DETERMINATION OF COPPER BY FLAME ATOMIC ABSORPTION SPECTROMETRY USING FLOW INJECTION ON-LINE PRECONCENTRATION WITH DOUBLE MICRO-COLUMNS

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ABSTRACT:

A flow injection spectrophotometric method is proposed for on-line preconcentration and determination of trace amounts of copper in water samples. The results show that copper can be determined using the sample pH in 6.98, sample flow rate of 2.5 ml min^{-1}, and the elution step using 0.1 mol/l^{-1} hydrochloric acid solution at flow rate of 2 ml min^{-1}. Under optimized conditions, the relative standard deviation of this method was 6.5% at 3 μg·l^{-1} (n=5), and the detection limit was 0.585 μg·l^{-1}. The analytical recovery was up to 93~109% and 94~106% respectively in detecting environment water and drinking water

INTRODUCTION

Copper is an essential micronutrient that plays a central role for a broad range of biological processes /1/. So the determination of copper in natural water samples is very important for environmental science. Due to the concentration of copper in some water samples being rather low (ppb level), some preconcentration steps must be included to assure the sensitivity of determination /2,3/. There are many methods for copper determination such as spectrophotometry /4,5/, inductively coupled plasma atomic emission spectroscopy (ICP-AES) /6/, inductively coupled plasma mass spectrometer (ICP-MS) /7/, graphite furnace atomic absorption spectrometry (GFAAS) /8/, flame atomic absorption spectroscopy (FAAS) /9/. The above methods mentioned are of high sensitivity and accuracy, But some restrictions for the present methods. For example, ICP-Based procedures found difficulties in treating samples with high salt solution /10/. Mass spectrometers are expensive and this limited the applications /11/. In many cases, the FAAS do not have sufficient sensitivity for the determination of trace elements.

In recent years, flow injection (FI) on-line preconcentration procedures now play an important role in trace metals analysis. Various adsorbents have been reported for the on-line preconcentration of trace metals in water samples. Now, the investigated materials include 8-hydroxquinoline immobilized onto silicone tubing /7/, chelating resin known as D412 /8/ and Chelex-100 /9/, micro porous silica /10/ and modified cellulose /11/, etc.

Herein we describe a flow injection packed with porous cellulose sphere modified by the open chain azacrown (PCS-OCAC) /12,13/ on-line enrichment for determination of Cu^{2+} in water samples. The results show that it is very beneficial to perform such procedures on-line and automatically.

EXPERIMENTAL

Apparatus

A FIA-3100 flow injection analyzer (Beijing Jitian Instruments Co., Ltd, China) was used for transporting samples. The sample solution was pumped to micro-column (200ul) packed with PCS-OCAC for preconcentration. Then the eluted solution was delivered to WFX-120 flame atomic absorption spectrometry (Beijing Ruili Instruments Co., Ltd, China) that was equipped with a copper hollow-cathode lamp for determination. The instrument was operated at the optimum conditions suggested by the manufacturer. The wavelength was set at 324.7 nm, the lamp current was adjusted to 3 mA and air-acetylene flame was employed (air 8 $Lmin^{-1}$ and acetylene 2 $Lmin^{-1}$). The peak height was used for quantification.

Two laboratory-built micro-columns (200ul) were used for packing with PCS-OCAC, which is shown in Fig 1.

Ultrapure water (18.3 MΩ) was produced by a Human UP-900 system provided by Nanjing Kejie Instruments Co., Ltd.

Reagents and Operating procedures

A standard copper (II) prepared according the standard procedure was used to detect the working calibration curve. The copper (II) solution was adjusted to pH values (6.98) by nitric acid and sodium hydroxide.

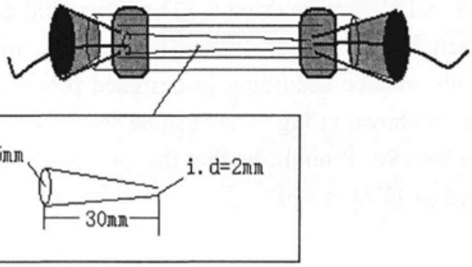

Fig. 1: The laboratory-built micro-column

The on-line determination system was designed as Fig 2.

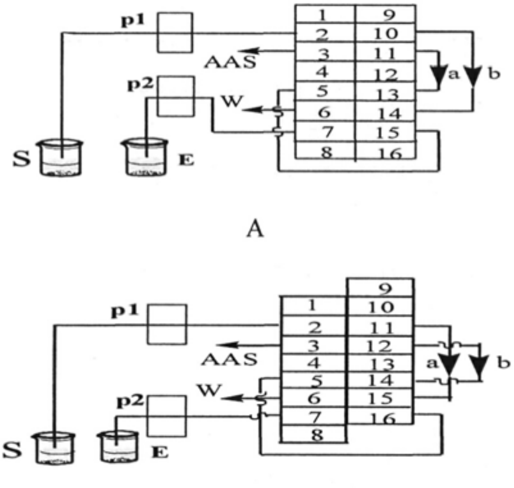

Fig. 2: Flow injection apparatus

RESULTS AND DISCUSSION

Effect of pH

In the flow injection analysis, the absorbance is affected by pH of sample solution. We adjusted to various pH values of sample solution (0.06μg·mL^{-1}) by nitric acid and sodium hydroxide (The nitric acid and sodium hydroxide were purchased from Chengdu kelong reagent Co., Ltd., China.), and then detected the absorbance according to designed procedure. The effect of pH on absorbance is shown in Fig. 3. As can be seen from Fig. 3, the optimal pH was found to be 6.98. It might be that the Cu^{2+} adsorbed by the adsorbent is easily replaced by H^{+} at this pH.

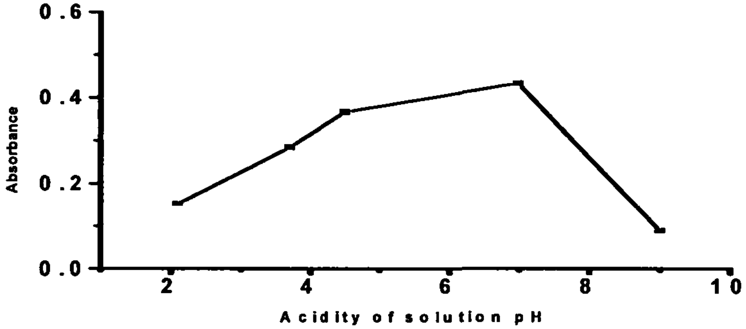

Fig 3: Effect of pH of sample solution on the absorbance

Effect of Preconcentration Time

Pre-concentration time can affect analysis sensitivity and sampling frequency. Pre-concentration time from 20 seconds to 120 seconds was tested under the conditions designed above. The result in Fig. 4 showed that the absorbance almost did not increase when preconcentration was more than 120 s. So the optimal preconcentration time was found to be 90 s. The results in Figure 4 showed that the absorbance will increase when pre-concentration time was no more than 90 seconds. So 90 seconds was selected as the optimal time for the further work.

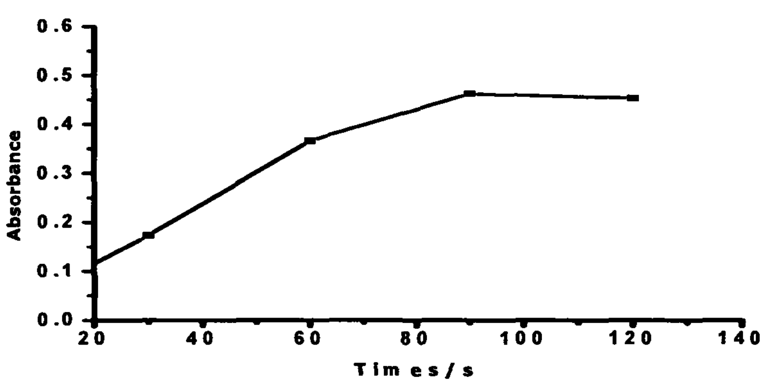

Fig 4: Effect of preconcenration time on absorbance

Selection of eluent and the effect of eluent concentration

In the study, nitric acid, sulfuric acid and hydrochloric acid were tested as eluents. (The sulphuric acid and hydrochloric were purchased from Chengdu kelong reagent Co., Ld, China.) The experimental results showed that the sensitivity of the eluent of nitric acid was higher than that of sulfuric acid and hydrochloric acid. Thus, nitric acid was selected as the eluent solution. Nitric acid concentration affects the absorbance of copper (II). The maximum absorbance of copper (II) (0.06 $\mu g \cdot mL^{-1}$) was 0.3713 under the conditions described above when nitric acid concentration was 0.1 $mol \cdot L^{-1}$. So the optimal concentration of nitric acid was found to be 0.1 $mol \cdot L^{-1}$.

Effect of preconcentration and elution rate

In the FIA, the flow rate of pre-concentration and elution could affect the sensitivity of the proposed method. We controlled the flow rate by changing the pump pressure. In this work, the effect of the preconcentration rate and elution rate were studied from 1 to 6 $mL \cdot min^{-1}$. As is shown in Fig. 5, the best results of preconcentration rate and elution rate were found to be 2.5 $mL \cdot min^{-1}$, 2 $mL \cdot min^{-1}$, respectively. At these flow rates, the absorbance of copper (II) (0.06 $\mu g \cdot mL^{-1}$) was up to maximum. So the flow rates were selected for further work.

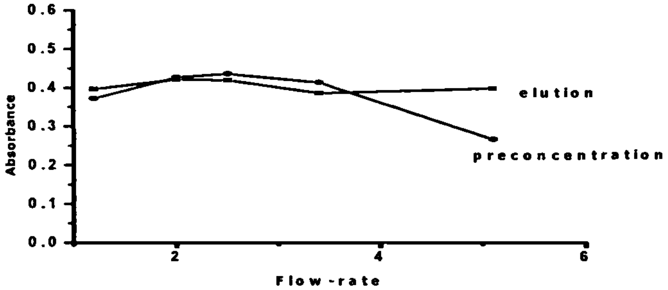

Fig 5: Effect of the flow rate of enrichment and elution on absorbance

On-line preconcentration of Cu

The micro-columns were introduced in a flow injection system for preconcentration of copper (II) and its performance was tested. The solution (0.1 ug·mL^{-1} or 0.6 ug·mL^{-1}) was passed through the column at a flow rate of 2.5 mL·min^{-1} for 6 min and the column was washed with 10 ml of 0.1 mol·L^{-1} nitric acid. The effluent was collected, and then determined by FAAS. The recovery was found to be 105% for 0.1 ug·mL^{-1} of copper (II) and 97% for of copper (II).

The effect of various ions

In order to check the applicability of present method to analysis of water samples, various ions were added to standard solution (0.06 ug·ml^{-1}). The results showed that no interference was observed from 200 times ions of K^+, Na^+, 50 times ions of Mg^{2+},Ca^{2+} or 10 times ions of Zn^{2+}, Fe^{3+},Cd^{2+}. So the present method may be applicable to the determination of copper in water samples.

Linearity and precision of the proposed method

In order to obtain a calibration graph, standard solutions were preconcentrated by PCS-OCA, and then eluted with nitric acid (0.1 mol·L^{-1}) directly into the FAAS to detect under the selected conditions. A linear correlation is observed with the correlation coefficient 0.9987. The regression equation was as follows: A= 0.0476C - 0.0013. To assess the reproducibility and accuracy of the proposed method, 0.05 ug·ml^{-1} standard solution (n=7) were investigated. The results showed that the relative standard deviation (RSD) was calculated as 6.5%. The results showed that the relative standard deviation (RSD) was calculated as 6.5%.

Application and determination of recovery

The proposed method was applied to the determination of trace copper (II) ions in environment water and drinking water. Standard solution was prepared for determination of recovery. The results are given in Table 1.

Table 1

The results for the determination of Cu^{2+} and recovery tests

Samples	Average ug.mL^{-1}	Sample + standard solution + ultrapure water mL	Experimental ug.mL^{-1}	Recovery %
Drinking water	0.0153	80+0+20	0.0130	108
		80+10+10	0.0124	94
		80+15+5	0.0145	106
		80+20+0	0.0149	105
Environment water	0.0328	80+0+20	0.0249	95
		80+10+10	0.0253	93
		80+15+5	0.0299	108
		80+20+0	0.0307	109

CONCLUSIONS

The proposed method was significant with regard to the development of a simple, reliable, and sensitive flow injection method for continuous on-line pre-concentration and determination of trace amounts of copper (II). The FIA-FAAS system described in this paper provides an automated alternative to the determination of copper in water samples, and the PCS-OCA had the strongest accumulation capacity on copper (II). Through pre-concentration, the absorbance can improve 28 times. Also, the system is cheaper than other instruments, but it can be applied to determine copper (II) in water samples. The relative standard deviation of this method was 6.5% and the detection limit was 0.585ug/L. Therefore, it preferably applied to the routine analysis of water samples.

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