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Dithizone immobilized silica gel on-line preconcentration of trace copper with detection by flame atomic absorption spectrometry

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ABSTRACT

A novel adsorbent-silica gel bound dithizone (H_2Dz-SG) was prepared and used as solid-phase extraction of copper from complex matrix. The H_2Dz-SG is investigated by means of FT-IR spectra and the SEM images, demonstrating the bonding of dithizone. The H_2Dz-SG quantitatively adsorb copper ions, and the retained copper is afterwards collected by elution of 10% (v/v) nitric acid. An on-line flow injection solid-phase extraction procedure was developed for trace copper separation and preconcentration with detection by flame atomic spectrometry. By loading 5.4 mL of sample solution, a liner range of 0.5–120 μg L^{-1}, an enrichment factor of 42.6, a detection limit of 0.2 μg L^{-1} and a precision of 1.7% RSD at the 40 μg L^{-1} level (n = 11) were obtained, along with a sampling frequency of 47 h^{-1}. The dynamic sorption capacity of H_2Dz-SG to Cu^{2+} was 0.76 mg g^{-1}. The accuracy of the proposed procedure was evaluated by determination of copper in reference water sample. The potential applications of the procedure for extraction of trace copper were successfully accomplished in water samples (tap, rain, snow, sea and river). The spiking recoveries within 91–107% are achieved.

1. Introduction

Water is one of the most important resources for human life, rapid and sensitive methods for controlling of water qualities are very important, while suitable techniques for quantification of water pollutions are always restricted because of heavy matrix interferences or low concentration of analytes. Even though atomic absorption spectrometry (AAS) [1–3], inductively coupled plasma atomic emission spectrometry (ICP-AES) [4] and inductively coupled plasma mass spectrometry [5] are powerful techniques for determination of trace heavy metal elements in water which are toxic for human body, some separation and preconcentration methods are usually highly necessary to pretreat samples [6]. Among those, solid phase extractions are commonly used and very favorable techniques [7,8].

Dithizone is an important and efficient chelating agent used to extract trace metal elements [9]. Employing dithizone as chelator, liquid–liquid extraction procedures were reported [10,11], where the analytes were efficiently separated from matrix, the procedures could be coupled with atomic absorption spectrometry or inductively coupled plasma atomic emission spectrometry, and the selectivity and the sensitivity of the mentioned methods were significantly improved. While in those common liquid–liquid extraction process, application of toxic organic solvents is inevitable in order to separate the complex of analyte and chelating agent from the sample matrix [11,12]. These organic solvents are usually harmful for organisms and environment. Nowadays, many new materials, i.e., silica gel and modified silica gel [13,14], ion imprinted polymer [15], resin [16], carbon nanotubes [17], polytetrafluoroethylene (PTFE) [18], zeolites [19], bio-adsorbent [20] and metal oxides [21] are exploited to be applied in solid-phase extraction techniques for metal analysis, where the use of organic solvents is eliminated, and mineral acids generally suffice the recovery of metal species from the adsorbent.

Silica gel, a commonly used solid-phase adsorbent and more easily functioned on its surface, has been widely used in separation and preconcentration of various trace metals [14,22,23]. In the present work, a novel solid phase extraction material was explored by immobilizing dithizone onto the surface of silica gel (H_2Dz-SG) through chemical reaction, which has strong complex ability with metal elements, thus could separate those elements efficiently from sample matrix by chelating reaction, and at the same time, the analyte retained on the solid phase of H_2Dz-SG could be easily collected by mineral acid. Copper was employed as model element, a novel flow injection on-line separation and preconcentration procedure coupled with flame atomic absorption spectrometry (FAAS) was developed.

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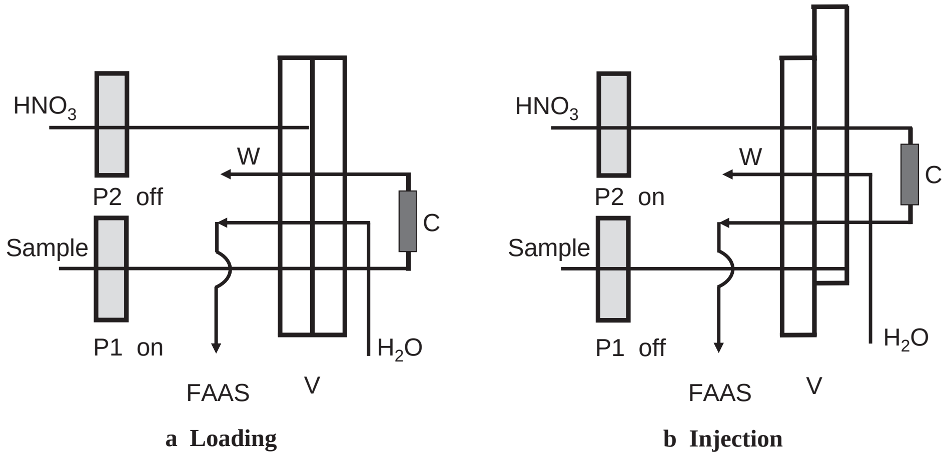


Fig. 1. Flow manifold for the on-line preconcentration of trace copper with dithizone immobilized silica gel with detection by flame atomic absorption spectrometry. C: mini-column packing with H_2Dz-SG; FAAS: flame atomic absorption spectrometer; P1, P2: peristaltic pump; V: two-position valve; W: waste. (A) Loading and (B) injection.

2. Experimental

2.1. Apparatus and measurements

An AAnalyst-200 atomic absorption spectrometer (AAS) (PerkinElmer, USA) is used with a copper hollow cathode lamp (Vigous Instrument Co., Ltd, Beijing, China) as the light source at a wavelength of 324.75 nm and operated at 5 mA with a 0.8 nm spectral bandpass. A burner height of 10 mm, an air flow rate of 8.24 L min^{-1} and a acetylene flow rate of 1.86 L min^{-1} are employed.

A LZ-2000 flow injection (FI) system (Zhaofa Institute for Laboratory Automation, Shenyang, China) is employed for on-line separation and preconcentration of copper. The flow manifold of the FI-FAAS system is shown in Fig. 1. Silicone pump tube (4.0 mm o.d. × 2.0 mm i.d.) is used to delivery the sample solution. Other external channels are connected with 0.5 mm i.d PTFE tube.

The characterization of the H_2Dz-SG composite is performed by FT-IR spectra recorded on a WQF-200 spectrometer (The Second Optical Instrument Factory, Beijing, China), and the SEM images are obtained by an JSM-6480LV scanning electron microscope (JEOL, Japan). The energy dispersive spectrometer (EDS) profiles were obtained by a X-ray spectrometer (EDAX, USA). The pH measurement is performed with a pHS-3C digital pH meter (Hangzhou East Star Equipment Factory, Zhejiang, China).

2.2. Reagents

The chemicals used are purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), unless otherwise specified. A 1000 mg L^{-1} copper stock solution is prepared by dissolving 0.2513 g of $CuSO_4 \cdot 5H_2O$ (AR, Shenyang No. 2 Reagent Co.) in 100 mL DI water and stored in dark. Standard solutions of various concentrations are obtained by step-wise dilution of this stock solution with DI water. A 10% (v/v) nitric acid (GR) is used as eluent. Other reagents used include: dithizone (AR, Beijing Yinghai Fine Chemical Factory), thionyl chloride (AR), carbon tetrachloride (AR), NaOH (AR), hydrochloric acid (GR), sulfuric acid (AR), phosphoric acid (AR). The pH value of the sample solution is adjusted with either 0.1 mol L^{-1} HNO_3 or NaOH. DI water is used throughout.

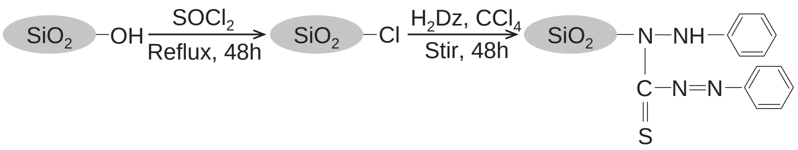
2.3. Immobilization of dithizone on silica gel and mini-column packing

As illustrated in Scheme 1, the immobilization of dithizone onto the surface of silica gel includes the silica activation, chlorination and chemical binding of dithizone.

Silica activation: 20 g silica gel (150–200 μm, Qingdao Ocean Chemical Factory, China) is activated by immersed into a 10 mL of HCl solution (6 mol L^{-1}) for 5 h to remove any metallic impurities. The silica gel is then filtered and rinsed with DI water to remove the excessive acid until neutral filtrate is obtained. The product is dried at 120 °C for 2 h.

Chlorination: 5 g of the activated silica gel is added into a 2-neck flask containing 30 mL thionyl chloride and refluxed at 77 °C for 48 h. The mixture is dried at 60 °C in a vacuum oven for 4 h and kept in a hermetic vessel after rotary evaporation.

Chemical binding of dithizone onto silica gel: The silica gel after chlorination is added into 30 mL dithizone–carbon tetrachloride solution (0.5 g dithizone). The mixture is stirred at room temperature for 48 h, and then filtered. The product is washed with carbon tetrachloride, ethanol and water sequentially to ensure a complete removal of the unreacted dithizone. After drying in vacuum at 60 °C for 4 h, 20 mg of the dithizone immobilized silica beads are used to pack a mini-column in a piece of PTFE tubing (3.0 mm o.d. × 2.0 mm i.d.). The mini-column is blocked at both ends with a small amount of glass wool to keep the silica beads in place. The mini-column is rinsed thoroughly by passing through 3.2 ml of NaOH solution (0.2 mol L^{-1}) at a flow rate of 6.5 mL min^{-1}. Afterwards, the mini-column is activated by passing through 10% (v/v) HNO_3 and DI water at a flow rate of 6.5 mL min^{-1} for 30 s and 60 s, respectively, and finally the mini-column is evacuated by air.



Scheme 1. Schematic diagram of the reaction process.

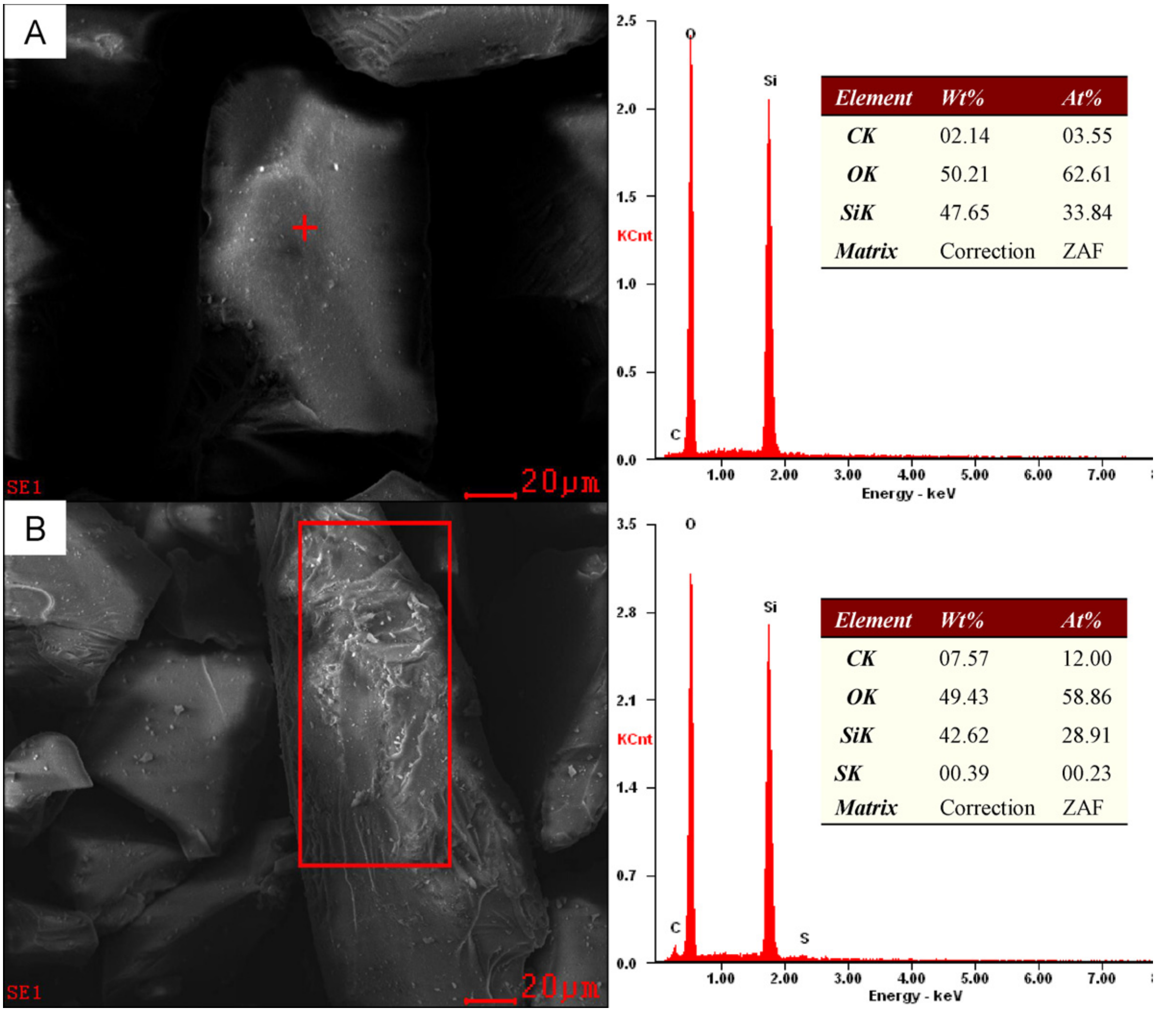


Fig. 2. The SEM images and the EDS profile of silica gel (A) and dithizone immobilized silica gel (B).

2.4. Operating procedure

The flow manifold is illustrated in Fig. 1. During the sample loading process, the two-position valve is set at the loading position. The sample solution at pH 5.5 is driven by peristaltic pump P1 at a flow rate of 6.5 mL min^{-1} to flow through the mini-column for 50 s, and during this process copper ions are retained onto the mini-column via coordination interaction with dithizone. In the meantime, DI water is used to clean the nebulizer of the atomic absorption spectrometer. After evacuating the sample loading tube and mini-column for 10 s, the two-position valve is switched to injection position. The retained copper are then recovered by elution with HNO_3 (10%, v/v) for 4 s at a flow rate of 6.5 mL min^{-1} in a reversed direction. The eluate is directly transferred into the flame atomic absorption spectrometer for quantification.

The mini-column is flushed with DI water for a period of 4 s at 6.5 mL min^{-1} after each cycle of the preconcentration-elution operation. It is evacuated with air before starting the next operation.

3. Results and discussion

3.1. Characterization of the dithizone immobilized silica and its adsorption mechanism for copper

Fig. 2 illustrated the SEM images, the EDS profiles as well as the compositions of the bare silica gel after activation by 6 M HCl and dithizone immobilization. It is obvious that the surface of the bare silica gel is smooth (Fig. 2A), while the surface of the H_2Dz-silica gel is rough (Fig. 2B). Sulfur is observed in the EDS profiles of the H_2Dz-silica gel (Fig. 2B), which is an indication of the immobilization of dithizone on the silica gel surface. Similar conclusions can be drawn from the FT-IR spectra. For pure silica gel, the absorption bands at 3459, 1641 and 1097 cm^{-1} are assigned to the stretching vibration for –OH, bending vibration for –OH and stretching vibration for –Si–O–, respectively (Fig. 3). Two new bands at 1544 and 1409 cm^{-1} are observed after the immobilization of dithizone, which are assigned to the bending vibration for –N–H and the stretching vibration for –N=N–, respectively. The absorption bands of the stretching vibration for –N–H and –C=S (1200–1050 cm^{-1}) are not identified because they are merged into the strong band at 1097 cm^{-1} from –Si–O–Si. However, the recognition of the bending absorption bands for the –N–H and stretching vibration for –N=N– groups well illustrate the immobilization of dithizone onto the silica.

The adsorption of copper can be attributed to the formation of penta-heterocycles chelating complex between Cu^{2+} and the dithizone molecule, where nitrogen and sulfur atoms serve as donors as illustrated in Scheme 2. The FT-IR spectrum of H_2Dz-SG after retaining Cu^{2+} shows red shift for the absorption bands of the bending vibration for –N–H and the stretching vibration for –N=N–, i.e., from 1544 to 1550 cm^{-1} and from 1409 to 1411 cm^{-1}, respectively. In the meantime, no shifts are observed for the stretching and bending

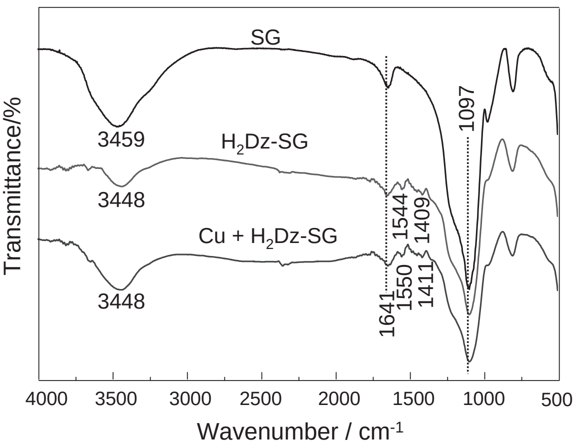
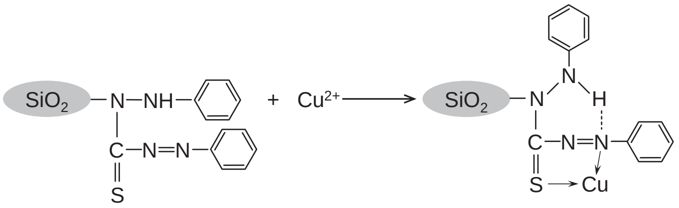


Fig. 3. FT-IR spectra of silica gel and dithizone modified silica gel before and after adsorption of copper.



Scheme 2. The adsorption of Cu^{2+} on the H_2Dz-SG.

vibration of the Si–OH group and the stretching vibration of Si–O–Si of silica gel. This indicates that the chelation between H_2Dz-SG and Cu^{2+} is a main factor for the adsorption, while the contributions from the functional groups on bare silica are negligible.

The bare silica gel and the H_2Dz-SG show significant difference for the adsorption efficiencies of copper. A very low adsorption efficiency of below 20% is recorded by the bare silica, while quantitative adsorption of copper is achieved when H_2Dz-SG is used.

3.2. *pH dependence of copper adsorption on H_2Dz-SG*

The chelation reaction between Cu^{2+} and dithizone depends strongly on the pH value of sample solution, as illustrated in Fig. 4. For the adsorption of copper by H_2Dz-SG, a significant increment in the sorption efficiency is recorded as the acidity of the sample solution is increased from pH 1 to 4. A maximum retention is observed within a range of pH 4–6. Thereafter, a further increase of the pH value gives rise to a significant decline of the sorption efficiency up to pH 12. These observations might be explained as follows: in a strong acidic medium (pH 1), the adsorption sites on the surface of H_2Dz-SG are occupied by the H_3O^+ ions, which entail a positively charged surface for H_2Dz-SG. The electrostatic repulsion between the Cu^{2+} and the surface of H_2Dz-SG is not favorable for the retention of copper, and thus no adsorption of copper is observed. On the other hand, at pH > 6 $Cu(OH)_2$ precipitation might be encountered because of hydrolysis. For further investigations, pH 5.5 is used for the sample solution.

3.3. *The sample loading process*

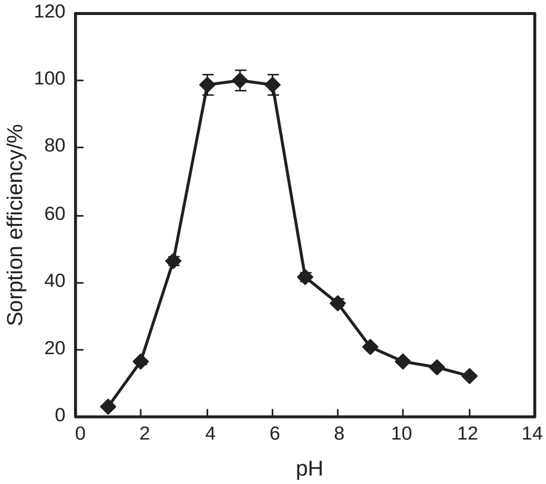


Fig. 4. The effect of pH on the sorption efficiencies of Cu^{2+} on H_2Dz-SG. H_2Dz-SG: 20 mg; sample volume: 5.4 mL; Cu^{2+} concentration: 100 μg L^{-1}; sampling flow rate: 6.5 mL min^{-1}; eluent: 10% (v/v) HNO_3; elution flow rate: 6.5 mL min^{-1}; elution time: 4 s.

The dependence of sorption efficiency of copper on the sample loading flow rate is investigated by fixing a copper concentration at 100 μg L^{-1}, a sampling volume of 5.4 mL, by varying the sample loading flow rate within a range of 3.5–7.5 mL min^{-1}. The results showed that when the sample loading flow rate is increased from 3.5 to 6.5 mL min^{-1}, no obvious variation of the sorption efficiency is observed. A decrease of the adsorption efficiency is encountered when further increasing the flow rate up to 7.5 mL min^{-1}. In practice, a sampling flow rate of 6.5 mL min^{-1} is employed in order to obtain a favorable sampling frequency and in the mean time remain the adsorption efficiency at a high level.

The effects of sampling time from 30 to 70 s are also investigated by fixing the other experimental parameters. It is reasonable that the detection sensitivity for copper will be favorable with a longer sampling time. However, too long a sampling time gives rise to a low sampling frequency. The present result showed that a sampling time of 50 s is appropriate when assessing the entire procedure in terms of sensitivity, enrichment factor and analytical frequency. Thus a sampling time of 50 s is adopted, corresponding to a sampling volume of 5.4 mL.

3.4. *The recovery of copper from H_2Dz-SG surface*

A few mineral acids, i.e., nitric acid, hydrochloric acid, phosphoric acid and sulfuric acid, are investigated as eluent for the collection of the retained copper on the H_2Dz-SG mini-column. The results showed that favorable elution efficiencies within the range of 10% (v/v) could be obtained when nitric acid, hydrochloric acid and sulfuric acid are employed, while phosphoric acid is not suitable for the recovery of the adsorbed copper. Among the there acids, nitric acid gives rise to better elution efficiency. The effect of HNO_3 concentration is investigated within the range of 2–12% (v/v). The results showed that improvement of the elution efficiency is observed when increasing the HNO_3 concentration up to 10% (v/v). Thereafter the recovery of copper dropped slightly when even higher concentrations of HNO_3 is employed. In practice, 10% (v/v) of HNO_3 solution is adopted as the eluent.

Table 1
Characteristic performance data of the procedure for copper analysis.

Sample volume	5.4 mL
Linear range	0.5–120 μg L^{-1}
Regression equation	$A = 2.9595 \times 10^{-3} C_{Cu}$ (μg L^{-1}) + 0.0021
Correlation coefficient	0.999
Enrichment factor	42.6
Detection limit (3σ, $n = 11$)	0.2 μg L^{-1}
RSD (40 μg L^{-1}, $n = 11$)	1.7%
Dynamic sorption capacity	0.76 mg g^{-1}
Sampling frequency	47 h^{-1}

Table 2
Comparisons of the analytical performance of the present system with those reported in the literature with similar detection techniques.

Adsorbent	Sample volume (mL)	Detection limit ($\mu g L^{-1}$)	RSD (%)	Ref.
3(1-Imidazolyl)propyl modified silica gel	11.2	0.2	1.4	[24]
NN-XAD	5.0	1.1	2.5	[25]
Styrene-divinylbenzene resin functionalized with (S)-2-[hydro -xyl-bis-(4-vinyt-phenyl)-methyll]pyrrolidine-1-carboxylic acid ethyl ester	13.2	1.1	1.0	[26]
Synthetic zeolites	5.0	0.1–0.4	2.6–2.8	[27]
Carbon nanotubes	4.3	0.11	2.4	[28]
Nb_2O_5–SiO_2	10.0	0.4	1.8	[29]
Polychlorotrifluoroethylene	17.4	0.02	1.8	[30]
Dithizone modified silica gel	5.4	0.2	1.7	This method

Table 3
The determination of trace copper in various water samples (*n* = 3, 95% confidence level).

Sample	Certified ($\mu g L^{-1}$)	Found ($\mu g L^{-1}$)	Spiked ($\mu g L^{-1}$)	Found ($\mu g L^{-1}$)	Recovery (%)
GBW(E)080039	100 ± 3	101 ± 5			
Tap water		1.32 ± 0.49	2.0	3.35 ± 0.84	102
Rain water		0.64 ± 0.48	2.0	2.56 ± 0.48	91
Snow water		1.21 ± 0.48	2.0	3.35 ± 0.84	107
Sea water		1.43 ± 0.48	2.0	3.46 ± 0.48	102
River water		1.54 ± 0.48	2.0	3.68 ± 0.84	107

By fixing a Cu^{2+} concentration at 100 $\mu g L^{-1}$ and an elution time of 4 s, we have investigated the effects of the elution flow rate in the range of 3.5–7.5 mL min^{-1} on the elution efficiency of the retained copper. The experimental results show an enhancement of the recovery of copper by increasing the elution flow rate up to 6.5 mL min^{-1}. However, when higher flow rates are used, significant decrease of the recovery is observed. This indicated that high elution flow rate is not favorable for the elution of copper. For further investigations, an elution flow rate of 6.5 mL min^{-1} is used.

When fixing the experimental parameters during the elution process, the collection of copper from the mini-column depends on the elution time. The recovery of copper by using elution time within a range of 1–6 s is investigated. The results indicated that elution efficiency more than 95% could be obtained when an elution time of 2–4 s is employed. In practice, a fixed elution time of 4 s is used.

3.5. *The interfering effects of foreign species*

The potential interfering effects of some foreign species, which are frequently encountered in environmental water samples, are tested using the present procedure by gradually increasing the amount of the foreign ions. At a copper concentration level of 10 $\mu g L^{-1}$ and within a ±5% error range, 10,000-fold of Na^+, K^+, 5000-fold of Ca^{2+}, Cl^-, 500-fold of Mg^{2+}, 100-fold of Pb^{2+}, Fe^{3+}, Co^{2+}, Ba^{2+}, 80-fold of Bi^{3+}, 60-fold of Ni^{2+}, Zn^{2+}, 50-fold of Cr^{3+}, 40-fold of Ag^+ and 30-fold of Mn^{2+} pose no interferences on the determination of copper. In common sense the contents of the above metals in sample digests or after appropriate dilution will not exceed the tolerant limits, therefore the present procedure can be directly employed, and no further treatment or masking reagents are needed.

3.6. *Performance and application of the procedure*

At the aforementioned experimental conditions, the analytical performance data are summarized in Table 1 for the preconcentration of trace copper by using the H_2Dz-SG beads as adsorbents with detection by flame atomic absorption spectrometry. Obviously, the present procedure provides a wide linear range of 0.5–120 $\mu g L^{-1}$. In addition, it provides a detection limit of 0.2 $\mu g L^{-1}$ along with a precision of 1.7% RSD at 40 $\mu g L^{-1}$ ($n = 11$). A dynamic sorption capacity of 0.76 mg g^{-1} copper is achieved.

A comparison of the characteristic performance data of the present system with some of the reported procedures based on solid-phase extraction with detection of FAAS has been summarized in Table 2. It is obvious that both the sensitivity and sample/reagent consumption of the present procedure are favorable or at least at the same level as those of the reported methodologies.

The method is validated by analyzing the copper concentration in a certified reference water sample, i.e., GBW (E) 080039 (The Second Institute of Oceanography, State Oceanic Administration, China). The obtained value for copper content agreed well with the certified value. Further, spiking recovery tests are also performed by employing a few water samples, i.e., tap water (laboratory), rain water (AnShan), snow water (AnShan), sea water (DaLian) and river water (YingNaHe, DaLian). The results are summarized in Table 3.

All the water samples except for the tap water are filtered through a cellulose membrane of 0.45-μm pore size. Before analysis, these water samples are adjusted to pH 5.5 with diluted HNO_3. It can be seen that satisfactory spiking recoveries within the range of 91–107% are achieved for the water samples, demonstrating the practical usefulness of the procedure.

4. Conclusions

The immobilization of dithizone on silica gel provides a useful adsorbent for the adsorption of trace amount of copper. The binding of dithizone effectively eliminates the drawbacks of liquid–liquid extraction procedure with dithizone as the chelating reagent, e.g., the consumption of large amount of organic solvent. This illustrates that the immobilization of chelating functional group or other binding sites on solid support is a practical approach for the improvement on the extraction efficiency. In the meantime, green analytical approaches are developed by avoiding or significantly reducing the amount of organic solvents.

Acknowledgments

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