On-line solid phase extraction coupled to flame atomic absorption spectrometry for the determination of trace copper and zinc in environmental and biological samples

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In this work, bamboo charcoal (BC) was used as a sorbent for on-line solid phase extraction (SPE) coupling with flame atomic absorption spectrometry (AAS) for trace copper and zinc determination in environmental and biological samples. Under the optimum pH of 5.5 (for Zn) and 7.0 (for Cu), trace copper and zinc were effectively adsorbed on the microcolumn and the retained cations were efficiently eluted with HCl or HNO_3 with an appropriate concentration and flow rate for on-line AAS determination. With a sample loading time of 60 s at a sample flow rate of $7.6 \, mL \, min^{-1}$, the enhancement factors of 39 (for Cu) and 30 (for Zn) and detection limits (3σ) of $0.60 \, \mu g \, L^{-1}$ (for Cu) and $0.36 \, \mu g \, L^{-1}$ (for Zn), respectively, were achieved. The sample throughput was $45 \, h^{-1}$. At the level of $20 \, \mu g \, L^{-1}$ of Cu(II) and Zn(II), the precision (RSD, $n = 11$) were found to be 0.26% and 1.6%, respectively. The proposed method has been successfully applied to the determination of copper and zinc in environmental and biological samples.

Keywords: bamboo charcoal; flow injection; on-line solid phase extraction; copper; zinc; flame atomic absorption spectrometry

1. Introduction

The effects of heavy metals such as lead, mercury, copper, zinc and cadmium on human health have been studied extensively. Trace elements, copper and zinc are essential to maintain the metabolism of the human body, however, at higher concentrations they can lead to poisoning. Excessive ingestion of them can cause accumulative poisoning, cancer, nervous system damage, etc. [1,2] Therefore, accurate determination of trace copper and zinc in environmental and biological samples is very important in aspects of ecology, hygiene and monitoring of environmental pollution.

Flame atomic absorption spectrometry (AAS) is most commonly employed for trace elements analysis; due to its high sensitivity, low operational and instrumental costs, easy operation and high sample throughput. However, the concentrations of copper and zinc in environmental and biological samples are usually below the detection limit of flame AAS, enrichment and separation procedures, such as ion exchange, adsorption, solvent extraction and coprecipitation, are often required before the determination in order to

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enhance the sensitivity. Conventional off-line procedures for separation and preconcentration, although effective, are usually time consuming and tedious, require large amounts of sample and reagents and are vulnerable to contamination and analyte loss [3]. On-line solid phase extraction (SPE) offers a number of important benefits. It reduces solvent use, solvent exposure, disposal costs and extraction time for sample preparation [4,5]. Up to now, multifarious materials such as C_{18}, various resins like Muromac A-1, CPG/quinolin-8-ol, Amberlite XAD-2, Chelex-100, polyurethane foam, PTFE beads, activated carbon and multi-walled carbon nanotubes [6–16] have been developed as sorbents in the microcolumns for the on-line SPE of trace elements before AAS detection. Activated carbon, a low cost material, has proved to be a good collector for numerous metal ions and metal complexes in water. Some authors reported the adsorption of metallic complexes onto activated carbon after complexation with chelating agents [17–22]. The disadvantage of those procedures is that they require a series of complexation steps. For this reason, the use of activated carbon loaded chelating agents for the extraction of ions was proposed recently [23–26]. However, in the mentioned method, the solid phases were not reversible since the chelating agent was apt to be eluted when the solid phase is washed for the determination of metal ions. Though Ensafi et al. have reported the effectiveness of SPE on Pb (II) based on activated carbon loaded with pyrogallol redn [27] and xylenol orange [28], the modified activated carbon phases can only be reused a few times without decreasing the enrichment factor of the solid phases. As its 'sister material', bamboo charcoal (BC), being extremely porous with a high-specific surface area, has been proved to be an efficient sorbent for the removal of various pollutants such as metal ions [29], ammonia [30], nitrate-nitrogen [31], phenols and dyes [32] from water. However, to the best of our knowledge, no paper has reported the use of BC on the on-line SPE of metal ions for the flame AAS determination. In this paper, BC was solitarily used as the sorbent for on-line SPE coupling with flame AAS for trace Cu and Zn determination. Simplification and automation of the procedure could possibly reduce the risk of operational errors and enhance the sample throughput. Under experimental conditions the column can be reused for at least 500 preconcentrations.

2. Experimental

2.1 *Apparatus*

TAS 990 atomic absorption spectrometer (Beijing Purkinje General Instrument Co., Ltd. Beijing, China) equipped with hollow cathode copper and zinc lamps (Beijing ShuGuang Ming Electronic Lighting Instrument Co., Ltd. Beijing, China) was used for the elements determination in the following conditions: wavelength, 325 nm for copper and 214.1 nm for zinc, both slit widths were 0.4 nm. The flame conditions ($2.2 \, \text{L min}^{-1}$ acetylene and $9.4 \, \text{L min}^{-1}$ air) were employed according to standard recommendations. The peak height absorbance was used for quantitative analysis.

A model FIA-3100 flow injection system (Vital Instruments Co. Ltd, Beijing, China), consists of two peristaltic pumps and a standard rotary injection valve (eight ports on the rotor and eight ports on the stator), was employed for the FI online SPE. The microcolumn used to capture the analyte in aqueous solution was made of a PTFE tube with an effective length of 1 cm and internal diameter of 2 mm. Tygon pump tubings were used to deliver samples and reagents. The rotation speed of the two peristaltic pumps, their stop and go intervals, and the actuation of the injection valve were

Table 1. Operational sequence of the FI on-line SSP system coupled with flame AAS for trace Cu and Zn determination.

Step	Function	Time (s)	Pumped medium	Flow rate (mL min^{-1})		Valve position
				Pump 1	*Pump 2*	
1 (Figure 1a)	Loading		Sample	7.6	–	Fill
		60	2.0 mol L^{-1} HCl for Cu	–	4.4	
			1.0 mol L^{-1} HNO$_3$ for Zn		5.4	
2 (Figure 1b)	Elution	20	2.0 mol L^{-1} HCl for Cu	off	4.4	Injection
			1.0 mol L^{-1} HNO$_3$ for Zn		5.4	

all programmed (Table 1). PTFE tubings (0.5 mm i.d.) were used for all connections. These connections were kept as short as possible to minimise the dead volumes.

A Model Qwave-2000 microwave digestion system (Questron Co., Missisauga Canada) was used to digest the samples. All instrumental parameters for the sample digestion were chosen according to the recommendations of EPA.

For pH measurements a Delta320 Mettler (Mettler Toledo, USA) pH meter was used.

2.2 *Reagents and materials*

All reagents (Sinopharm Chemical Reagent Co., Ltd) used were of the highest available purity and at least of analytical grade. Doubly deionised water (DDW, 18.2 MΩ cm^{-1}) obtained from a WaterPro water system (Labconco Corporation, Kansas City, MO, USA) was used throughout the experiments.

The BC was obtained commercially from Suichang Maitanweng Ecologic Development Co., Ltd. Zhejiang, China. The BC was sieved with 80 and 100 meshes and orderly refluxed with thick hydrochloric acid for 1 h, filtrated and washed with DDW several times and finally blast dried at 353K for 12 h before use.

The Cu(II) and Zn(II) stock solutions (1000 mg L^{-1}) were prepared by dissolving 1.0 g of copper and zinc metal powder (99.999% purity) in nitric acid (1:1) and then diluting to 1000 cm^3 with DDW. The working solutions were prepared by series dilution of the stock solution immediately prior to their use.

The certified reference materials (CRM, from NRCSM, Beijing, China): GBW07605 (bush leaves and branches) were analysed to check the accuracy of the developed method.

2.3 *Sample preparation*

A certain amount of the sample (0.0250 g for bush leaves and branches) was mixed with 4 mL of concentrated HNO$_3$ and 1 mL HClO$_4$ and digested with Qwave-2000 microwave digestion system, then, gently heated on a hot-plate until white fumes appeared. After cooling, the clear digest was transferred into a 50 mL calibrated flask and diluted to volume with DDW after adjusting its pH to the optimum range.

2.4 *Microcolumn preparation*

25 mg of BC was packed into the microcolumn. The microcolumn was end-capped with glass wool (to prevent the BC from being swept out by a liquid flow) and connected to the

(a) Sample Loading

2.0 mol L^{-1} HCl/

1.0 mol L^{-1} HNO$_3$

P2: on

Sample

P1: on

W

W

DT

AAS

(b) Elution

2.0 mol L^{-1} HCl/

1.0 mol L^{-1} HNO$_3$
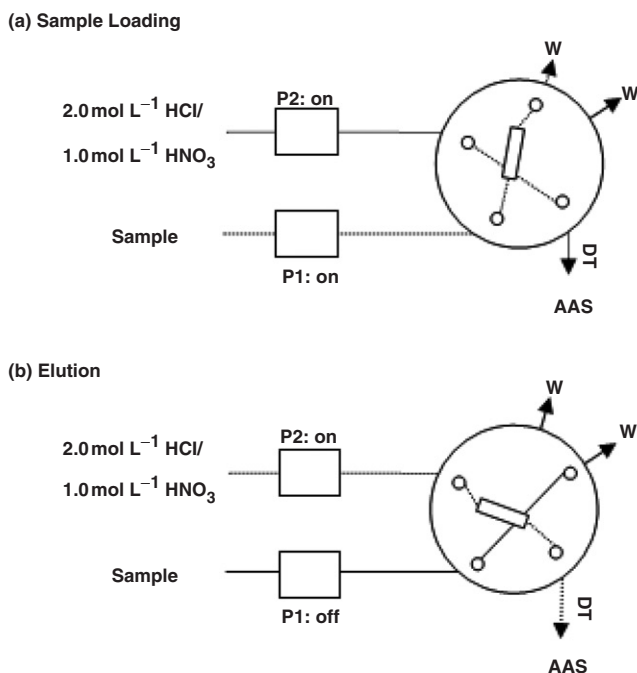
P2: on

Sample

P1: off

W

W

DT

AAS

Figure 1. Manifold for the FI on-line SSP coupled with flame AAS system for Cu and Zn determination.
Notes: P1 and P2: peristaltic pumps; DT: delivery tubing; W: waste. Valve position: (a) Sample loading; (b) Elution.

injector valve. The packed column was sequentially washed with DDW, 2 mol L^{-1} HCl and DDW until no copper or zinc signal was detected with flame AAS.

2.5 *Procedures for FI on-line SPE coupled with flame AAS for determination of trace copper and zinc*

The FI manifold and its operation sequence for the on-line SPE are shown in Figure 1 and Table 1, respectively. In step 1 (Figure 1(a)), the injection valve was in the fill position and pump 1 was activated so that the sample solution was loaded onto the microcolumn; the effluent from the column was flowing to waste. At the same time, pump 2 started to introduce diluted HCl or HNO$_3$ solution to flame AAS for baseline. In step 2 (Figure 1(b)), pump 2 started to work while pump 1 was stopped and the injection valve turned to the inject position to introduce diluted HCl or HNO$_3$ solution for eluting the analytes retained on the column. A complete cycle of SPE and elution required 80 s with a sample loading time of 60 s.

3. Results and discussion

3.1 *Sample loading*

In the SPE studies, the influence of pH on the aqueous solution is one of the main factors for recoveries of heavy metal ions. The effect of sample acidity on the preconcentration
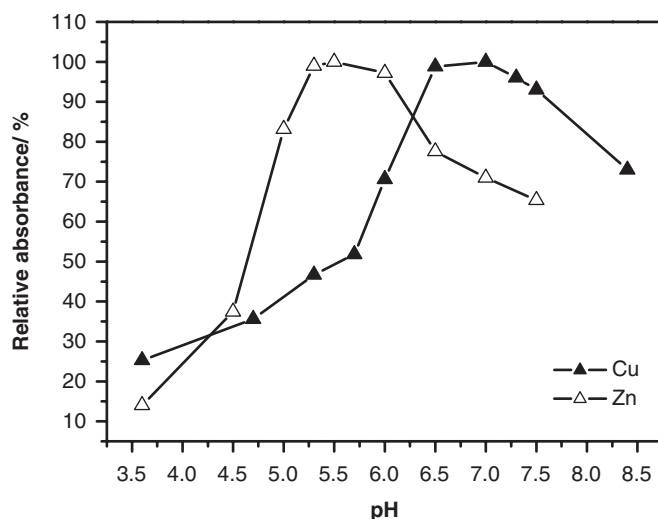
Figure 2. Effect of sample acidity on the absorbance of $20\,\mu g\,L^{-1}$ Cu and $20\,\mu g\,L^{-1}$ Zn.
Notes: All other conditions as in Figure 1 and Table 1.

efficiency was investigated in a series of pH values from 3.5 to 8.5 (adjust with $0.1\,mol\,L^{-1}$ HAc–NaAc or NH_4Cl–NH_3H_2O buffer), keeping the other parameters constant. As shown in Figure 2 that the retention for Cu(II) and Zn(II) varies significantly with change in the pH value. The relative absorbance for Zn(II) reached maximum at the pH value about 5.3, whereas the relative absorbance of Cu(II) was less than 50% under the same pH value. With the increase of pH, the absorption of Cu(II) increased, and high recovery efficiency was achieved at a pH range of 7.0–7.5. To achieve high efficiency and good selectivity for the adsorbent, pH of 5.5 and 7.0 were chosen for the separation and preconcentration of Zn(II) and Cu(II), respectively, in further experiments.

The influences of sample loading rate on the preconcentration of $20\,\mu g\,L^{-1}$ Cu(II) and $20\,\mu g\,L^{-1}$ Zn(II) were studied at the sample loading time 60 s. The results are shown in Figure 3. It was found that the absorbance of the analytes increased linearly as sample loading rate increased up to at least $7.6\,mL\,min^{-1}$.

Investigations were made on the effect of sample loading time on the preconcentration of $20\,\mu g\,L^{-1}$ Cu(II) and $20\,\mu g\,L^{-1}$ Zn(II) at a sample loading rate of $7.6\,mL\,min^{-1}$. The absorbance of the analytes increased almost linearly up to 120 s. At a preconcentration time of 120 s, the enhancement factors for Cu(II) and Zn(II) were 84 and 72, respectively, which indicated that the microcolumn has great sorption capacity.

3.2 Analytes elution

The choice of eluent, eluent concentration and flow rate of elution are important for the analytical performance of an FI on-line preconcentration system. The influence of a variety of eluents was investigated with $2.0\,mol\,L^{-1}$ HCl, HNO_3 and H_2SO_4 solutions at a flow rate of $4.0\,mL\,min^{-1}$ for 20 s, respectively. The experimental results showed that the optimal elutions were HCl for Cu(II) and HNO_3 for Zn(II), respectively. Accordingly, HCl and HNO_3 were selected, respectively, for the examination of the
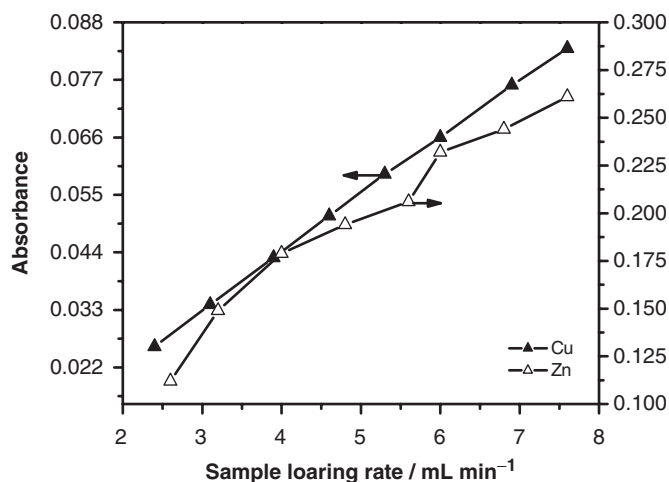
Figure 3. Effect of sample loading rate on the absorbance of $20\,\mu g\,L^{-1}$ Cu and $20\,\mu g\,L^{-1}$ Zn.
Notes: All other conditions as in Figure 1 and Table 1.

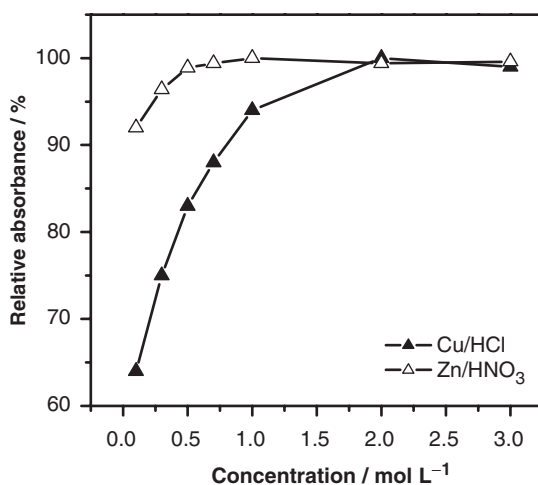Figure 4. Effect of eluents concentrations on the relative absorbance of $20\,\mu g\,L^{-1}$ Cu and $20\,\mu g\,L^{-1}$ Zn.
Notes: Eluents flow rate were $4.0\,mL\,min^{-1}$. All other conditions as in Figure 1 and Table 1.

effect of eluent concentration and flow rate. As shown in Figure 4, for the determination of copper, the relative absorbance of copper increased significantly and no stable absorbance was obtained as the concentration of HCl incremented from 0.1 to $2.0\,mol\,L^{-1}$. However, a plateau in absorbance was reached with a further increase in HCl concentration (above $2.0\,mol\,L^{-1}$). Similarly to the determination of copper, a plateau in relative absorbance also appeared in the determination of zinc when the HNO_3 concentration was above $1.0\,mol\,L^{-1}$. Therefore, $2.0\,mol\,L^{-1}$ of HCl and $1.0\,mol\,L^{-1}$ HNO_3 were selected as the eluents for the elution of the adsorbed Cu(II) and Zn(II), respectively. Using the selected elutions, the influence of flow rate was checked in the range of 2.4 to $6.4\,mL\,min^{-1}$. The results are shown in Figure 5. It was
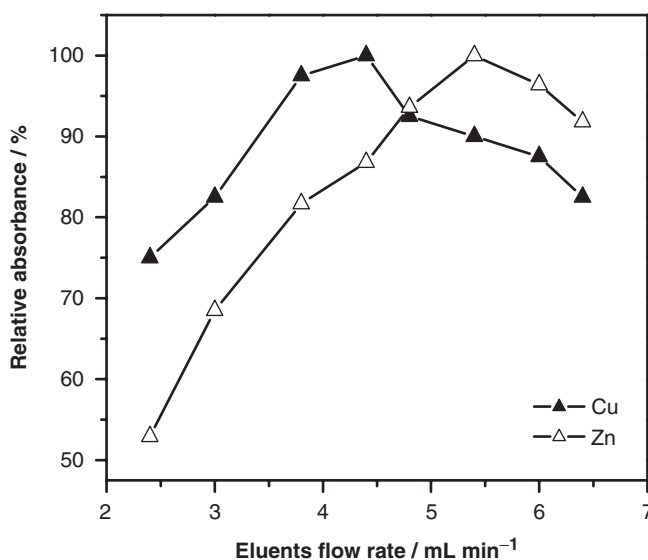
Figure 5. Effect of eluents flow rate on the relative absorbance of $20\,\mu g\,L^{-1}$ Cu and $20\,\mu g\,L^{-1}$ Zn. Notes: All other conditions as in Figure 1 and Table 1.

Table 2. Effect of coexisting ions on the absorbance of $20\,g\,L^{-1}$ Cu and $20\,g\,L^{-1}$ Zn under the conditions listed in Figure 1 and Table 1. (Results are the average of triplicate measurements).

Coexistingion	Cu		Zn	
	Concentration (mg L^{-1})	Recovery (%)	Concentration (mg L^{-1})	Recovery (%)
K(I)	5.0	99 ± 1	1.0	101 ± 1
	10	97 ± 1	2.0	96 ± 1
	5.0	101 ± 1	0.5	100 ± 1
Na(I)	10	97 ± 1	2.0	97 ± 1
	20	87 ± 3	3.0	87 ± 4
	5.0	101 ± 1	0.03	102 ± 2
Mg(II)	10	98 ± 1	0.06	96 ± 1
	15	94 ± 2	0.1	93 ± 1
	5.0	102 ± 2	0.08	98 ± 1
Ca(II)	10	95 ± 1	0.1	96 ± 2
	0.1	101 ± 2	0.05	101 ± 2
Cd(II)	0.3	100 ± 2	0.1	97 ± 2
	0.6	95 ± 2		
	2	99 ± 2		
Zn(II)	8	95 ± 2		
Cu(II)			0.5	99 ± 1
			1.0	96 ± 1
Fe(III)	0.3	98 ± 1	0.06	99 ± 1
	0.6	95 ± 2	0.1	96 ± 1
Mn(II)	2	102 ± 1	0.5	98 ± 1
	5	95 ± 1	1.0	95 ± 1
Pb(II)	2	101 ± 1	0.5	99 ± 2
	4	98 ± 1	1.0	96 ± 2
	8	96 ± 2		

Table 3. Analytical performance of FI on-line SPE system coupled with flame AAS for determination of Cu and Zn under the conditions in Figure 1 and Table 1.

Analyte	Cu	Zn
Preconcentration time (s)	60	60
Enhancement factor	39	30
Sampling frequency (h^{-1})	45	45
Sample consumption (mL)	7.6	7.6
Eluent consumption (mL)	4.4	5.4
Precision (RSD for $20 \, \mu g \, L^{-1}$, $n = 11$)/%	0.26	1.6
Detection limit (3σ) ($\mu g \, L^{-1}$)	0.60	0.36
Range of calibration graph ($\mu g \, L^{-1}$)	1.0–40	1.0–30
Calibration function ($n = 6$)	$A = -0.0017 + 0.0319C$	$A = -0.00097 + 0.00995C$
(A, peak height absorbance, C in $\mu g \, L^{-1}$)		
Correlation coefficient	0.9997	0.9987

Table 4. Analytical results for the determination of trace Cu and Zn in the certified reference material and real samples under the conditions in Figure 1 and Table 1 (mean $\pm \sigma$, $n = 3$).

Sample	Concentration of Cu				Concentration of Zn			
	Certified	Added	Found	Recovery (%)	Certified	Added	Found	Recovery (%)
GBW 07602 ($\mu g \, g^{-1}$)	5.18 ± 0.01	0	5.17 ± 0.01		20.6 ± 1.2	0	20.4 ± 0.8	
Tap water ($\mu g \, L^{-1}$)	–	0	2.27 ± 0.01		–	0	2.03 ± 0.03	
		2	4.30 ± 0.01	102 ± 1	–	2	4.01 ± 0.04	99 ± 2
Mineral water ($\mu g \, L^{-1}$)	–	0	5.04 ± 0.01		–	0	4.06 ± 0.03	
		2	7.02 ± 0.01	99 ± 1	–	2	6.02 ± 0.04	98 ± 2

found that the optimal eluent flow rates were $4.4 \, mL \, min^{-1}$ for Cu(II) and $5.4 \, mL \, min^{-1}$ for Zn(II), respectively. (It was noted that the use of HCl and HNO_3 as eluents may cause some problems such as corrosion of the injection valve or the nebulizer, so prompt and thorough washing of the valve and nebulizer with DDW after experiments is strongly recommended.)

3.3 *Test for interferences*

The effect of potential coexisting ion interferences encountered in copper and zinc determination by the proposed method was examined under the optimised conditions given in Table 1. The results are shown in Table 2. Up to $10 \, mg \, L^{-1}$ of K(I), Na(I), Mg(II) and Ca(II), $8 \, mg \, L^{-1}$ of Mn(II), Zn(II) and Pb(II), $0.6 \, mg \, L^{-1}$ of Fe(III) and Cd(II) had no significant interference with the determination of $20 \, \mu g \, L^{-1}$ Cu(II). The tolerable concentrations of K(I), Na(I), Ca(II), Mg(II), Cd(II), Cu(II), Fe(III), Mn(II) and Pb(II) for the determination of $20 \, \mu g \, L^{-1}$ Zn(II) were found to be 2.0, 2.0, 0.08, 0.06, 0.1, 1.0, 0.1, 1.0 and $1.0 \, mg \, L^{-1}$, respectively.

Table 5. Comparison of the essential features of FI-flame AAS methods developed for the determination of Cu and Zn.

Analyte	Sorbent	Sample	EF (min)	DL ($\mu g\,L^{-1}$)	f (h^{-1})
Cu	Multi-walled carbon nanotubes [16]	Environ & bio samples	25	0.11	45
Cu	Active carbon modified with ligands [26]	Natural waters, soil and blood	–	0.65, 0.42, 0.52	–
Cu, Zn	Poly(aminophosphonic acid) [33]	Natural water	19	1.6, 0.4	48
Cu	Amberlite XAD-2/3, 4-dihydroxybenzoic acid [34]	Rice flour and starch	27	0.27	33
Cu, Zn	XAD-4/2,6-dihydroxyphenyldiazoaminoazobenzener [35]	Natural water	28, 31	0.3, 0.2	30
Cu	Silica gel/3-(1-imidazolyl)propyl groups [36]	Water	20–26 36–42	0.4, 0.2	27
Zn	Polyurethane foam/2-[20-(6-methylbenzo-thiazolylazo)]-4-bromophenol [37]	Natural water	48	0.37	23
Cu	Chitosan biopolymer/8-hydroxyquinoline [38]	Natural water	25	0.4	26
Cu	RP-18-1-nitroso-2-naphthol [39]	Alloy steel	16	2.0	90
Cu	Activated carbon/Ammonium pyrrolidine-dithiocarbamate [17]	Water	35	1.5	40
Cu, Zn	BC[This work]	Water	30, 39	0.6, 0.36	45

Notes: EF Enrichment factor, DL detection limit, f sampling frequency.

3.4 *Performance of the FI on-line sorption separation preconcentration flame AAS analytic system*

The analytical characteristic performance data for the FI on-line SPE coupled with flame AAS system are presented in Table 3. With a sample loading time of 60 s at a sample loading flow rate of $7.6\,mL\,min^{-1}$, the enhancement factors were 30 for zinc and 39 for copper, respectively at a sample throughput of $45\,h^{-1}$, compared with the conventional flame AAS method. The detection limits (3σ) were $0.36\,\mu g\,L^{-1}$ for zinc and $0.60\,\mu g\,L^{-1}$ for copper, respectively. The precision (RSD, $n = 11$) was found to be 0.26% and 1.6% at the level of $20\,\mu g\,L^{-1}$ of Cu(II) and Zn(II), respectively.

To evaluate the accuracy and the application performance of the developed method, the CRM, GBW07605 (bush leaves and branches) and two water samples were analysed. As is shown in Table 4, the determined concentrations of copper and zinc in the CRM by the present method using simple aqueous standards for calibration showed good agreement with the certified value. The recoveries of $2\,\mu g\,L^{-1}$ of Cu(II) and $2\,\mu g\,L^{-1}$ of Zn(II) spiking for water samples were both above 98%.

4. Comparison with alternative sorbents

Table 5 compares the sorbents reported in the literature for the adsorption of Cu(II) and Zn(II). From the table, the BC microcolumn described in this work showed fast sorption/desorption kinetics, reusability and had low analytical cost. The experimental results demonstrate that BC microcolumn is capable of FI on-line SPE system coupled with flame AAS for interference-free determination of trace copper and zinc in the environmental and biological samples.

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