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Determination of trace copper in water samples by flame atomic absorption spectrometry after preconcentration on a phosphoric acid functionalized cotton chelator

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Abstract: This paper reports the preparation of a phosphorylated cotton chelator (PCC) by solid phase esterification of phosphoric acid (PA) onto defatted cotton fibres using urea as the catalyst. The synthesized PCC was employed for the preconcentration of copper from water samples prior to its determination by flame atomic absorption spectrometry (FAAS). The preconcentration of copper was studied under both batch and column techniques. The pH range for the quantitative preconcentration of copper was 4.0–7.0. The sorption time required for each sample was less than 30 min by the batch method. The copper sorption capacity of the PCC was found to be 15.3 mg/g at the optimum pH value. Elution with 1.0 mol dm^{-3} hydrochloric acid was found to be quantitative. Feasible flow rates of the copper solution for quantitative sorption onto the column packed with PCC were 0.5–4.0 ml min^{-1}, whereas the optimum flow rate of the hydrochloric acid solution for desorption was less than 1.5 ml min^{-1}. An 80-fold preconcentration factor could be achieved under the optimum column conditions. The tolerance limits for common metal ions on the preconcentration of copper and the number of times of column reuse were investigated. The proposed method was successfully applied for the preconcentration and determination of trace copper in natural and drinking water samples by FAAS.

Keywords: phosphoric acid; PCC; trace copper; preconcentration; FAAS; determination.

INTRODUCTION

Determination of heavy metals at trace levels in environmental and food samples is of great importance nowadays due to the non-degradability, bioaccumulation and high toxicity of heavy metals in the environment and living organisms. Most heavy metals have a high affinity for thiol groups, carboxyl groups and/or amine groups; hence, they attack and inactivate enzymes and protein sites where these kinds of groups are present. It also has been demonstrated

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that heavy metals bind to cell membranes, obstructing transport processes through the membranes. Therefore, heavy metals are of particular importance from the ecotoxicological point of view.[1]

Copper, an important metal in many industries, is considered as an essential micronutrient for human health and plays an important role in carbohydrate and lipid metabolism and in the maintenance of heart and blood vessel activity. The requirement of an adult human is about 1–5 mg of copper per day, but excess amounts in the body can be toxic.[2] Acute symptoms from excessive ingested copper include salivation, epigastria pain, nausea, vomiting, diarrhoea, intravascular haemolytic anaemia, acute hepatic and renal failure, shock, and coma.

Flame atomic absorption spectrometry (FAAS) is a simple and well available technique for the determination of heavy metals in diverse samples. Due to the limited sensibility of FAAS and to the low concentration levels of heavy metal in natural samples, prior to FAAS analysis some preconcentration procedures based on liquid–liquid extraction,[3] ion exchange[4] and solid phase extraction[5] have been developed. Solid phase extraction of heavy metals is considered superior to liquid–liquid extraction due to its simplicity, rapidity, low cost, and higher recovery. Macromolecular chelators have been found to be more selective for solid phase extraction in comparison to ion exchangers. Among different kinds of support materials used to design macromolecular chelator, cellulose appears attractive due to its good porosity, high hydrophilicity, low swelling, chemical resistance, wide availability and easy biodegradability.[6]

Cellulose sorbents containing diverse functional groups or reagents, such as pyrocatechol,[6] iminodiacetate,[7] diethylenetriaminetetraacetic acid,[8] triethylenetetraminepentaacetic acid,[9] 8-hydroxyquinoline,[10] 2,3-dihydroxypyridine,[11] 8-hydroxyquinoline-5-sulphonic acid,[12] hexamethylenedithiocarbamates,[13] methyliminodiacetic acid,[14] have been reported for metal preconcentration. Lásztity *et al.*[15] examined oxime, sulphoxine and 2,2'-diamino-diethylamine cellulose based macromolecular chelators for platinum. Aoki *et al.*[16] investigated 6-deoxy-6-mercaptocellulose and its S-substituted derivatives for their sorption characteristics. Dietz *et al.*[17] functionalized acetoacetamide chelating groups onto microcrystalline cellulose and studied its affinity for Fe(III), Cu(II) and U(VI). In addition to cellulose, thiol cotton fibre (a functionalised cellulose sorbent)[18–20] were also employed for methylmercury, selenium and multielement preconcentration.

This paper presents the preparation of a phosphorylated cotton chelator (PCC) by solid phase esterification of phosphoric acid (PA) onto defatted cotton fibre using urea as the catalyst. The synthesized PCC was employed for the preconcentration of copper in water samples prior to its determination by FAAS. The preconcentration of Cu on a column packed with PCC was investigated. The optimum conditions for the preconcentration and desorption procedures were also elucidated. By applying the proposed method, the Cu contents in natural and drinking water samples were determined.

EXPERIMENTAL

Reagents and Instrumentation

All chemicals were of analytical reagent grade unless otherwise stated. Doubly distilled deionised water was used throughout this study. A copper stock solution (200 µg ml^{-1}) was prepared by dissolving 0.3802 g of $Cu(NO_3)_2 \cdot 3H_2O$ (Merck) in 500 ml of water. Working solutions were prepared by diluting the stock solution to the required volumes. The esterification agent was prepared by dissolving 1.67 g of urea in 1 l of 0.5 mol dm^{-3} PA and then the pH value of the solution was adjusted to 3.5 with NaOH.

The glassware was washed with chromic acid, soaked in 10 % HNO_3 overnight and subsequently cleaned with doubly distilled water before use.

A Perkin–Elmer Model 5100PC flame atomic absorption spectrophotometer was used for the determination of copper under the manufacturer's recommended conditions. The calibration curve (0.25–5.0 µg ml^{-1}) for copper was established with solutions prepared from the 200 µg ml^{-1} stock solution.

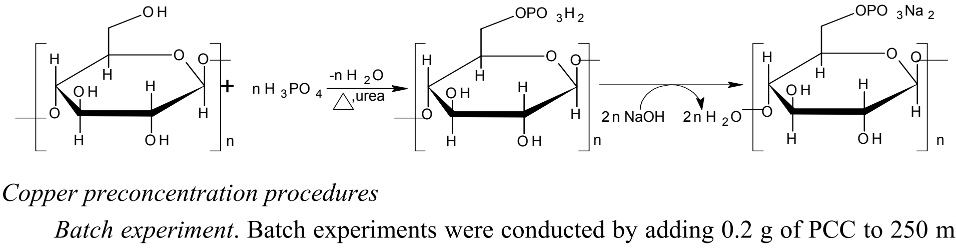
The reference measurements were made on Jobin-Yvon Panorama ICP–AES instrument using the axial viewing configuration. The operating condition was as follows: RF power 1.0 kW, nebuliser pressure 3.0 bar, plasma gas flow 16.0 l min^{-1}, auxiliary gas flow 1.7 l min^{-1}, sample uptake rate 0.8 ml min^{-1}, stabilization time 15 s, read time 1 s, emission line for Cu 324.754 nm.

Preparation of PCC

The PCC was prepared according to a method similar to one given in the literature but free of any solvent.[21]

Thus, defatted cotton fibre, purchased from a local drugstore, was mixed with the previously mentioned esterification agent in the ratio 1:12 (fibre:esterification agent, w/v) and stirred for 30 min. The esterification agent/fibre slurry was placed in a stainless steel tray and dried at 50 °C in a forced air oven. After 24 h, the esterification reaction between PA and fibre was initiated by raising the oven temperature to 120 °C for 90 min. After cooling, the PA-modified cotton fibre was extensively washed to neutral pH with doubly distilled deionised water. After filtration, the PA-modified cotton fibre was transformed into the Na form by suspension in a suitable amount of 0.10 mol dm^{-3} NaOH and stirring for 60 min. Subsequently, the residual alkali was removed by washing thoroughly with doubly distilled deionised water. The PCC was then dried at 50 °C to constant weight and stored in a desiccator before use as the extractant for preconcentration.

The preparation of PCC can be schematically expressed by the following Equation:



Copper preconcentration procedures

Batch experiment. Batch experiments were conducted by adding 0.2 g of PCC to 250 ml shaking flasks containing 100.0 ml of copper solution having different concentrations or initial pH values. The initial pH values of the solution were previous adjusted with dilute HNO_3 or NaOH using a pH meter. After sealing to prevent volume change during the experiments, the flasks were maintained at ambient temperature (20±2 °C) and agitated at 150 rpm in a rotary shaker for predetermined time intervals. The PCC was separated by filtration through a membrane filter (0.45 μm). The filtrate was analysed for the concentration of the remaining copper ions by FAAS. When the copper ion concentration in the filtrate was too low to be analysed by FAAS, the copper sorbed by the PCC was eluted into a suitable volume of 1.0 mol dm^{-3} hydrochloric acid for its determination.

Column procedure. A glass column (10 mm×200 mm) was packed with 0.1 g of PCC, then 100 ml doubly distilled deionised water was passed through the column for cleaning and preconditioning. A copper solution at the optimum pH value was loaded onto the column with a peristaltic pump at a flow rate of 2 ml min^{-1}, after which the column was washed with 5 ml of doubly distilled deionised water. The copper sorbed on the column was preconcentrated into a 5.0 ml volumetric flask by eluting with 5.0 ml of 1.0 mol dm^{-1} hydrochloric acid at a flow rate of 1 ml min^{-1}. The copper ion in the eluate was determined by FAAS.

RESULTS AND DISCUSSION

Batch experiment

Influence of initial pH. Preliminary studies indicated that the initial pH of the solution significantly affected Cu sorption. Hence, in all the experimental parameters affecting copper sorption by the PCC, the influence of the initial pH was studied first. The initial pH of copper solution was systematically examined over a range from 0.5 to 7.0, thus avoiding copper precipitation. As can be seen from Fig. 1, the percent copper sorbed was the lowest at the initial pH 0.5. The amount of Cu sorbed increased with increasing pH until a plateau was reached at about pH 4.0. These results show the strong pH dependence of Cu sorption on PCC. Thus, pH 4.5 was selected for the subsequent experiments.

At the optimal initial pH, the sorption equilibrium of Cu was attained after about 30 min.

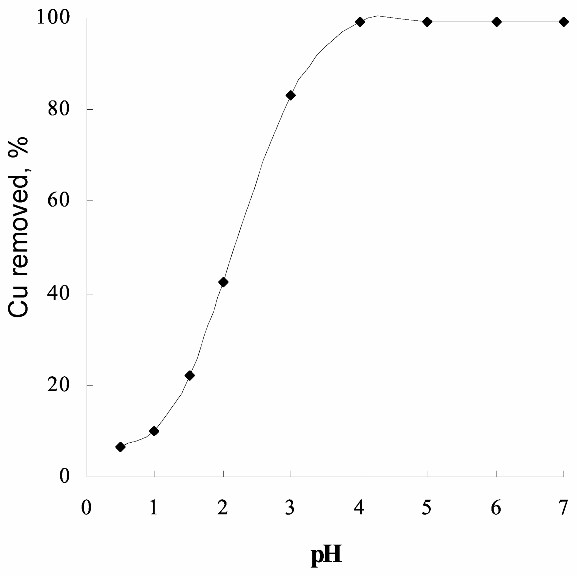


Fig. 1. Influence of the initial pH on the removal of Cu by PCC (Batch experiment: Cu concentration: 20 mg dm^{-3}; PCC dose: 2 g dm^{-3}; contact time: 1 h).

Effect of initial copper concentration. The influence of copper concentration on the sorption percent of Cu and sorption capacity of PCC for copper was investigated. As shown in Fig. 2, when the copper concentration was increased from 5 to 70 mg dm^{-3}, the percent Cu sorbed on the PCC decreased from 99.4 to 44.4 %.

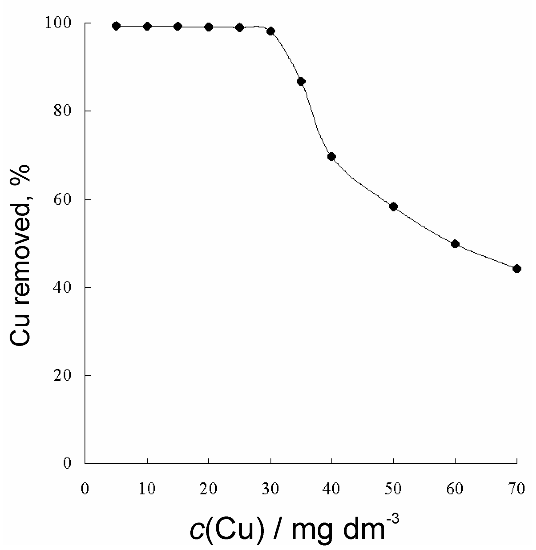


Fig. 2. Effect of the initial copper concentration on the removal of Cu by PCC (Batch experiment: PCC dose: 2 g dm^{-3}; contact time: 1 h; pH 4.5).

Using the data in Fig. 2, the Langmuir equation was employed to study the sorption isotherm of Cu.

The Langmuir equation is based on the assumption that maximum sorption corresponds to a saturated monolayer of sorbate molecule on the sorbent surface, that the energy of sorption is constant and that there is no transmigration of sorbate in the plane of the surface.

The linear Langmuir equation is as follows:

$$c_e/q_e = 1/(aQ_m) + c_e/Q_m$$

where c_e (mg dm^{-3}) is the concentration of the Cu solution at equilibrium, q_e (mg/g) is the amount of Cu sorbed at equilibrium, Q_m is the maximum sorption capacity and represents the practical limiting sorption capacity when the sorbent surface is fully covered with a monolayer of sorbate molecules and a is the Langmuir constant.

The Langmuir sorption isotherm of Cu sorbed on PCC is shown in Fig. 3. The experimental result indicate that the sorption isotherm of Cu trapped on PCC fitted the Langmuir model ($R^2 = 0.9988$). The maximum sorption capacity (Q_m) of PCC for Cu, obtained from the slope ($1/Q_m$) of the linear plot of c_e/q_e *versus* c_e, was 15.27 mg/g. The capacity of the PCC for other divalent metals is 12.62 mg/g for cobalt, 13.89 mg/g for zinc and 12.91 mg/g for nickel.

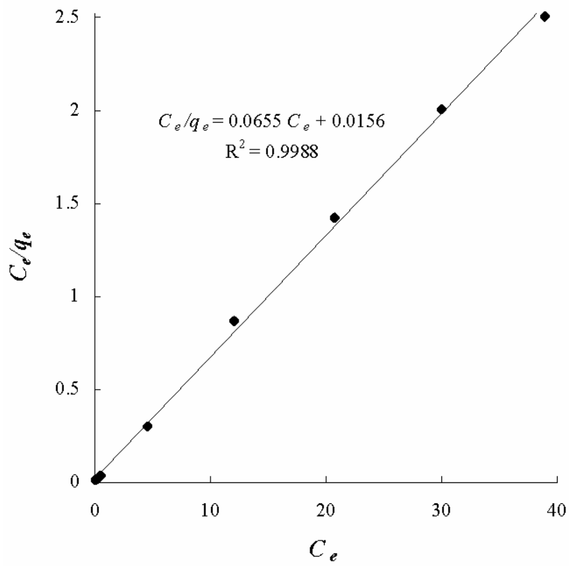


Fig. 3. Langmuir sorption isotherm of Cu by PCC.

Column procedure

Column operation conditions. The column operation conditions were examined with different volumes of a solution containing 20.0 μg copper at the optimum pH value. The volume of the copper solution was varied in the range of 50––500 ml under the optimum conditions, keeping the other variable constant. The experimental results indicated that the sorption was almost constant up to 400 ml. However, for convenience, all experiments were conducted with 100 ml of aqueous phase. The flow rate of the copper solution was varied from 0.5–5 ml min^{-1}. Figure 4 shows that the flow rate in the range 0.5–4 ml min^{-1} did not affect the copper sorption. A flow rate of 2 ml min^{-1} was used in all further experiments. Preliminary observations indicated that copper was eluted quantitatively with 5.0 ml of 1.0 mol dm^{-3} hydrochloric acid. It was found that a flow rate lower than 1.5 ml min^{-1} did not affect the elution of copper (Fig. 4). Therefore, 5.0 ml of 1.0 mol dm^{-3} hydrochloric acid and eluant flow rate of 1.0 ml min^{-1} were used in the present work. Thus, the quotient of the largest sample volume and the eluant volume was 80. After elution, the column was washed to neutral pH with doubly distilled deionised water and then 5 ml of 0.10 mol dm^{-3} sodium hydroxide was passed through before finally thoroughly washing with sufficient doubly distilled deionised water for reuse of the PCC.

Interference of foreign ions. The interference of common foreign metal ions on the preconcentration of copper were investigated by adding individual foreign metal ions to 100 ml of a 200 μg dm^{-3} copper solution at the optimum pH value and determining the recoveries of copper applying the proposed procedure. The tolerance limits of the foreign metal ions, defined as the largest amount making the recoveries of copper less than 95 %, were found to be 2.000 g dm^{-3} for Na$^+$and K$^+$, 1.000 g dm^{-3} for Ca^{2+}, 0.500 g dm^{-3} for Mg^{2+}, 100 mg dm^{-3} for Co^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}. As the contents of these metal ions in common samples are within the tolerated concentration range, they will not interfere with the preconcentration of copper.

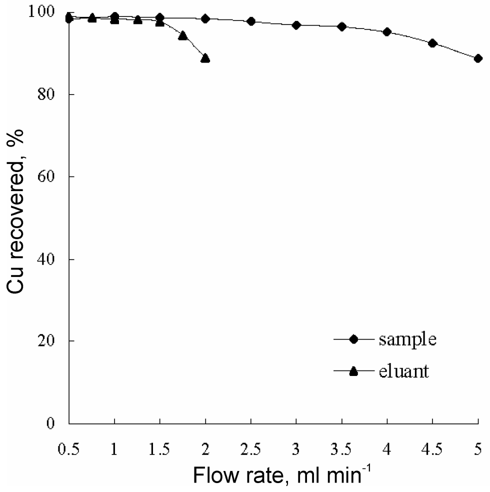


Fig. 4. Influence of the sample and eluant flow rate on the removal of Cu by PCC (Column experiment: Cu – 20 µg; sample volume – 100 ml; sample/eluant flow rate – 2/1 ml min^{-1};pH 4.5).

Regeneration of column. The stability and potential regeneration of the column were investigated. Twenty sorption–elution cycles were performed by making four runs on the same day and the next four runs one day later. The column was stored in doubly distilled deionised water. As shown in Fig. 5, the column was relatively stable up to at least 20 preconcentration–elution cycles without an obvious decrease in the recovery of copper.

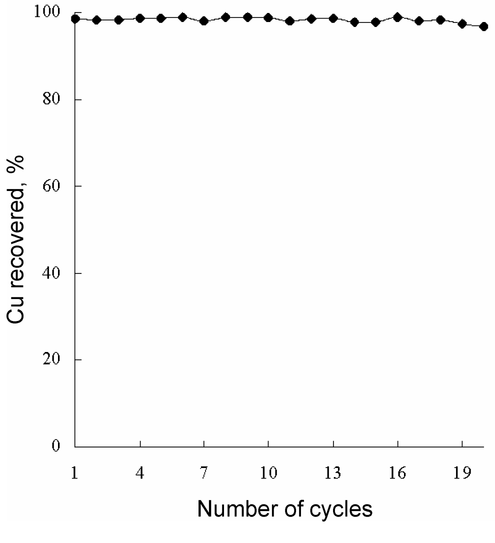


Fig. 5. Effect of recycle time on the removal of Cu by PCC (Column experiment: Cu – 20 µg; sample volume – 100 ml; sample/eluant flow rate – 2/1 ml min^{-1}; pH 4.5).

Copper determination in real water samples

In order to check the validity of the proposed method, the method was applied to determine trace amounts of copper in natural and drinking water samples. The natural water samples were collected from the Mirror Lake, the Yangtze River in or around Wuhu city, China. The drinking water sample was purchased from a local supermarket. The natural water samples were filtered through a membrane filter (0.45 μm), and then 100.0 ml of the filtrates or drinking water were subjected to the recommended column procedure for the preconcentration and determination of copper ions directly and after standard addition. The analysis was repeated five times and the results obtained were compared with the values determined by ICP–AES in Table I. It could be seen that the recovery obtained from the real water samples (97.9–102.1 %) was comparable to that gained by ICP–AES (97.8–100.5 %, data not shown), and the performance of the method was very good in natural and drinking water samples. Finally, the relative standard deviation of the copper determination in the examined real water samples ranged between 2.6 and 4.1 %.

TABLE I. The results of copper determination in natural and drinking water samples

Sample	Copper				
	Added μg dm^{-3}	Found μg dm^{-3}	Recovery %	*RSD* %	ICP–AES μg dm^{-3}
Lake water	0	23.5	–	3.6	24.4
	100	125.6	102.1	2.7	124.9
River water	0	28.6	–	3.8	28.2
	100	126.9	98.3	2.6	126.0
Nongfu spring® natural drinking water	0	8.4	–	4.1	8.2
	100	106.3	97.9	3.4	107.8

CONCLUSIONS

A simple, accurate and sensitive method for the preconcentration and determination of copper by FAAS in large volumes of water samples using PCC as the extractant has been developed. The preconcentration technique used in this work is very inexpensive since only 0.10 g of sorbent is required in column operation and which could be repeatedly used at least 20 times. An 80-fold preconcentration factor can be achieved under the optimum column conditions. The duration of the preconcentration step, which includes preconcentration of the sample and regeneration of the column, is about 70 min for 100 ml of sample solution. Moreover, as copper can be sorbed quantitatively over a wide pH range, no buffer was required to control precisely the pH values. The detection limit achieved was satisfactory for the examined samples. The proposed method was employed for preconcentration and determination of copper in natural and drinking water samples by FAAS with satisfactory results. In conclusion, the proposed method is excellent in regards to simplicity, sensitivity, selectivity, reliability, accuracy and column stability.

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ИЗВОД

ОДРЕЂИВАЊЕ ТРАГОВА БАКРА У УЗОРЦИМА ВОДЕ ПЛАМЕНОМ АТОМСКОМ АБСОРПЦИОНОМ СПЕКТРОСКОПИЈОМ ПОСЛЕ ПРЕКОНЦЕНТРИСАЊА НА ПАМУЧНОМ ХЕЛАТОРУ ТРЕТИРАНОМ ФОСФОРНОМ КИСЕЛИНОМ

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У раду је приказано добијање фосфорисаног памучног хелатора (PCC) естерификацијом фосфорне киселине (PA) у чврстој фази, на одмашћеним памучним влакнима помоћу урее као катализатора. Добијени PCC употребљен је за преконцентрисање бакра из узорака воде ради одређивања пламеном атомском абсорпционом спектроскопијом (FAAS). Преконцентрисање бакра испитивано је техникама груписања и колоне у области pH 4,0–7,0. Време сорпције за сваки узорак у методи груписања износи мање од 30 min. Добијено је да капацитет PCC за сорпцију бакра износи 15,3 mg/g при оптималној pH вредности. Квантитативно испирање постигнуто је раствором 1,0 mol dm^{-3} хлороводоничне киселине. Проток раствора бакра потребан за квантитативну сорпцију у колони са PCC пуњењем изоси 0,5–4,0 ml min^{-1}, док је оптимални проток раствора хлороводоничне киселине потребног за десорпцију мањи од 1,5 ml min^{-1}. Фактор преконцентрисања од око 80 може се постићи под оптималним условима у колони. Иситивани су границе толеранције за преконцентрисање металних јона сличних бакру и број поновних коришћења колоне. Предложени метод успешно је примењен за преконцетрисање бакра у траговима и његово одређивање у узорцима природне и пијаће воде методом FAAS.

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