Silica gel surface modified with sulfanilamide for selective solid-phase extraction of Cu(II), Zn(II) and Ni(II)

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A new chelating matrix has been prepared by immobilising sulfanilamide (SA) on silica gel (SG) surface modified with 3-chloropropyltrimethoxysilane as a sorbent for the solid-phase extraction (SPE) Cu(II), Zn(II) and Ni(II). The determination of metal ions in aqueous solutions was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES). Experimental conditions for effective sorption of trace levels of Cu(II), Zn(II) and Ni(II) were optimised with respect to different experimental parameters using the batch and column procedures. The presence of common coexisting ions does not affect the sorption capacities. The maximum sorption capacity of the sorbent at optimum conditions was found to be 34.91, 19.07 and 23.62 $mg\,g^{-1}$ for Cu(II), Zn(II) and Ni(II), respectively. The detection limit of the method defined by IUPAC was found to be 1.60, 0.50 and 0.61 $\mu g\,L^{-1}$ for Cu(II), Zn(II) and Ni(II), respectively. The relative standard deviation (RSD) of the method under optimum conditions was 4.0% ($n = 8$). The method was applied to the recovery of Cu(II), Zn(II) and Ni(II) from the certified reference material (GBW 08301, river sediment) and to the simultaneous determination of these cations in different water samples with satisfactory results.

Keywords: silica gel (SG); sulfanilamide (SA); Cu(II), Zn(II) and Ni(II); solid-phase extraction (SPE); ICP-OES

1. Introduction

Heavy metals in the environment, even at low concentrations, have been a major preoccupation for many years because of their toxicity towards aquatic life, human beings and the environment [1,2]. As they do not degrade biologically like organic pollutants, their presence in industrial effluents or drinking water is a public health problem due to their absorption and therefore possible accumulation in organisms.

Although inductively coupled plasma atomic emission spectrometry (ICP-OES) and atomic absorption spectrometry (AAS) are among the most widely used methods for trace metal determination, they are usually insufficient due to the matrix interferences and the very low concentration of metal ions. Therefore, a separation/pre-concentration step is required [3].

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In order to overcome these problems, separation and pre-concentration of given analytes become necessary, particularly when they exist at trace levels of concentration.

Nowadays, SPE method is one of the most effective multi-elemental pre-concentration methods because of its advantages of the ease of use, the high pre-concentration factor and flexibility to choose the solid phase for optimum results [4]. So, solid-phase extraction (SPE) has been widely used for the isolation and concentration of target analytes, and the clean-up of samples (removal of matrix interferences) in pharmaceutical, clinical, environmental and food chemistry [5].

Many methods of pre-concentration of metal ions from solutions have been described. However, the methods of particular interest are those which involve inorganic solid surfaces modified with chelating groups increasing selectivity [6,7]. In this case, a relevant aspect is to establish the experimental conditions for anchoring the groups that will bind the analyte traces [8]. Among many types of solid phase use in SPE, silica gel immobilised with various organic compounds as metal chelating agent has received great attention for its good mechanical and thermal stability and it is less susceptible to swelling, shrinking and microbial and radiation decay [9,10]. The selectivity of the immobilised surface towards metal ions depends on various factors such as size of the modifier, activity of the loaded group and characteristic of the hard-soft acid-base. Silica gel is an amorphous inorganic polymer composed of internal siloxan groups (Si–O–Si), and with silanol groups (Si–OH) distributed on the surface [11,12]. The active hydrogen atom of the silanol groups of silica gel has the ability to react with agents containing organosilyl groups, to give some organic nature to the precursor inorganic support [13,14]. The modified silica gel generally exhibits higher sorption capacities than those of organic polymer-based resins. Reactive sites of silica gel exist in large number, and therefore the number of organic molecules immobilised is high which results in good sorption capacity for metal ions.

There are several recent reports on the use of functionalised silica gel for metal enrichment. Silica gel functionalised with eriochrome black T (ECB-T) [15], Lucigenin (bis-N-methylacridinium nitrate) [16], 8-hydroxyquinoline [17], salicyldoxime [18], 1-(2-thiazolylazo)-2-naphthol [19], dithizone [20], acid red-88 [21], acid alizarin violet-N [22], didecylaminoethyl-b-tridecylammonium [23], 3-methyl-1-phenyl-4-stearoyl-5-pyrazolone [24], formylsalicylic acid [25], thiourea [26], 2-mercaptobenzothiazole [27], dithiocarbamate [28], salicyldehyde [29], o-vanillin [30], 2-hydroxy-5-nonylacetopheneoxime [31], amine derivatives [32], 3-aminopropyltriethoxysilane [33], ofloxacin [34], diaminothiourea [35], 5,5′-dithiobis(2-nitrobenzoic acid) [36], N-S Schiff base [37] and H_2Salphen (L) [38] is reported as a chelating collector for metal ions, Zn(II), Mg(II), Ca(II), Fe(II), V(IV), Fe(III), Cu(II), Cd(II), Co(II), Ni(II), Pb(II), Hg(II), Ag(I), Au(III) and Pt(II), etc.

In this work, sulfanilamide chemically modified silica gel was employed as an effective solid-phase selective sorbent for Cu(II), Zn(II) and Ni(II). Parameters that can affect the sorption and elution efficiency of the metal ions were studied in batch and column modes. Then, the method was validated by analysis of the standard reference material (GBW 08301, river sediment) and applied to the analysis of water samples with satisfactory results.

2. Experimental

2.1 Reagents and solutions

All reagents were of analytical grade and all solutions were prepared with double distilled water. Standard labware and glassware used were repeatedly cleaned with HNO_3 and rinsed with double distilled water, according to a published procedure [39].

Standard stock solutions of Cu(II), Zn(II) and Ni(II) ($1 \, mg \, mL^{-1}$) were prepared by dissolving analytical grade salts in double distilled water with addition of hydrochloric acid and further diluted daily prior to use. Silica gel (80–120 mesh, Qingdao Ocean Chemical Company, Qingdao, China) and sulfanilamide (The Third Reagent Factory, Shanghai, China) were used in this work. 3-chloropropyltrimethoxysilane (CPS) was purchased from Wuhan University Chemical factory (Wuhan, China). The standard reference sediment material (GBW 08301, river sediment) was provided by the National Research Center for Certified Reference Materials (Beijing, China).

2.2 *Apparatus*

An IRIS Advantage ER/S inductively coupled plasma spectrometer (TJA, USA) was used for all metal-determinations. The operation conditions and the wavelengths were summarised in Table 1.

The pH value was controlled with a pHs-10C digital pH meter (Xiaoshan Instrument Factory, China). Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR apparatus (USA).

A YL-110 peristaltic pump (The General Research Academe of Colored Metal, Beijing, China) was used in the separation/pre-concentration process. A self-made glass microcolumn (100 mm × 4 mm i.d.) was used.

2.3 *Sample preparation*

River water was collected from Yellow River, Lanzhou, China. Lake water was collected from Qinghai Lake, Qinghai, China. To oxidise organic matter such as humic acid, the samples were digested by oxidising UV-photolysis in the presence of 1% H_2O_2 (w/v) using a low pressure Hg-lamp which was integrated in a closed quartz vessel [40,41].

The certified reference material (GBW 08301, river sediment) was digested according to literature [42]. A portion (50–100 mg) of the certified sediment sample was accurately weighed into a 50 mL container (or beaker) and aquaregia (12 mL concentrated

Table 1. Instrumental and operating conditions for ICP-AES measurements.

Parameter	Type or amount
R.F. Power (kw)	1.15
Carrier gas (Ar) flow rate ($L \, min^{-1}$)	0.6
Auxiliary gas (Ar) flow rate ($L \, min^{-1}$)	1.0
Coolant gas (Ar) flow rate ($L \, min^{-1}$)	14
Nebulizer flow (psi)	30
Pump rate ($r \, min^{-1}$)	100
Observation height (mm)	15
Integration time (s)	
on-axis	20
off-axis	5
Wavelength (nm)	Cu 324.754, Zn 213.856, Ni 231.604

hydrochloric acid and 4.0 mL of concentrated nitric acid) was added to the sample. The container was covered with a watch glass and the mixture was evaporated on a hot plate at 95°C almost to dryness. Then 8.0 mL of aquaregia was added to the residue and the mixture was again evaporated to dryness. After cooling, resulting mixture was filtered through a 0.45 μm polytetrafluoroethylene (PTFE) millipore filter. The sample was diluted to 10 mL with double distilled water and was analysed by the pre-concentration procedure.

2.4 *Preparation of silica gel-bound 3-chloropropyl phase*

Activation of silica gel surface was first accomplished by reflux in concentrated hydrochloric acid for 4 h to remove any adsorbed metal ions, then filtered and repeatedly washed with water until the filtrate is neutral and dried in an oven at 160°C for 8 h to remove surface adsorbed water. Then 10.0 g of dry silica gel was suspended in 150 mL dry toluene containing 10 mL of 3-chloropropyltrimethoxysilane and refluxed overnight. The product silica gel phase was filtered off, washed with toluene, ethanol and diethyl ether and dried in an oven at 60°C for 6 h. The product was silica gel-bound 3-chloropropyl phase (SG-CP).

2.5 *Preparation of silica gel-bound sulphanilamide*

Chemically immobilised silica gel with sulfanilamide was synthesised according to the procedure described. 2.0 g of sulfanilamide was dissolved in 150 mL dry and hot toluene, then 10 g of dry SG-CP was added to the solution. The reaction mixture was refluxed for 8 h, then the resulting phase was filtered, washed with toluene, ethanol and dried in an oven at 80°C for 7 h. The product was silica gel-bound sulfanilamide (SG-SA).

2.6 *Procedure*

2.6.1 *Batch procedure*

The data are given on the simple mean of three replicate, whereas those of applications were repeated eight times from which the statistical evaluation is pertained.

A total of 25 mg of SG-SA sorbent was suspended with constant stirring for 30 min in 10 mL of $1.0 \, \mu g \, mL^{-1}$ of Cu(II), Zn(II) and Ni(II) at the desired pH value. Then the mixture was shaken vigorously for 30 min to facilitate sorption of the metal ions onto the SG-SA. After extraction, the bound metal ions were eluted with HCl of optimum concentration and the concentrations of the desorbed metal ions were measured by ICP-OES.

2.6.2 *Column SPE procedure*

About 50 mg of functionalised silica gel sorbent was packed in a glass column (100 mm × 4 mm i.d.) plugged with a small portion of glass wool at both ends. Before use, the column was treated with $2 \, mol \, L^{-1}$ HCl or HNO_3 and washed with doubly distilled water until free from acid. A suitable aliquot of the sample solution containing $1.0 \, \mu g \, mL^{-1}$ of Cu(II), Zn(II) and Ni(II) in a volume of 50 mL was passed through the column after adjusting its pH 5.0, at a flow rate of $1.5 \, mL \, min^{-1}$ controlled with a peristaltic pump. The bound metal ions were stripped off from the gel column with

2.0 mol L^{-1} HCl. The concentration of the metal ions in the eluate was determined by ICP-OES.

3. Results and discussion

3.1 *FTIR spectra*

The modified SG-CP and SG-SA was confirmed by IR absorption spectrum analysis. Comparing the IR spectrum (Figure 1) of the SG-SA with SG-CP, several new bands appeared in the region of 1100–1600 cm^{-1}. The bands around 1571.72 and 3422.46 cm^{-1} assigned to the bending vibration and stretching vibration of N-H in the SG-SA [43,44]. The peaks at 1442.03 and 1486.37 cm^{-1} are due to the benzene ring characteristic vibrations in the SA. Over the observed wavenumber region, the bands of –SO$_2$– cannot be observed distinctly because the peaks region of –SO$_2$– is close to the strong peaks region of the longitudinal SiO$_2$ lattice vibration.

The above experimental results suggest that strong interaction exists at the interface of SG-CP and SA, and SG is successfully modified by SA. Due to the existence of a donating nitrogen atom group, SA was expected to increase both the stability and selectivity of its complex towards ions [45].
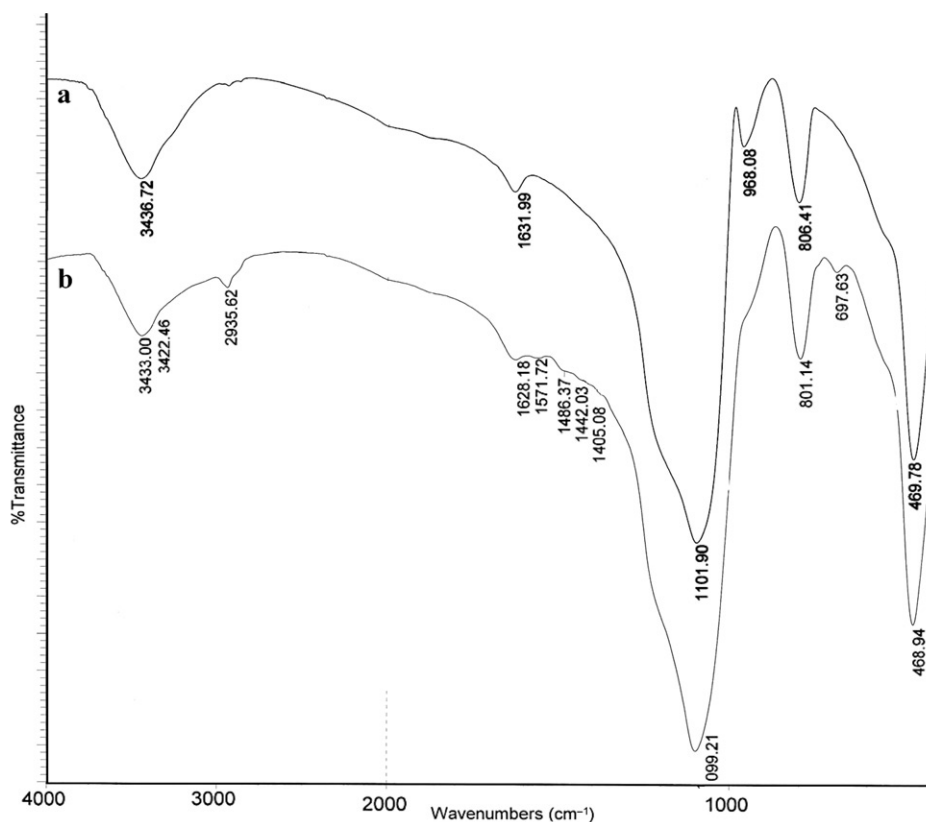
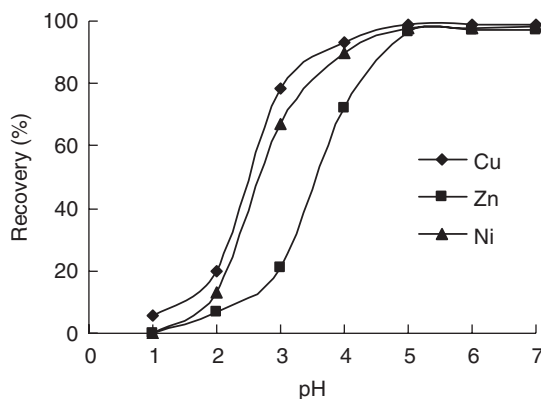Figure 1. FT-IR spectra: (a) SG-CP (b) SG-SA.

Figure 2. Effect of pH on sorption of $1.0\,\mu g\,mL^{-1}$ Cu(II), Zn(II) and Ni(II) on SG-SA. Other conditions: shaking time 30 min, temperature 25°C.

3.2 *Effect of pH*

The acidity of a solution has two effects on metal sorption. First, proton in acid solution can protonate binding sites of the chelating molecules. Secondly, hydroxide in basic solution may complex and precipitate many metals. Therefore, pH of a solution is the first parameter to be optimised. The reaction between Cu(II), Zn(II) and Ni(II) and the sorbent (SG-SA) can be influenced by changes of pH value. In order to determine this parameter, the effect of the pH on Cu(II), Zn(II) and Ni(II) sorption onto SG-SA was investigated over the range from 1 to 7 using the batch procedure. The sorption experiments were triplicates. It can be seen from Figure 2 that the sorption quantity of Cu(II), Zn(II) and Ni(II) increases with the increases of pH values in the studied pH ranges. Below pH 2.0, the sorption quantity is very low owing to the protonation of the SG-SA. After pH 5.0, the increasing rate is relatively very slow, and the sorption capacity is near the maximum capacity. At pH 5.0 it was possible to carry out the determination of Cu(II), Zn(II) and Ni(II). So, pH 5.0 was chosen as the optimum pH for further studies.

3.3 *Effect of shaking time*

The effect of shaking time is another important factor in the evaluation process of the affinity of SG-SA to Cu(II), Zn(II) and Ni(II). To determine the rate of loading of Cu(II), Zn(II) and Ni(II) on the SG-SA, the batch procedure was carried out. The contact time was varied from 5 to 40 min and the results are shown in Figure 3. The sorption of Cu(II), Zn(II) and Ni(II) increased during the first 5 min and then levels off as equilibrium was reached during the 15 min at pH 5.0. The results indicate that kinetics of sorption equilibrium is very fast so that 15 min of stirring was enough to reach maximum values of separation. Therefore, it is suitable for an application in flow system or using in the pre-concentration of trace metal ions.

3.4 *Effect of flow rate*

The flow rate of sample solutions through the packed volume is a very important parameter because the retention of elements on sorbent depends upon the flow rate of the
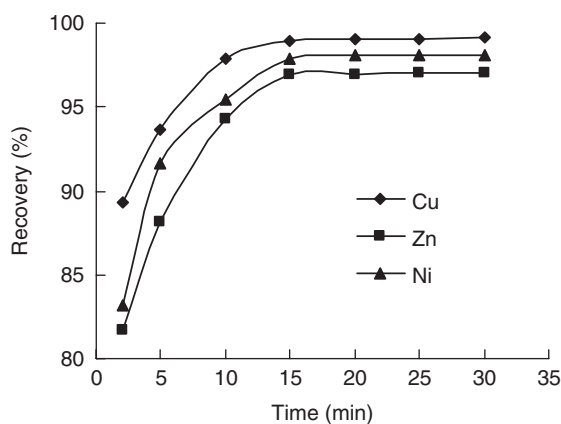
Figure 3. Effect of shaking time of Cu(II), Zn(II) and Ni(II) $(1.0 \mu g\,mL^{-1})$ sorption on SG-SA. Other conditions: pH 5.0, temperature 25°C.
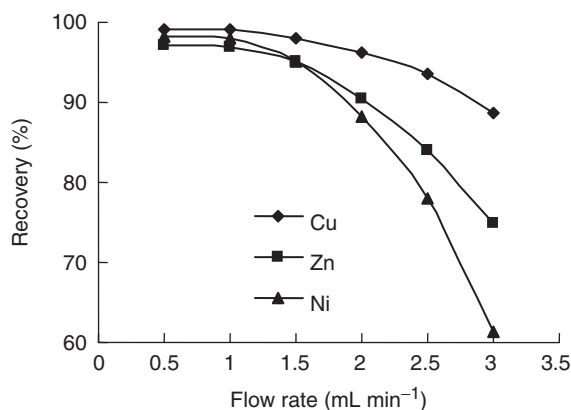

Figure 4. Effect of solution flow rates on the sorption of Cu(II), Zn(II) and Ni(II). Other conditions: 50 mg of SG-SA, volume 50 mL, pH 5.0, temperature 25°C.

sample solutions. In this study, different flow rates $(0.5–3.0\,mL\,min^{-1})$ were investigated using the column procedure. As shown in Figure 4, the results indicated that the flow rate has strong influence on the sorption of Cu(II), Zn(II) and Ni(II). Quantitative recoveries of both metals were obtained with $1.5\,mL\,min^{-1}$. However, at flow rates greater than $1.5\,mL\,min^{-1}$, there was a decrease in the percentage of sorption and the recovery of the Cu(II), Zn(II) and Ni(II) less than 95%. Thus, a flow rate of $1.5\,mL\,min^{-1}$ was selected for column procedure.

3.5 *Sorption capacity*

The capacity of the sorbent is an important factor because it determines how much sorbent is required to quantitatively remove a specific amount of metal ions from the solutions [46]. The sorption capacity was tested following the batch procedure. Thus, 20 mg of SG-SA was equilibrated with 50 mL of various concentrations of Cu(II), Zn(II) and Ni(II).
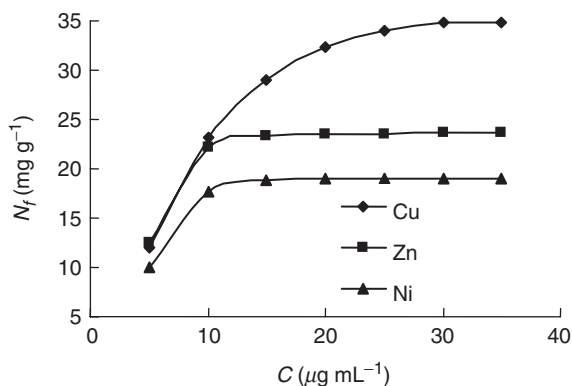
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Figure 5. Sorption isotherm of Cu(II), Zn(II) and Ni(II) on sorbent at 25°C.

Table 2. Thermodynamic parameters of Langmuir's sorption isotherm at 25°C.

Elements	Equation	N_s (mg g^{-1})	r	N_f
Cu(II)	$y = 0.02287x + 0.1794$	43.73	0.9962	34.91
Zn(II)	$y = 0.04143x + 0.0274$	24.13	0.9999	19.07
Ni(II)	$y = 0.05118x + 0.03839$	19.54	0.9998	23.62

The results are shown in Figure 5. The number of milligrams adsorbed per gram of sorbent (N_f) versus the equilibrium concentration of cation is illustrated. Figure 5 shows the process that conforms to the Langmuir model. Such isotherms are generally associated with monolayer sorption.

The Langmuir equation was used to calculate the maximum retention capacity (N_s) [47,48]. The general form of Langmuir isotherm is:

$$Y = \frac{KC}{1 + KC} \tag{1}$$

where Y is the fraction of sorbent surface covered by adsorbed species, K is a constant and C is the equilibrium concentration of the cation solution. In our case, $Y = N_f/N_s$, where N_f represents the number of mg cation adsorbed per gram of sorbent (mg g^{-1}) at equilibrium concentration. After linearisation of the Langmuir isotherm, Equation (1), we obtain the Langmuir isotherm Equation (2) [49]:

$$\frac{C}{N_f} = \frac{C}{N_s} + \frac{1}{KN_s} \tag{2}$$

All these sorption studies were based on the linearisation form of the Langmuir isotherm derived from C/N_f as a function of C. The correlation coefficients (r) are higher than 0.99 (Table 2) indicated that the Langmuir isotherm is an adequate description of the sorption of metal ions on sorbent. The maximum retention capacity from the experimental data was 34.91, 19.07 and 23.62 mg g^{-1} for Cu(II), Zn(II) and Ni(II), respectively. The theoretical sorption capacity (N_s) (Table 2) was calculated. The results were compared

with experimental data. The differences can be explained by the errors of experimental uncertainties.

In addition, according to the test results, high metal capacity values were found to be of Cu(II), Zn(II) and Ni(II) higher than other metal ions by the SG-SA. This can be attributed to the strong affinity of Cu(II), Zn(II) and Ni(II) to bind and complex formation with SG-SA. It is well known that binding of metal ions to the chelate compound either in solution or loaded on solid support is mainly dependent on several factors [50]. First is the nature, charge and size of the metal ions. Second is the nature of the donor atoms which are mainly oxygen, sulfur, nitrogen or phosphorus. These donor atoms direct the selective extraction and binding characteristics of such chelate containing compounds to certain metal ions based on different selectivity. This selectivity controls the factor governing such trends. Third is the buffering conditions which favour certain metals extraction and binding to active donors or groups. These factors make Cu(II), Zn(II) and Ni(II) be completely adsorbed by the SG-SA and other ions cannot be enriched.

3.6 *Maximum sample volume, enrichment factor and elution condition*

The enrichment factor was studied by the recommended column procedure using increasing volume of investigated metal ions solution and keeping the total amount of investigated metal ions loaded constant to 1.0 μg. The maximum sample volume can be up to 200 mL with 95% recovery.

Several pre-concentration papers employing modified silica gel use nitric acid as eluent [50,51], as well as hydrochloric acid [52]. In this work, the elution condition was studied in column procedure using various concentrations and volumes of HCl for the desorption of retained Cu(II), Zn(II) and Ni(II). The results show that 2.0 mL of 0.01 mol L^{-1} HCl was sufficient for 95% recovery for Zn(II) and Ni(II) and 2.0 mL of 2.0 mol L^{-1} HCl was sufficient for 95% recovery for Cu(II) with time of 25 min. Quantitative recoveries of *three* metals were obtained with 2.0 mL of 2.0 mol L^{-1} HCl. Therefore, the high enrichment factor of 100 was obtained.

3.7 *Effect of coexisting ions*

The effect of different cations and anions on the sorption of Cu(II), Zn(II) and Ni(II) on SG-SA were studied using the batch procedure. The results showed that in excess of 4000 μg mL^{-1} of K$^+$, Na$^+$, Cl$^-$, NH$_4^+$; 1000 μg mL^{-1} of Ca^{2+}, Mg^{2+}, NO$_3^-$, SO$_4^{2-}$; 200 μg mL^{-1} of Cd^{2+}, Pb^{2+}, Mn^{2+}, Cr^{3+}, Co^{2+} and 50 μg mL^{-1} of Fe^{3+}, PO$_4^{3-}$ ions do not affect the separation process. The results showed that high concentrations of the ions tested did not interfere with separation and determination of the analytes.

3.8 *Accuracy and precision of the method*

In order to find the reproducibility in the determination of analytes, the dynamic procedure repeated eight times under optimum conditions. The relative standard deviation (RSD) of the method were lower than 4.0%, which indicated that the method had good precision for the analysis of trace Cu(II), Zn(II) and Ni(II) in solution samples. In accordance with the definition of IUPAC, the detection limit of the method was calculated based on three times of the standard deviation of eleven runs of the blank solution.

Table 3. Analysis results for the determination of Cu(II), Zn(II) and Ni(II) in standard reference material.

Analyte	Found by present method ($\mu g\,g^{-1}$)[a]	Certified value ($\mu g\,g^{-1}$)	Relative error (%)
Cu(II)	52 ± 2.0	53 ± 6.0	−1.89
Zn(II)	247 ± 5.0	251[b]	−1.59
Ni(II)	31 ± 1.0	32[b]	−3.13

Notes: [a] $\overline{x} \pm s$ ($n = 8$). $\overline{x}$ average value for eight determinations, s standard deviation.
[b] Reference value.

The detection limits (3σ) were found to be 1.60, 0.50 and 0.61 ng L^{-1} for Cu(II), Zn(II) and Ni(II), respectively.

The accuracy of the proposed pre-concentration methodology was evaluated by means of Cu(II), Zn(II) and Ni(II) determination in certified sample material (GBW 08301). The results showed in Table 3, good agreement was obtained between the estimated content by the proposed method and the certified values of Cu(II), Zn(II) and Ni(II). The results also indicated that the developed pre-concentration method for Cu(II), Zn(II) and Ni(II) was not affected by potential interferences from the major matrix elements of the analysed standard materials.

3.9 *Application of the method*

The proposed method was then applied for the determination of Cu(II), Zn(II) and Ni(II) in Yellow River water and Qinghai Lake water samples by ICP-OES. For the analysis of water samples, the standard addition method was used and the results for the recovery of both metals are presented in Table 4. As shown in Table 4, the recoveries of analytes were in the range of 94–104%.

4. Comparison with other metal ion sorbents

The sorbent of SG-SA is easily prepared and exhibits good characteristics for sorption and pre-concentration of heavy metal ions because it contains multiple functional groups. The sorption capacity on sorbent of SG-SA was compared with those of other modified different supporter represent in Table 5. The sorption capacity for Cu(II), Zn(II) and Ni(II) are higher than those obtained with most of the sorbents listed in Table 5. The quantitative recoveries of the present sorbent and the faster sorption and desorption are another distinct advantages. In comparison to the commonly used silica gel sorbents, SG-SA has a similar pre-concentration factor and good detection limit values for all three metal ions.

5. Conclusions

We had successfully synthesised a novel chemically modified silica gel containing sulfanilamide and applied to solid phase extraction and pre-concentration of Cu(II),

Table 4. Analytical results for the determination of Cu(II), Zn(II) and Ni(II) in water samples.

Water samples	Added	Founded	Recovery (%)	RSD (%)
		($\mu g\,L^{-1}$)		
Yellow River water				
Cu(II)	0	70.11 ± 1.50	–	–
	10.0	79.66 ± 1.20	95.5	0.9
	50.0	119.49 ± 1.40	98.76	1.1
Zn (II)	0	6.71 ± 0.50	–	–
	5.0	11.79 ± 0.08	101.6	3.4
	10.0	17.07 ± 0.50	103.6	2.8
Ni(II)	0	4.08 ± 0.03	–	–
	5.0	9.01 ± 0.07	98.6	1.9
	10.0	13.95 ± 0.10	98.7	1.6
Qinghai Lake water				
Cu(II)	0	50.19 ± 1.90	–	–
	10.0	59.67 ± 1.20	94.8	1.0
	50.0	99.34 ± 0.90	98.3	1.2
Zn(II)	0	3.18 ± 0.06	–	–
	5.0	8.19 ± 0.02	100.2	3.8
	10.0	13.22 ± 0.05	100.4	3.3
Ni(II)	0	1.69 ± 0.03	–	–
	5.0	6.65 ± 0.06	99.2	1.4
	10.0	11.53 ± 0.05	98.4	0.9

Note: The value following '$\pm$' is the standard deviation. ($n = 8$).

Table 5. Comparison of sorption capacities ($mg\,g^{-1}$) on some sorbents used for the separation and pre-concentration of the studied ions.

Supporter	Functional ligand	Metal ion ($mg\,g^{-1}$)			Reference
		Cu(II)	Zn(II)	Ni(II)	
Amberlite XAD-2	Chromotropic acid	8.50	9.65	6.07	[53]
	2-Aminoacetylthiophenol	24.09	196.12	17.60	[54]
Poly (vinylpyridine)	Xylenol orange	1.599	1.68	2.60	[55]
	Dithiazone	32.38	42.50	34.63	[56]
Silica gel	Dalicyldoxime	5.08	2.615	2.35	[18]
	Didecylaminoethyl-b-tridecylammonium	165.20	1.63	–	[23]
	Sulfanilamide	34.91	19.07	23.62	This work

Zn(II) and Ni(II) by ICP-OES. The proposed methodology was simple and of low cost. The simultaneous pre-concentration of Cu(II), Zn(II) and Ni(II) showed the versatility of the system, increasing the analytical frequency. The determination of Cu(II), Zn(II) and Ni(II) in certified reference material showed good accuracy. The proposed procedure can be successfully applied for the determination of Cu(II), Zn(II) and Ni(II) in water samples.

The most important characteristics of the SG-SA are its excellent selectivity towards Cu(II), Zn(II) and Ni(II) over other ions and the high sorption capacity. In addition, the preparation of SG-SA is relatively simple and rapid. The data in this paper revealed that the proposed method is simple, sensitive and reliable.

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