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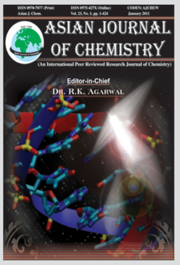

Selective Trace Analysis of Bismuth in Water and Sediment Samples Based on Solid Phase Extraction Using a Modified Silica Gel Containing Oxygen and Nitrogen Donor Atoms

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A new selective method is described for the solid phase extraction and preconcentration of trace level bismuth in aqueous solutions by using gallic acid modified silica gel (GASG) in a acidic medium (pH 1.0) prior to determination by flame atomic absorption spectrometry (FAAS). In the column experiments, Bi(III) can be adsorbed on gallic acid modified silica gel at pH 1.0 with 94.69 % retention, whereas the retention of other common coexisting metal ions such as Pb(II), Cd(II), Cu(II), Zn(II), Co(II), Ni(II), Mn(II) and Fe(III) is less than 10 %. The adsorption equilibration for Bi(III) was achieved within 10 min. At optimum conditions, the adsorption capacity of the extractant is 7.25-7.73 mg/g, preconcentration factor is 250 and detection limit is 0.26 ng/mL. Gallic acid modified silica gel is stable in 4 mol/L HCl-pH 7.0 buffer solutions. The procedure was validated by analysis of a standard reference sediment material (GBW07350, China). The new solid phase extractant has been used for the preconcentration of low level of Bi(III) in lake sediment, wastewater and lake water samples, recoveries of 95.4-101 % were obtained. It is shown that low level of Bi(III) can be effectively preconcentrated by this new selective solid phase extractant.

Key Words: Bi(III), Gallic acid, Silica gel, Selective solid phase extraction.

INTRODUCTION

Bismuth has been widely used in semiconductors, cosmetic preparations, medicine for the treatment of syphilis, peptic ulcers and dermatological disorders, alloys, metallurgical additives and in the preparation and recycling of uranium nuclear fuels[1]. As the use of bismuth increases, it has spread in the environment and the chance of exposure of organism to bismuth has increased[2,3]. A variety of techniques have been described for the determination of bismuth with adequate detection limits[3]. Atomic absorption spectrometry (AAS) provides a convenient, rapid and sensitive technique for the determination of bismuth in metallurgical, biological and pharmaceutical materials[4-7]. However, due to the presence of bismuth in environmental samples at low levels, its separation from other elements present and also the use of a preconcentration step prior to bismuth determination is usually necessary. Solvent extraction[8,9], Mg-W cell-electrodeposition[2], flow injection on-line sorption preconcentration[7,10-12] and solid phase extraction[6,13-15] has attracted considerable attention. For its experienced with several major advantages over the classical liquid extraction technique and these include the fast, simple application, amenability to automation, disposal costs and extraction time for sample preparation, the SPE approach has gained rapid acceptance for organic micropollutants, metal ion extraction and preconcentration in the last two decades[16]. Solid phase extraction is based on the utilization of a major constituents as bonded stationary phases mainly silica gel immobilized with different functional groups including C18, C8, cyano, hydroxy, diol, amine and phenyl to meet all the analytical needs for extraction as well as separation of the analyte of interest[17]. Various papers dealing with the potential use of chelating ligands immobilized on the silica gel support for the separation, preconcentration and determination of metal ions from the aqueous phase of different origins are available[18-23].

Gallic acid is one kind of natural phenolic compound widely existed in plants and has shown pharmacological properties, *e.g.*, strong antimutagenic, anticarcinogenic and antioxidant activities[24-26] and also as a selective reagent for the separation of bismuth[27]. This work aims to synthesize a gallic acid modified silica gel (GASG) and to use the chelating matrix as a solid phase extractant for the selective extraction, preconcentration of trace levels of bismuth in aqueous media prior to it's determination by flame atomic absorption spectrometry.

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Different experimental conditions, for example the effect of sample pH, the type and volume of eluting solvent, option kinetics, the effect of flow rates on the extraction efficiency and maximum sorption capacity of the modified silica gel for bismuth ion recovery, have been studied.

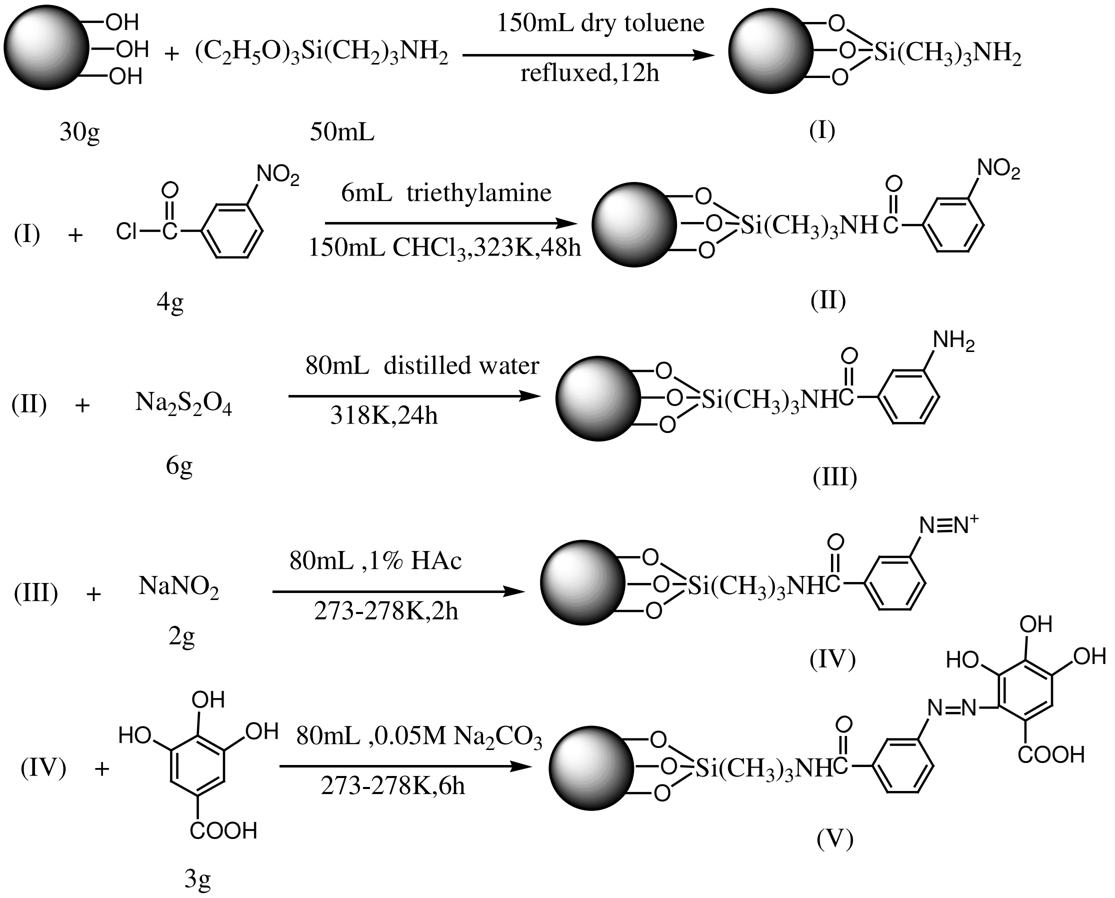
EXPERIMENTAL

A flame atomic absorption spectrometer of Beijing Rayleigh Analytical Instrumentation Corporation (model WFX-1E2, Beijing, China), equipped with air-acetylene flame was used for metal ion determination. The pH measurements were conducted by a PHS-2C pH-meter (Dazhong instrumentation corp., Limited. Shanghai, China). Infrared measurements were performed using a model WQF-300 spectrometer (Beijing, China) and KBr pellets. A micro-column (110 mm × 4 mm i.d.) was used to study the metal ion sorption on the chelating matrix and washed with 4.0 M HCl, 4.0 M HNO_3, ethanol and deionized water successively before using. The flow rate of solution through the column was controlled using a peristaltic pump (FIA-3100, Beijing Titan Instruments Co., Ltd).

The silica gel (60-100 mesh size) was made in the Haiyang Chemical Factory, Qingdao, China. gallic acid were purchased from China Medicine (group) shanghai Chemical Reagent corporation. 3-Aminopropyl triethoxysilane was procured from Wuhan Tianmu Science & Technology Development Co. Ltd. The stock solutions of metal ions (1.0 mg/mL) were prepared from the analytical reagent grade corresponding metal salts in nitric acid, hydrochloric acid or sulphuric acid by dissolving the appropriate amount in deionized water. All working solutions were diluted according to requirements. HCl (pH 0.0-2.0), acetate-acetic acid buffer (pH 3.0-5.0), phosphate buffer (pH 6.0-7.0), NH_3-NH_4Cl buffer (pH 8.0-9.0) were used for pH adjustment. All chemicals used were of analytical reagent grade.

Preparation of gallic acid modified silica gel: In order to remove any adsorbed metal ions and increase the content of -OH, silica gel was activated by successively immersing it in 6 mol/L HNO_3 and then in 6 mol/L HCl for 24 h. It was filtered and washed with deionized water until free from acid and then dried for 12 h in a furnace at 393 K and finally degassed at 373 K under vacuum for 10 h. Immobilization of gallic acid on the silica gel was performed in five steps as shown in **Scheme-I**. This gallic acid derivative of silica gel was ready for use after washing with 0.05 mol/L Na_2CO_3, 1 mol/L HCl and then with distilled water to remove HCl. The residue was heated at 333 K for 6 h and used for heavy metal ion enrichment. In the IR spectrum of GASG bands corresponding to the NH-vibration (3303 cm^{-1}) and the strong band of the CH-vibration (2926 cm^{-1}) can be seen. The band appeared at 1450 and 1650 cm^{-1} was contributed to -N=N- and C=O stretching vibration, respectively.

Batch experiments: Gallic acid modified silica gel (0.1 g) was equilibrated with a suitable amount of metal ions solution and buffer solution in a glass stoppered bottle (250 mL) for a fixed period of time and the unextracted heavy metal ion in



Scheme-I: Surface modification process on silica gel the solution phase was measured by FAAS. This method was used to study the sorption kinetics and the maximum adsorption capacity.

Column experiments: For the column experiments, GASG was packed in a glass tube and a solution containing metal ions was adjusted to a suitable pH and percolated at a certain flow rate. The metal ions retained on the column were eluted with a suitable eluant and determined by FAAS. This method was used to study effect of pH, sorption selectivity, effect of flow rate.

Sample and sample preparation: 0.500 g certified reference material (aquatic Sediment reference material, GBW 07350) or lake sediment was added to a closed polytetrafluoroethylene (PTFE) beaker. Then, 7, 4 and 4 mL of concentrated HNO_3, $HClO_4$ and HF were added, respectively. The mixture was heated at 368 K for 12 h and evaporated nearly to dryness. After cooling, the residue was dissolved to 50 mL of 1.0 mol/L HCl and the solution was filtered.

Lake water and wastewater samples were obtained from Hefei, Anhui, China. These water samples were filtered (0.45 μm) and then acidified with 2 % HNO_3. The samples were analyzed within 3 days after collection.

RESULTS AND DISCUSSION

Effect of pH: The pH value is one of the important factors controlling the extraction of metal ions from aqueous solutions. The adsorption of metal ions on GASG with different pHs was examined by a column experiment. The metal ion solutions were adjusted to a fixed pH and passed through a column filled with GASG (0.35 g) at a flow rate of 3.0 mL/min. The extracted metal ions were then eluted using 15 mL eluent (2 mol/L HNO_3) from the column and determination by FAAS. Fig. 1 has shown the effect of pH on the retention of metal ions on the GASG. It was found that the retention for most of the metal ions varies significantly with change in the pH. About 94.69 % of Bi(III) is sorbed on GASG at pH 1.0, whereas the adsorption of other metal ions, such as Pb(II), Cd(II), Cu(II) , Zn(II), Co(II), Ni(II), Mn(II) and Fe(III) is less than 10 % under the same experimental conditions. These metal ions will not interfere with the extraction of Bi(III) if the solutions are controlled at pH 1.0. Therefore, pH 1.0 was chosen for the separation and preconcentration of Bi(III) in the following studies.

Selective extraction of Bi(III): To assess the possibility of analytical applications for the proposed selective separation procedure, the effects of some foreign ions, which interfere with the determination of Bi(III) were examined by using column methods. For this purpose, 20 mL of the test solution containing 100 μg of Bi(III) and Pb(II), Cd(II), Cu(II), Zn(II), Co(II), Ni(II), Mn(II), Fe(III) ion at pH 1.0 was passed through the column filled with 0.35 g GASG at a flow rate of 3.0 mL/min. The amount of metal ion extracted was determined after elution. The adsorption capacity, distribution ratio and selectivity coefficient were calculated, respectively, by the following equations:

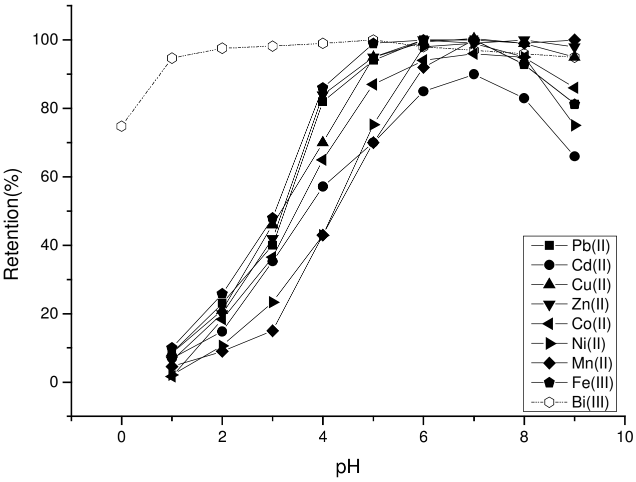


Fig. 1. Effect of pH (0.0-9.0) on the recovery of heavy metal ions from aqueous solution

$$Q = \frac{V(C_0 - C_e)}{m} \quad (1)$$

$$K_d = \frac{Q}{C_e} \quad (2)$$

$$k = \frac{K_0(Bi)}{K_d(M)} \quad (3)$$

where C_0 = initial concentration of metal ions (μg/mL), C_e = equilibrium concentration of metal ions (μg/mL), V = volume of metal ions solutions, m = mass of the modified silica gel (g) and Q = represents the adsorption capacity (mg/g); K_d = distribution ratio (mL/g); k = denotes the selectivity coefficient of Bi(III) with respect to other common coexisting metals, indicating the selectivity factor of the functionalized silica gel. The results showed (Table-1) that K_d is as large as 1628.68, which is several hundreds of times higher than that for the common coexisting metal ions. k is also large than some reported ion imprint adsorbent[28,29]. This result indicates that the presence of foreign metal ions did not interfere with the recoveries and the determination of Bi(III). The new solid phase extractant has good selectivity for separation and recovery of Bi(III) in the presence of Pb(II), Cd(II), Cu(II), Zn(II), Co(II), Ni(II), Mn(II) and Fe(III).

Effect of eluant: The elution behaviour of Bi(III) from GASG was examined in the column experiment. The effects of different acids such as HCl, HNO_3, H_3PO_4, EDTA and citric

TABLE-1
ADSORPTION OF METAL IONS ON GASG AND THE DISTRIBUTION RATIO, SELECTIVITY COEFFICIENT OF Bi(III) WITH RESPECT TO OTHER METAL IONS AT pH = 1.0

Metal ion	Bi(III)	Pb(II)	Cd(II)	Fe(III)	Co(II)	Ni(II)	Mn(II)	Zn(II)	Cu(II)
Added (μg)	100	100	100	100	100	100	100	100	100
Adsorption (μg)	95.69	8.51	7.01	10.00	1.68	2.12	4.55	6.36	8.64
K_d	1268.68	5.32	4.30	6.35	0.98	1.24	2.72	3.88	5.40
k	–	238	295	200	1294	1023	466	327	235

acid were tested at different concentrations on the desorption of bismuth from the column. The result was shown that using of H_3PO_4, EDTA, HCl and citric acid only does not give quantitative results. The analyte retained by the sorbent could be quantitatively desorbed (recovery > 95 %) with at least 2 mol/L HNO_3. The more concentrated HNO_3 solutions did not change the elution yield or elution kinetics.

Effect of flow rate: The degree of bismuth adsorbed on gallic acid modified silica gel was studied at various flow rates (1.0-15.0 mL/min). The optimum flow rate (recovery > 95 %) for bismuth extraction is between 1.0 and 6.0 mL/min (Fig. 2). To avoid the long time extraction, the flow rate less than 1.0 mL/min were not employed. However, at flow rate value more than 6.0 mL/min, there was a decrease in the percentage of adsorption, probably because the Bi(III) cannot be adsorbed sufficiently by the modified silica gel. For desorption, Bi(III) can be desorbed quantitatively by the present matrix at a flow rate of 1.0-4.0 mL/min. Above 4.0 mL/min, the recovery for Bi(III) was < 95 %. The flow rate was maintained at 3.0 mL/min throughout the column experiment.

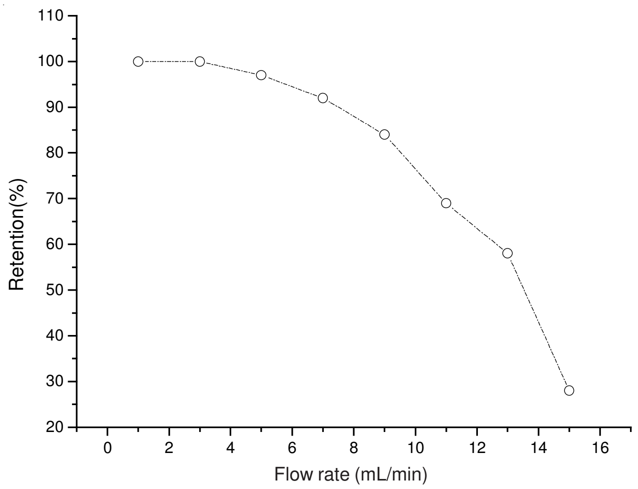


Fig. 2. Effect of flow rate (1.0-15.0 mL/min) on the recovery of Bi(III)

Kinetics of Bi(III) extraction: The time taken for the extraction of Bi(III) ion and the attainment of the equilibrium condition by gallic acid modified silica gel is of considerable importance. Gallic acid modified silica gel (0.1 g) was equilibrated by shaking with 200 mL of a solution containing 4 mg of Bi(III) ion at pH 1.0 for different time intervals (2, 5, 10, 15, 20, 25, 30, 40, 50 and 60 min) and the recommended batch experiment was applied. The concentration of Bi(III) ion in the supernatant solution was determined and the amount of bismuth adsorbed was calculated using eqn. 1. The profile of saturation of the present extractant as a function of time Bi(III) ion was shown in Fig. 3. It is notable that Bi(III) is > 92 % extracted in 10 min. The fast extraction rate indicates that gallic acid modified silica gel is highly suitable for the preconcentration of trace Bi(III) from aqueous solutions.

Adsorption capacity: The adsorption capacity of the sorbent is an important parameter to determine how much sorbent is required to quantitatively adsorb a specific amount of metal ion from solution. For investigation of the adsorption capacity of bismuth on gallic acid modified silica gel at pH

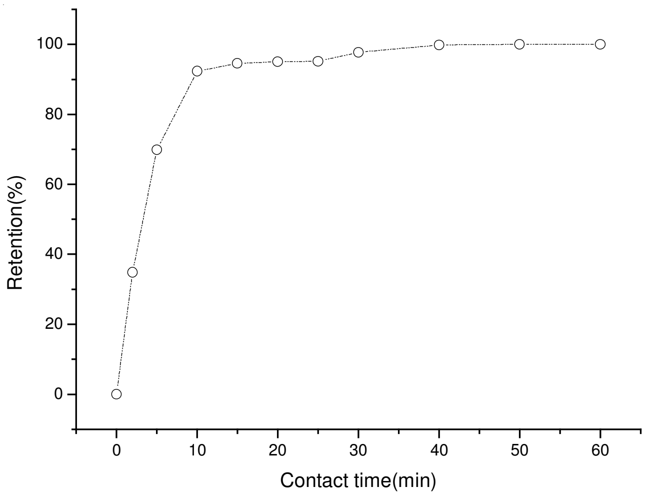


Fig. 3. Kinetics of adsorption

1.0 by using the batch experiments at 290 K, the same volumes of Bi(III) ion solutions in the concentration range of 20-180 μg/mL was stirred with the same amount (0.1 g) of gallic acid modified silica gel for 1 h. The bismuth in the supernatant were determined by FAAS and the amount of bismuth adsorbed was calculated using eqn. 1. The result was shown in Fig. 4. The adsorption capacity is found to be 7.25-7.73 mg/g of gallic acid modified silica gel at the optimum conditions. This is satisfactory for the trace analysis of Bi(III) in aqueous solutions.

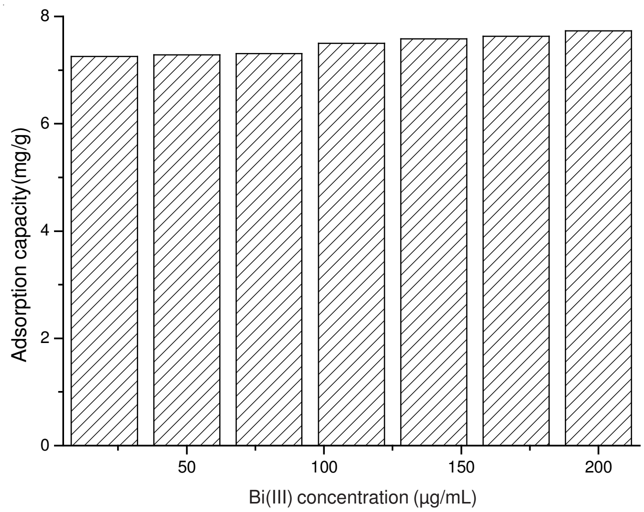


Fig. 4. Effect of initial concentration for Bi(III) adsorption on gallic acid modified silica gel. (290 K, pH = 1.0)

Stability and reusability of gallic acid modified silica gel: To determine the stability of gallic acid modified silica gel, 0.1 g of the present matrix was shaken with 5 mL of different aqueous solutions between 4.0 mol/L HCl and pH 7.0 for 1 h and then filtered, washed with deionized water,then added into 20 mL solution containing 100 μg Bi(III) and stirred for 1 h, the Bi(III) in the supernatant was determined by FAAS. The result was shown in Table-2. There is no difference in extraction percentage between before and after treatment. GASG is thus fairly stable in these media.

The reusability of the present matrix was examined after several loading and elution cycles. It was found that the adsorption capacity does not decreasing. The trace amount of

TABLE-2
STABILITY OF THE GASG (n = 4)

No.	Solutions	Average adsorption capacity (mg/g)	RSD (%)
1	4 mol/L HCl	7.05	3.54
2	3 mol/L HCl	7.12	2.33
3	2 mol/L HCl	7.14	2.50
4	1 mol/L HCl	7.19	2.05
5	0.5 mol/L HCl	7.15	1.58
6	pH = 1.0 buffer solution	7.08	2.73
7	pH = 2.0 buffer solution	7.18	1.35
8	pH = 3.0 buffer solution	7.22	1.88
9	pH = 4.0 buffer solution	7.14	1.76
10	pH = 5.0 buffer solution	7.24	1.85
11	pH = 6.0 buffer solution	7.26	1.60
12	pH = 7.0 buffer solution	7.26	1.21

bismuth in natural water samples can be quantitatively retained after ten repeated uses and the adsorption capacity can be reach 95 % compare to the untreated one. The behaviour of stability and reusability strongly supports the fact that the ligand is chemically bonded to silica gel and not simply physically adsorbed on the surface of silica gel.

Preconcentration and recovery of Bi(III): Solutions containing 10 μg of Bi(III) ion in various volumes were made up and passed through the column packed with 0.35 g of GASG and bismuth preconcentrated on the column was eluted and determined by the above-mentioned procedure. The feed volumes for loading and preconcentration factors are given in Table-3. The result shown the maximum preconcentration factor is 250.

TABLE-3
PRECONCENTRATION FACTORS AND
RECOVERY OF Bi(III) (n = 4)

Volume of solution passed (mL)	Concentration (ng/mL)	Average recovery (%)	RSD (%)	Preconcentration factor
100	100	96.70	0.96	10
500	20	99.06	0.41	50
1000	10	97.26	0.92	100
2000	5	96.66	0.81	200
2500	4	93.50	1.21	250

Analytical precision and detection limits: Under the selected conditions, eight portions of standard solutions were enriched and analyzed simultaneously following the general procedure. The relative standard deviations (RSDs) of the method was 3.66 %, which indicated that the method had good precision for the analysis of trace Bi(III) in sample solutions. In accordance with the definition of IUPAC[30,31], the detection limit of the method was calculated based on three times of the standard deviation of 11 runs of the blank solution. The detection limit (3σ) of the proposed method was 0.26 ng/mL.

Analytcal performance: An aquatic Sediment reference material (GBW 07350, China) was used for method validation. The average recovery of Bi was 96.22 % (n = 4, RSD = 2.64 %). Good agreement was obtained between the estimated content by the proposed method and the certified values for Bi ions. These results also indicate that the developed preconcentration method for Bi is not affected by potential interferences from the major matrix composition of the analyzed aquatic sediment.

Analysis of natural water samples: At the optimum conditions, water samples (1000 mL) were passed through the column for preconcentration and determination of the target metal ions directly. The recoveries of Bi from lake sediment and water samples are satisfactory (Table-4). The method developed in this paper for determination of trace amount of Bi in environmental samples has been proved to be reliable.

TABLE-4
DETERMINATION OF Bi(III) IN WATER
AND LAKE SEDIMENT SAMPLES (n = 4)

Sample	Added (μg/L)	Found	Recovery (%)
Lake sediment	–	0.38 ± 0.06 μg/g	–
Wastewater	–	4.9 ± 0.99 μg/L	–
	5	9.5 ± 1.53 μg/L	95.9
	10	14.24 ± 1.22 μg/L	95.4
Lake water	–	ND	–
	5	4.8 ± 0.09 μg/L	96
	10	10.02 ± 0.12 μg/L	101

ND: Not detected.

Conclusion

The results presented in this paper demonstrate the feasibility of using silica gel modified with gallic acid for selective extraction and preconcentration of trace amount of Bi(III) from aqueous solutions. This solid phase extraction method shows high selectivity, fast extraction kinetics and high adsorption efficiency. The satisfactory results for standard reference sediment materials analysis indicated the accuracy and sensitivity of the method and the proposed method is widely applicable for the measurement of trace Bi(III) in a variety of environmental samples.

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