIPTSC.

Selective separation of Hg^{2+} ion from natural water

Surface water samples were collected from the River Nile water (Mansoura, Dameitta, Ras EL-Bar) and tap water from Mansoura city. All samples were filtered using a sintered glass G4 and the suspended matter is determined (Table 3). The pH, total dissolved salts (TDS), dissolved oxygen (DO) and total alkalinity (mg CaCO$_3$ l^{-1}) were determined according to previous methods [28]. The samples were acidified with concentrated HNO$_3$ to pH ~ 2 and preserved in polyethylene vessel. The organic matter was digested prior to the separation process. 0.5 g of K$_2$S$_2$O$_8$ and 5 ml of 98% (w/v) H$_2$SO$_4$ were added to 500 ml of the water sample and heated for 30 min at 95 °C. After cooling to room temperature, 100 mg of silica-IPTSC, and 1 ml (of 5 x 10^{-3}) EDTA solution was added to the sample and the pH was adjusted to 5 and stirred for 30 min then filtered off. To the filtrate, another 100 mg of silica-HIPTSC was added and the pH was again controlled.

Table 2
Separation of Hg(II) from binary mixtures [a]

Diverseion	Amount taken, mg	Recovery % of Hg^{2+}
Na$^+$	25	100.0 (0.076)[b]
Mg^{2+}	25	99.8 (0.100)
Ca^{2+}	25	99.6 (0.153)
Co^{2+}	25	99.9 (0.080)
Ni^{2+}	25	100.0 (0.480)
Cu^{2+}	25	99.5 (0.900)
Zn^{2+}	25	99.7 (0.980)
Pb^{2+}	25	100.0 (0.585)
Cd^{2+}	25	99.4 (0.600)

[a] Sample containing 1 mg Hg^{2+}, 25 mg of diverse ions and 1g of the modified silica in 500 ml water.

[b] Values in parentheses are RSD's based on three replicate analyses.

The sample was then stirred for 30 min and filtered. The total residue was gathered and the collected Hg(II) was eluted by 5 ml of 0.1 moll^{-1} HCl, to give a

concentration factor of 100-folds. The eluate was analyzed as previously described.

The quality of waters is mentioned in Table 3. The tap, Nile and Sea water samples were analyzed for Hg(II) by the described procedure. Preliminary investigation showed that the method is selective to sorb Hg(II) with high efficiency. Samples of wastewater from Talkha (Table 4) showed high concentrations of Hg(II) (the water of this area is relatively polluted by agricultural effluents and domestic sewage and was chosen because many water creatures were dead).

Table 3
Water quality measurements for the water samples collected from different locations.

Location	Parameters				
	pH	TDS (gl^{-1})	TSM (gl^{-1})	TDO $(mg\ O_2l^{-1})$	Alkalinity $(mg\ CaCO_3l^{-1})$
Tapwater (Mansoura city)	7.22	0.12	4.00	6.38	125.00
Nile river (Mansoura city)	7.83	0.50	4.00	5.54	144.00
Wastewater (Talkha from Meat Antar)	8.25	0.55	4.00	7.85	180.00
Nile water (Dameitta city)	8.20	29.20	321.00	5.56	185.00
Waste water (Ras El-Bar from Elborg)	8.14	14.30	150.00	6.24	154.00
Sea water (Port Said from Suezcanal)	8.19	46.10	346.00	5.74	132.00

Table 4
Analysis of water samples using CVAAS for determination of Hg^{2+} in ng ml^{-1} (otherwise indicated) after preconcentration with silica-HIPTSC 0.4 g l^{-1}, pH 5, stirring time 30 min at 25 °C.

Sample location	Experimental	
	value, (X)	RSD (%)
Tap water (Mansoura city)	ND	-
Nile river (Mansoura city)	0.12	1.9
Wastewater (Talkha from Meat Antar)	0.32	3.0
Nile water (Dameitta city)	0.05	2.0
Wastewater (Ras El-Bar from Elborg)	0.25	2.5
Sea water (Port said from Suez canal)	0.02	2.0

ND: not detected

The RSD % was found to be 1.9–3.5. The Hg(II) was not found in Tap water of Mansoura city. In other water samples, Hg(II) was detectably low or present in the permissible level.

Conclusion

The described work, offers a simple and fast procedure for selective sorption and preconcentration of Hg(II) using silica gel modified with HIPTSC. The elution step does not need organic solvents as in the other procedures. The method was found free from interferences and the quantitative recoveries (better than 98%) from binary mixtures and natural water samples can be achieved.

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