



Determination of trace copper in food samples by flame atomic absorption spectrometry after solid phase extraction on modified soybean hull

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ABSTRACT

Soybean hull was chemically modified with citric acid and used as a solid phase extraction adsorbent for the determination of trace amounts of Cu^{2+} in food samples by flame absorption spectrometry (FAAS). The effect of pH, sample flow rate and volume, elution flow rate and volume and co-existing ions on the recovery of the analyte were investigated. The results showed that Cu^{2+} could be adsorbed on the modified soybean hull at pH 8.0 and eluted by 2.0 mL of 1.0 mol L^{-1} HCl. Under the optimized conditions, the adsorption capacity of modified soybean hull was found to be 18.0 mg g^{-1} for Cu^{2+} . The detection limit of the proposed method was 0.8 ng mL^{-1} for Cu^{2+} with an enrichment factor of 18. The analytical result for the certified reference tea sample (GBW07605) was in a good agreement with the certified value. The proposed method has also been successfully applied to the determination of trace Cu^{2+} in dried sweet potato, lake water and milk powder, the recovery of Cu^{2+} for spiked samples was between 91% and 109.6%.

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1. Introduction

Copper is an essential element not only for mammals but also for plants, and plays an important role in carbohydrate and lipid metabolism. It has many biological effects as an essential element as well as a toxic one [1]. In general, a daily copper intake of $1.5\text{--}2 \text{ mg}$ is essential and copper at nearly 40 ng mL^{-1} is required for normal metabolism of many living organisms [1,2]. However, copper at higher levels is toxic and severe oral intoxication will affect mainly the blood and kidneys. And copper can be present in foods naturally, as a result of pollution, or from the storage or processing of foods. Because of these, the trace copper content in foods must be controlled on a daily basis and the European Commission has fixed the limit of $2 \text{ } \mu\text{g mL}^{-1}$ for copper in drinking water and the allowed limit of copper is set to $1.3 \text{ } \mu\text{g mL}^{-1}$ in the USA similar to that in Canada ($1.0 \text{ } \mu\text{g mL}^{-1}$) [3,4]. Therefore, there is an increasing need to monitor copper levels in food samples at ever decreasing concentrations. For this purpose, very sensitive, simple, rapid and inexpensive methods are necessary.

Sensitive and accurate determination of metals at trace level is one of the important points of analytical chemistry [5,6]. The quantification of trace metals in food samples has routinely been done by inductively coupled plasma optical emission spectrometry (ICP-OES) [7], inductively coupled plasma mass spectrometry

(ICP-MS) [8,9], graphite furnace atomic absorption spectrometry (GFAAS) [10] and flame atomic absorption spectrometry (FAAS) [11–13]. Compared with other techniques, FAAS has the characteristics of good precision and simplicity with lower cost. However, direct determination of trace metals at trace level by FAAS is often difficult, not only because of its insufficient sensitivity, but also because of matrix effects. To solve this problem, separation–preconcentration procedures are often involved prior to analysis by FAAS. Preconcentration is a very important issue for improvement of sensitivity, and separation is an efficient technique to reduce the interference of sample matrix [14]. Various separation–preconcentration procedures have been used for this purpose, including liquid–liquid extraction [15], solid phase extraction [16,17], ion exchange techniques [18], coprecipitation [19] and cloud point extraction [20,21].

Recently, solid phase extraction (SPE) technique has become increasingly popular for the enrichment of metal ions prior to their determination. Compared with traditional liquid–liquid extraction method, SPE has the following advantages: (i) high preconcentration factor; (ii) simple operation; (iii) rapid phase separation; (iv) can be combined with different detection techniques and (v) time saving and cost saving [14].

It is well known that the adsorption medium plays a key role in improving the selectivity of SPE and much more attention has been paid to the investigation of new adsorption materials for SPE in recent years [22]. Many adsorption materials, such as chelating resins, silica gel, carbon sorbents, inorganic based sorbents, biological adsorption material and nanomaterials have been used in SPE

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[14,22,23]. Recently, it has been showed that materials obtained from modified agriculture wastes, such as peanut shell, saw dusts, exhibit a large adsorption capacity towards heavy metal ions such as Cu^{2+} , Zn^{2+} , Ni^{2+} , Cr(V) , and Pb^{2+} [24–26]. Modified peanut shell has been used as adsorbent of SPE for the preconcentration of trace Pb^{2+} and Cd^{2+} in food samples with a very larger adsorption capacity in our previous work [27], which indicated that material obtained from agriculture wastes was a potential adsorbent for SPE. In this paper, modified soybean hull was proved another potential adsorbent for SPE. The adsorbent was prepared with a similar preparation procedure as our precious work [27], and packed in a homemade micro-column. The SPE preconcentration procedure was combined with FAAS for the determination of trace Cu^{2+} in food samples.

2. Experimental

2.1. Apparatus

TAS-986 atomic absorption spectrometry (Beijing Purkinje General Instrument Co., Ltd., Beijing, China) with copper hollow cathode lamps (KY-1) was used for the determination. The optimum operation conditions were as follow: wavelength 324.7 nm, spectrum band width 0.2 nm, lamp current 3 mA, flow rate of acetylene 1600 mL min^{-1} . The pH values were controlled with a PHS-3C pH-meter (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). A HL-2D constant flow pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) and a self-made polytetrafluoroethylene (PTFE) micro-column ($30 \text{ mm} \times 4.0 \text{ mm}$, i.d.) packed with modified soybean hull were used in SPE process.

2.2. Standard solutions and reagents

The stock standard solutions (1.000 g L^{-1}) of Cu^{2+} was prepared by dissolving appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) in deionized water. HCl (pH 1.0–2.0), acetate–acetic acid buffer (pH 3.0–5.0) and $\text{NH}_3\text{--NH}_4\text{Cl}$ buffer (pH 8.0–10.0) were used for pH adjustment. Different stock solutions of potentially interfering ions (1.000 g L^{-1}) were prepared according to the conventional method. Working solutions were prepared by appropriate dilutions of stock solutions. All reagents used were analytical-reagent grade. The laboratory glassware was kept in a 5% (v/v) HNO_3 solution overnight. Afterwards, it was rinsed thoroughly with deionized water and dried.

2.3. Preparation of the adsorbent

The cleaned and sieved (0.074 mm) soybean hull powder was added to $50 \text{ mL } 1 \text{ mol L}^{-1} \text{ NaOH}$ for 1 h with magnetic stirring. Then the supernatant was removed after standing, and the powder was washed to neutral by deionized water, and dried at 50°C . Subsequently, the powder was mixed with $50 \text{ mL } 0.6 \text{ mol L}^{-1}$ citric acid, and esterification reaction could be occurred between citric acid and cellulose (the soybean hull has a relative high cellulose content) at 70°C water bath with magnetic stirring. After washed to neutral by deionized water, the obtained powder was heated at 200°C for 1.5 h. The resulting powder was washed with deionized water for several times in order to eliminate the potential impurities, and then was dried at 50°C for future use.

2.4. Preparation of micro-column

A total of 50 mg of modified soybean hull powder was filled into a PTFE micro-column ($30 \text{ mm} \times 4.0 \text{ mm}$, i.d.) plugged with a small portion of absorbent cotton at both ends. Before use, methanol and

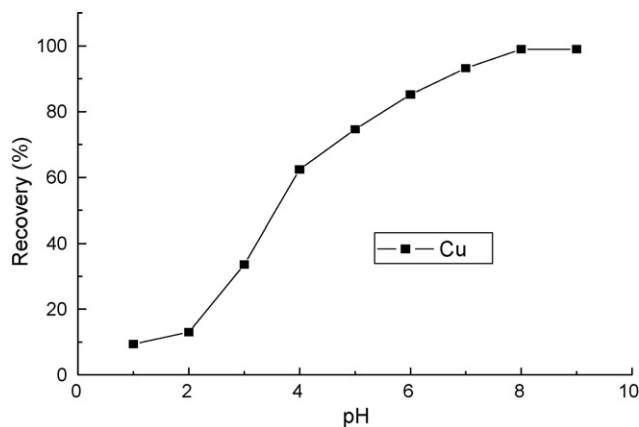


Fig. 1. Effect of pH on the adsorption (recovery, %) of Cu^{2+} on modified soybean hull. The concentration of target analytes: $\text{Cu}^{2+} 5.0 \mu\text{g mL}^{-1}$, sample flow rate: 3.0 mL min^{-1} , sample volume: 50 mL , eluent flow rate: 0.5 mL min^{-1} .

deionized water were passed through the column in sequence in order to clean it.

2.5. Procedure of column experiments

In the column experiments, a 50.0 mL sample or standard solution containing Cu^{2+} was adjusted to pH 8.0 and was passed through the column by using a peristaltic pump at 3.0 mL min^{-1} of sample flow rate. Afterwards, Cu^{2+} retained on the column was eluted with $2.0 \text{ mL } 1.0 \text{ mol L}^{-1}$ of HCl at elution flow rate of 1.0 mL min^{-1} . Finally, the analyte in the effluents was determined by FAAS.

2.6. Sample preparation

Certified reference tea sample (GBW07605): 0.5000 g of certified reference tea sample was weighed into a 100 mL porcelain crucible, and then the powder was incinerated at electric furnace. When there is no white smoking emission from the incinerated powder, the porcelain crucible with the powder was heated in a muffle furnace with temperature of $500 \pm 25^\circ\text{C}$ for 5 h. After cooling, the residue was dissolved in $500 \text{ mL } 1\% \text{ (v/v) HNO}_3$.

Dried sweet potato: 0.3000 g of sweet potato (purchased in the supermarket) was treated by the similar preparation procedure with that for certified reference tea sample.

Lake water. Lake water was collected from Xiliu Lake, Zhengzhou, China. Before use, the water sample was filtered through a $0.45 \mu\text{m}$ membrane filter (Tianjin Jinteng Instrument Factory, Tianjin, China) and the pH value was adjusted to 8.0 with $\text{NH}_3\text{--NH}_4\text{Cl}$ buffer.

Milk powder. Milk powder was purchased in the supermarket, and 0.5000 g of milk powder was treated by the similar procedure with that for certified reference tea sample.

3. Results and discussion

3.1. Effect of pH

pH value plays a key role in the SPE procedure. An appropriate pH value can not only improve the adsorption efficiency, but also depress the interference of the matrix. The adsorption behavior of Cu^{2+} on modified soybean hull was studied according to the procedure of column experiments. Fig. 1 is effect of pH on the adsorption (recovery, %) of Cu^{2+} on modified soybean hull. It can be seen that Cu^{2+} was adsorbed quantitatively (recovery larger than 90%) on modified soybean hull within a pH range of 7–9. The precipitate was observed when pH larger than 9, for further experiments, pH

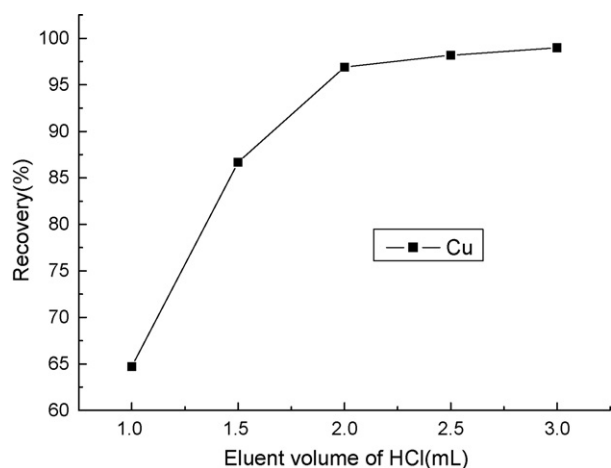


Fig. 2. Effect of eluent volume on the recovery of analytes. The concentration of target analytes: Cu^{2+} $0.1 \mu\text{g mL}^{-1}$, HCl concentration: 1.0 mol L^{-1} , HCl flow rate: 0.5 mL min^{-1} , sample flow rate: 3.0 mL min^{-1} .

8.0 was chosen for preconcentration of Cu^{2+} . These could possibly be explained that citric acid could be bonded onto soybean hull through esterification reaction between cellulose and citric acid during the preparation procedure for adsorbent. Certainly, not all the carboxyls of citric acid could be converted into ester, so there are carboxyls on the surface of the adsorbent. When the pH value is larger than 7, carboxylic acid has better complexation capability for Cu^{2+} .

3.2. Optimization of elution conditions

It is obvious from Fig. 1 that the adsorptions of Cu^{2+} decrease sharply with the decrease of pH value. For this reason, various concentrations ($0.5\text{--}2.0 \text{ mol L}^{-1}$) of HCl were studied for the elution of retained analytes (50 mL standard solution containing $0.1 \mu\text{g mL}^{-1}$ of Cu^{2+} was passed through the column) from the column with elution flow rate of 1.0 mL min^{-1} . The results showed that quantitative recoveries ($>90\%$) could be obtained when the HCl concentration was higher than 1.0 mol L^{-1} .

The elution volume and elution flow rate could affect the elution efficiency remarkably. By keeping the eluent concentration of 1.0 mol L^{-1} HCl, the effect of elution volume on the quantitative elution of analytes was investigated according to the procedure of column experiments. 3.0 mL of 1.0 mol L^{-1} HCl was used to elute the analytes on the modified soybean hull, the eluent was collected at 0.5 mL intervals. Fig. 2 showed the recovery of analytes in each portion determined by FAAS. As can be seen, the recovery of analytes was larger than 95% when eluent volume was larger than 2.0 mL . That means quantitative elution could be obtained when elution volume was higher than 2.0 mL . And it was also found that quantitative elution could be obtained with elution flow rate varying among $0.2\text{--}1.2 \text{ mL min}^{-1}$. Thus, the elution conditions used in the following experiments were as follows: the eluent concentration was 1.0 mol L^{-1} HCl, elution volume was 2.0 mL and the elution flow rate was 1.0 mL min^{-1} .

3.3. Effect of sample flow rate and sample volume

The sample flow rate should be optimized to ensure quantitative retention along with minimization of the time required for sample processing. It was found that the flow rate in the range of $1.0\text{--}3.0 \text{ mL min}^{-1}$ had no significant effect on the recoveries of Cu^{2+} according to the procedure of column experiments. It means that the adsorption kinetics of the modified soybean hull is very excel-

Table 1
Tolerance limits of co-existing ions.

Substance	Maximum tolerable amount	Recovery (%)
K^+ , Na^+	2.0 mg mL^{-1}	95.9
Ca^{2+}	1.0 mg mL^{-1}	93.7
Mg^{2+}	1.0 mg mL^{-1}	99.3
Al^{3+}	$10 \mu\text{g mL}^{-1}$	107.2
Fe^{3+}	$10 \mu\text{g mL}^{-1}$	101.7
Pb^{2+}	$15 \mu\text{g mL}^{-1}$	96.7
Co^{2+}	$20 \mu\text{g mL}^{-1}$	94.1
Mn^{2+}	$10 \mu\text{g mL}^{-1}$	96.1
Ni^{2+}	$10 \mu\text{g mL}^{-1}$	95.2

lent to the studied ion. For further experiments, 3.0 mL min^{-1} was chosen as the sample flow rate.

In order to obtain a high or achievable preconcentration factor of very dilute analyte solutions from large volumes, it is imperative to investigate the effect of sample volume on the retention of analytes on the modified soybean hull. It was found that quantitative recovery for Cu^{2+} was obtained when sample volumes were less than 50 mL . So 50 mL was chosen as the sample volume.

3.4. Effect of concomitant

The effect of some co-existing ions on the preconcentration and determination of the studied analytes was investigated. In this experiment, the solutions of $0.5 \mu\text{g mL}^{-1}$ Cu^{2+} containing the added interfering ions were treated according to the procedure of column experiments. The content of target analytes in the effluent was determined in order to calculate the recovery of the studied elements. The tolerances of the co-existing ions, defined as the maximum concentration that could achieve $>90\%$ recovery of the target analytes, are given in Table 1. It can be seen that the presence of major cations had no obvious influence on the target element adsorption under the selected conditions.

3.5. Column regenerability and adsorption capacity

The regenerability and stability of the column was investigated by passing the analytes and then passing 2.0 mL of 1.0 mol L^{-1} HCl and 10 mL of deionized water through the column packed with 50 mg of modified soybean hull. It was observed that the column could be reused up to 30 runs with the recoveries of the target ion larger than 90% .

The adsorption capacity of modified soybean hull was studied in order to evaluate the amount of adsorbent required to quantitatively concentrate the analytes from a given solution. The method used was adapted from the recommended by Maquieira et al. [28]. The adsorption capacities of Cu^{2+} was 18.0 mg g^{-1} .

3.6. Analytical performance

Under the optimized conditions, the analytical performance of the method was evaluated. Based on the definition of IUPAC, the detection limits (3σ) of this method was 0.8 ng mL^{-1} for Cu^{2+} , the relative standard deviation (RSD) were 1.7% ($c=40 \text{ ng mL}^{-1}$, $n=7$). The calibration graph for the preconcentration procedure was $A=0.00236C-0.0003814$ ($R=0.998$) for $4\text{--}150 \text{ ng mL}^{-1}$, and the calibration graph without preconcentration was $A=0.000132C-0.00728$ ($R=0.999$). The enrichment factor (EF, calculated as the ratio of the slopes of the calibration graphs with preconcentration and direct aspiration, respectively) was 18.

For comparative purposes, the performance characteristics of the proposed method and other selected off-line SPE/FAAS systems reported in the literature are given in Table 2. The proposed procedure shows larger adsorption capacity and lower detection limit

Table 2
Comparative data from some recent studies on off-line SPE/FAAS system.

Analyte/Absorbent	Adsorption capacity	Detection limit	Enrichment factor	Sample flow rate	Eluent/volume
Cu ²⁺	–	1.46 ng mL ⁻¹	60	600 mL 2.0 mL min ⁻¹	10 mL HNO ₃ (2.0 M) [29]
Pb ²⁺	Pb: 12.63 mg g ⁻¹	Pb: 0.58 ng mL ⁻¹			
Cu ²⁺	Cu: 15.38 mg g ⁻¹	Cu: 0.86 ng mL ⁻¹			
Cd ²⁺	Cd: 6.09 mg g ⁻¹	Cd: 0.65 ng mL ⁻¹	200 (100 for Cd(II))	2000 mL (Cd 1000 mL) 2.0 mL min ⁻¹	10 mL HCl (0.05–0.5 M, 0.1–0.5 M) [30]
Ni ²⁺	Ni: 4.62 mg g ⁻¹	Ni: 0.92 ng mL ⁻¹			
Cu ²⁺	Cu: 2.55 mg g ⁻¹	Cu: 1.14 ng mL ⁻¹	37	250 mL 5.0 mL min ⁻¹	7 mL HCl (1.0 M) [31]
Fe ³⁺	Fe: 4.05 mg g ⁻¹	Fe: 2.01 ng mL ⁻¹			
Zn ²⁺	Zn: 2.82 mg g ⁻¹	Zn: 0.14 ng mL ⁻¹			
Cu ²⁺	18.0 mg g ⁻¹	0.8 ng mL ⁻¹	18	50 mL 3.0 mL min ⁻¹	2.0 mL HCl (1.0 M) (this work)

Table 3

Analytical results for copper in the certified reference material (GBW07605).

Species	Founded ($\mu\text{g g}^{-1}$)	Certified ($\mu\text{g g}^{-1}$)
Cu	18.9 ± 0.2	17.3 ± 0.3

Table 4

Analytical results for Cu²⁺ in food samples (mean ± CI^a, n = 3).

Sample	Added	Found	Recovery
Dried sweet potato ($\mu\text{g g}^{-1}$)	0	46.9 ± 4.0	–
	15	61.6 ± 5.2	98%
	30	79.8 ± 4.7	109.6%
Lake water (ng mL ⁻¹)	0	14.1 ± 1.0	–
	20	34.4 ± 2.7	101.5%
	40	53.4 ± 4.5	98.3%
Milk powder ($\mu\text{g g}^{-1}$)	0	6.8 ± 0.7	–
	10	15.9 ± 1.7	91%
	15	22.1 ± 2.5	102%

^a CI is confidence intervals, which was calculated with 95% confidence level.

over other SPE off-line methods. Moreover, the absorbent used in this work was easily prepared from agriculture wastes. In this work, relative smaller sample volume (50 mL) and eluent volume (2.0 mL) and relative larger sample flow rate (3.0 mL min⁻¹) were used, which means much shorter analysis time.

3.7. Sample analysis

For real sample analysis, the standard calibration curve was employed. In order to establish the validity of the proposed procedure, the method has been applied to the determination of trace copper in the certified reference materials (GBW07605 tea sample). The analytical results were listed in Table 3. As can be seen, a good agreement between determined values and the certified values could be obtained.

The method was also applied to the determination of trace Cu²⁺ in dried sweet potato, lake water and milk powder. The analytical results and the recoveries for the spiked samples were given in Table 4. It can be seen that the recovery for the spiked samples is between 91% and 109.6%.

4. Conclusions

A simple, rapid and reliable method was developed for the preconcentration and FAAS determination of trace Cu²⁺ in food samples by using modified soybean hull as micro-column packing material. The adsorption behavior of Cu²⁺ on modified soybean hull had been systematically studied. It was found that modified soybean hull showed a high adsorption capacity for Cu²⁺, and the analytes retained on its surface can be easily desorbed. Hence, modified soybean hull showed great potential as an adsorbent for the preconcentration of trace metal ions in samples with complicated matrix.

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