Preconcentration of Cu(II), Fe(III) and Pb(II) with 2-((2-aminoethylamino)methyl)phenol-functionalized activated carbon followed by ICP-OES determination

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ABSTRACT

A procedure for separation and preconcentration trace amount of Cu(II), Fe(III) and Pb(II) by 2-((2-aminoethylamino)methyl)phenol-functionalized activated carbon (AC-AMP) packed column has been proposed. Under the optimized conditions (pH 4, flow rate 2.0 mL min^{-1}), Cu(II), Fe(III) and Pb(II) were retained on the column, then quantitatively eluted by 2 mL 1 mol L^{-1} nitric acid solution and determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The tolerance limits of electrolytes were very high. The adsorption capacity of AC-AMP was found to be 12.1, 67.1, and 16.2 mg g^{-1} for Cu(II), Fe(III), and Pb(II), respectively. According to the definition of International Union of Pure and Applied Chemistry, the detection limits (3σ) of this method for Cu(II), Fe(III) and Pb(II) were 0.27, 0.41 and 0.16 µg L^{-1}, respectively. The relative standard deviation under optimum conditions is less than 3.0% ($n = 11$). The proposed method has been validated by analyzing a certified reference material and successfully applied to the preconcentration and determination of Cu(II), Fe(III), and Pb(II) in actual samples with satisfactory results.

1. Introduction

Heavy metal pollution has become a more serious environmental problem in the last several decades as a result of its toxicity and insusceptibility to the environment, and therefore rapid and sensitive methods must be accessible for determination of these metals in actual samples [1,2]. Inductively coupled plasma-optical emission spectrometry (ICP-OES) is widely recognized as a suitable technique for the determination of metals. However, the direct determination of metal ions at trace levels is limited due to their low concentrations and matrix interferences. This limitation can be overcome by the use of a separation or preconcentration step before the detection procedure.

Various separation–preconcentration techniques such as liquid–liquid extraction [3], electro-deposition, coprecipitation [4], cloud point extraction [5], membrane filtration [6], dispersive liquid–liquid microextraction (DLLME) [7,8] and solid-phase extraction (SPE) [9] have been successfully employed to determine trace levels of metals. SPE is preferred by many researchers on account of good enrichment factors, rapid phase separation, time and cost saving [10,11]. The basic principle of SPE is the concentration and purification of analytes from solution by sorption on a solid sorbent [9]. Among many types of sorbent employed in SPE, activated carbon has received great interest due to its advantages of large specific surface area, high thermal resistance, porous structure and low cost [12,13].

Activated carbon is a hydrophobic adsorbent which adsorbs non-polar or slightly polar substances in aqueous solutions, metal ions to be preconcentrated need to be transformed to corresponding metal chelates [14]. Based on this, activated carbons are usually modified via physically adsorbing of various organic reagents which introduce additional heteroatoms so that sorbents with a high selectivity towards certain metal ions be obtained [12,15]. Pyrocatechol violet [16], N,N′-etylenebis-(ethane sulfonamide) [17], 8-hydroxyquinoline [18], bis(2-hydroxy acetophenone) ethylendiimine [19], diarylazobisphenol [20], and 1,10-phenanthroline [21] are typical example. Generally speaking, chemical bonding is more stable than physical loading.

In the presented work, a new activated carbon chemically modified with 2-((2-aminoethylamino)methyl)phenol was synthesized. The prepared sorbent of AC-AMP has a high selectivity for the solid-phase extraction of Cu(II), Fe(III) and Pb(II). The influences of the some analytical parameters on the quantitative recoveries of the analytes were investigated in detail. This proposed method was applied to the preconcentration and determination of trace amount of Cu, Fe and Pb from actual samples with satisfactory results.

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2. Experimental

2.1. Apparatus

An IRIS Advantage ER/S inductively coupled plasma emission spectrometer (TJA, USA) (RF power supply: 1.15 kW; Ar carrier gas flow rate: 0.6 L min^{-1}; Ar auxiliary gas flow: 1.0 L min^{-1}; Ar coolant gas flow rate: 14.0 L min^{-1}; viewing height: 15 mm; wavelength of element: Cu 327.396 nm, Fe 259.940 nm and Pb 216.999 nm) was used for metal ions determination. A pHS-10C digital pH meter (Xiaoshan Instrument Factory, China) was used for the pH adjustments. Infrared spectra (4000–400 cm^{-1}) in KBr were recorded on a Nicolet NEXUS 670 FT-IR spectrometer, Nicolet (Madison, WI, USA). An YL-110 peristaltic pump (General Research Institute for Nonferrous Metals, Beijing, China) was used in the pre-concentration process. A PTFE (polytetrafluoroethylene) column (45 mm × 3.0 mm i.d.) was used in this study.

2.2. Reagents and standard solutions

Reagents of analytical and spectral purity were used for all experiments and doubly distilled deionized water was used throughout.

Salicylaldehyde and N,N′-dicyclohexylcarbodiimide (DCC) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Activated carbon (AC), gas chromatographic grade, 100–200 mesh (Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China) and ethylenediamine (EDA) (The First Reagent Factory) were used in this work.

Buffer solutions of HCl–NaCl (pH 1, 2), CH$_3$COONa–CH$_3$COOH (pH 3–6), CH$_3$COONH$_4$ (pH 7) were used. Standard stock solution of Cu(II), Fe(III) and Pb(II) (1 mg mL^{-1}) were prepared by dissolving spectral pure grade chemicals and made up in 1 mol L^{-1} nitric acid. The standard working solution was diluted daily prior to use.

2.3. Sample preparation

Tuckahoe was purchased from Anning market, Lanzhou, China. The certified reference material (GBW 08501, Peach Leaf) was purchased from National Research Center for Certified Reference Materials (Beijing, China, http://www.nrccrm.org.cn/eng/index_en.asp). All biological samples were dried in an oven at 80 °C to constant weight. 0.500 g samples were weighted and transferred to a digestion tube, and then 5 mL of concentrated HNO$_3$ were added into it. The tube was left at room temperature for one night. Then it was placed in a digester block and heated slowly until the temperature was up to 165 °C. This temperature was maintained until ceasing the evolution of brown fumes. After the tube was cooled down, 1.3 mL perchloric acid was added into it. Then the temperature was raised to 210 °C until evolution of white fumes begins. The volume was adjusted to 100 mL with doubly distilled deionized water when the tube was cooled down.

Lake water was collected from South Lake, Lanzhou, China. Tap water sample was taken from our research laboratory. The water samples were filtered through a 0.45 μm polytetrafluoroethylene (PTFE) millipore filter, acidified to pH 2 with diluted HNO$_3$ prior to storage in precleaned polyethylene bottles for use. The samples were analyzed within 2 weeks after collection.

2.4. Modification process

Activated carbon powder was first purified with 10% (v/v) hydrochloric acid solution for 24 h so as to remove the metal ions and other impurities sorbed on it. Then 5 g of purified activated carbon was suspended in 100 mL of 5 mol L^{-1} nitric acid solution under stirring and heating for 5 h at 60 °C. The mixture was filtered and
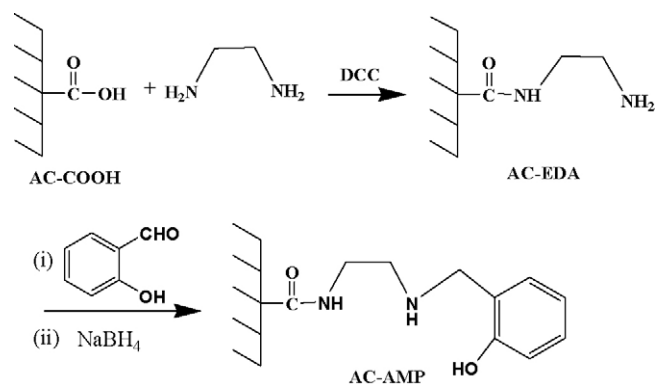

Fig. 1. Synthesis route of AC-AMP.

washed with deionized water to neutral and dried under vacuum at 80 °C for 8 h. The product was carboxylic derivative of activated carbon (AC-COOH).

The AC-COOH were functionalized with ethylenediamine to prepare activated carbon-bound ethylenediamine (AC-EDA) as described previously [11]. A 4.5 g amount of AC-COOH was suspended in 100 mL of ethylenediamine under stirring and heating, then 2.0 g of N,N′-dicyclohexylcarbodiimide (DCC) was added into the suspension and refluxed for 48 h. The product (AC-EDA) was filtered off, washed with ethanol and dried under vacuum at 80 °C for 8 h.

For the synthesis of 2-((2-aminoethylamino)methyl)phenol-modified activated carbon (AC-AMP), a 4.0 g amount of AC-EDA was treated with 2 mL salicylaldehyde in 100 mL of anhydrous ethanol. The mixture was refluxed with stirring for 12 h. After filtered and washed with anhydrous ethanol to remove the remnant salicylaldehyde, the product was treated with NaBH$_4$ in anhydrous ethanol medium at room temperature during 24 h [22]. The final product (AC-AMP) was washed with double-distilled water and acetone and then dried under vacuum at 80 °C for 6 h. The synthesis route of AC-AMP was described in Fig. 1.

2.5. Column SPE procedure

A total of 30 mg adsorbent was slurried in water and filled into a PTFE column (45 mm × 3.0 mm i.d.). The ends of the column were plugged with a small portion of glass wool to retain the adsorbent in the column. After cleaning by passing through ethanol, 0.1 mol L^{-1} HCl solution and doubly distilled deionized water once more, the column was conditioned to the desired pH with buffer solution. Each solution was passed through the column at a flow rate of 2.0 mL min^{-1} after adjusting to the desired pH. Afterwards, the metal ions retained on column were eluted with 1 mol L^{-1} HNO$_3$ solution at a flow rate of 0.5 mL min^{-1}. The analytes in the elution were determined by ICP-OES.

3. Results and discussion

3.1. FT-IR spectra

The modified activated carbon was confirmed by IR analysis. Fig. 2 shows the FT-IR spectra of AC-COOH and AC-AMP, respectively. The bands of AC-COOH at 1703.67 cm^{-1} was assigned to free carboxylic acids absorb [23]. The band at 3399.17 cm^{-1} could be assigned to νN–H and νO–H [11,24]. The peaks of 2922.01 cm^{-1} and 2864.34 cm^{-1} were caused by νC–H [24]. The observed features of 1590.74 cm^{-1} and 1526.25 cm^{-1} were assigned to νC=C [25]. The peak at 1334.99 cm^{-1} resulted from νC–N [25]. Peaks of 1000–1300 cm^{-1} were ascribed to νC–O and νC–C [23,25].
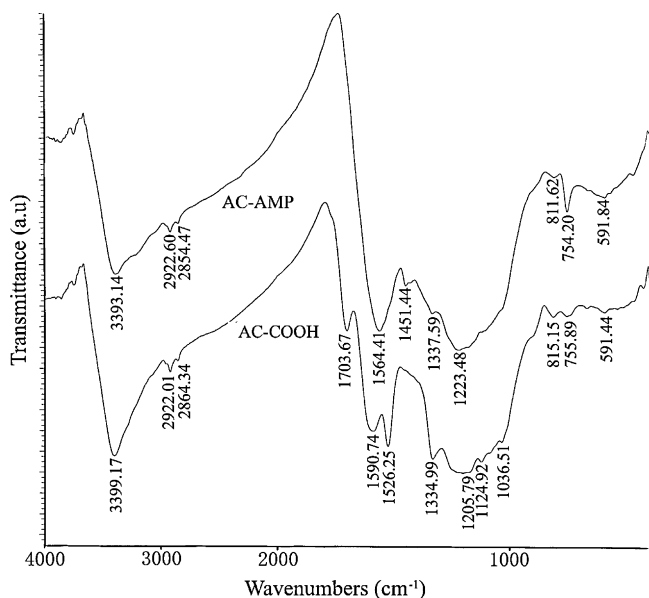
Fig. 2. FT-IR spectra of AC-COOH and AC-AMP.

Comparison of the IR spectrum of AC-AMP with AC-COOH, the new peak at 1451.44 cm^{-1} resulted from δCH$_2$ and stretching vibrations of aromatic C=C bonds. A strong band at 754.20 cm^{-1} was caused by δC–H of the aromatic ring in 2-((2-aminoethylamino)methyl)phenol. The intensive feature at 1564.41 cm^{-1} was assigned to νC=C [25]. Consequently, the above results showed that activated carbon was successfully modified by 2-((2-aminoethylamino)methyl)phenol.

3.2. Effect of the pH

The acidity of a solution is one of the most important factors affecting the adsorption process because proton in acid solution can protonate binding sites of the chelating molecules, and hydroxide in basic solution may complex and precipitate many metals. The adsorption of AC-AMP toward several metal ions, namely Ca(II), Mg(II), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) was tested at different pH values (pH 1–7) following the column SPE procedure at a flow rate of 0.5 mL min^{-1}. The result (Fig. 3) showed that the adsorption percentage increases with the increase of pH and Cu(II), Fe(III), and Pb(II) could be retained quantitatively by AC-AMP from pH 4 to 7.

In addition, Ca(II), Mg(II), Co(II), and Mn(II) ions were not enriched by AC-AMP at pH 4; Ni(II), Zn(II) and Cd(II) could be
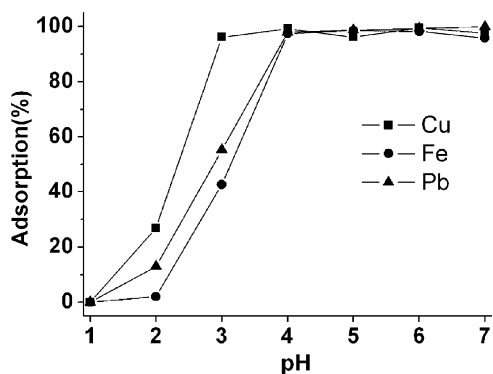

Fig. 3. Effect of pH on analyte adsorption; Cu(II), Fe(III) and Pb(II): 1.0 μg mL^{-1}; sample volume: 10 mL. AC-AMP amount: 50 mg; flow rate: 0.5 mL mim^{-1}.
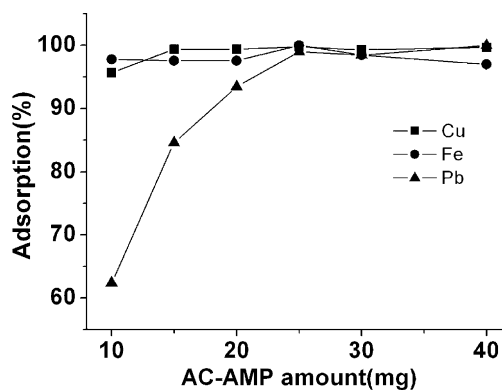

Fig. 4. Effect of AC-AMP amount on analyte adsorption; Cu(II), Fe(III) and Pb(II): 1.0 μg mL^{-1}; sample volume: 10 mL; pH 4; flow rate: 0.5 mL mim^{-1}.

adsorbed by AC-AMP about 20–40% at pH 4; Cr(III) and Hg(II) could be adsorbed by AC-AMP about 40–60% at pH 4, but they did not interfere with enrichment and determination of Cu(II), Fe(III) and Pb(II). To avoid hydrolyzing at higher pH and determine these elements simultaneously, pH 4 was selected as the enrichment acidity for further study.

3.3. Effect of AC-AMP amount

In the adsorption step, an appropriate amount of solid-phase filled to column should be used in order to obtain quantitative retention of metals. On the other hand, an excess amount of the sorbent also prevents the quantitative elution of the retained metals by a small volume of eluent. The influences of the amount of AC-AMP filled to the column were also investigated at pH 4. The result (Fig. 4) showed that quantitative recoveries for the examined analytes were obtained in the range of 25–50 mg of AC-AMP. Quantitative retention for Pb(II) was not obtained when mass of extractant was smaller than 25 mg. Accordingly, the column was filled with 30 mg of AC-AMP in further experiments.

3.4. Influence of elution condition on recovery

Since the adsorption of cations at pH < 2 was negligible, we expected elution would be favoured in acidic solution. So various concentrations of HCl and HNO$_3$ were studied for the desorption of retained Cu(II), Fe(III) and Pb(II) that followed analytical procedure. The result (Table 1) showed that higher recoveries for the metal ions were achieved with HNO$_3$ than when using HCl as eluent. The effect of the eluent volume on the recovery of metal ions was also

Table 1
Elution recovery (%) for Cu(II), Fe(III) and Pb(II) adsorbed on AC-AMP ($n = 3$).

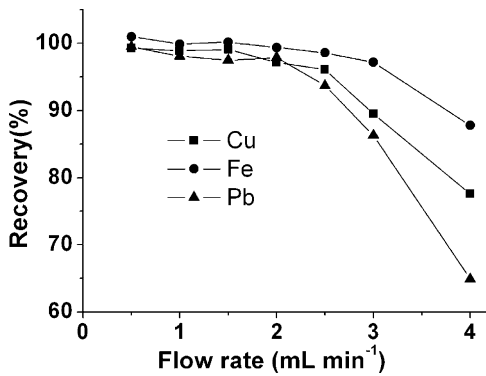|	5 mL HCl			5 mL HNO$_3$		
Concentration (mol L^{-1})	0.2	0.5	1	0.2	0.5	1
Cu	71.9	86.8	95.4	76.7	90.2	99.8
Fe	82.5	100.7	99.5	88.6	100.5	100.9
Pb	95.6	100.9	102.7	98.6	99.8	102.2
	1 mol L^{-1} HNO$_3$					
Eluent volume (mL)	1	1.5	2	2.5	3	4
Cu	56.6	82.1	96.7	97.8	98.8	101.2
Fe	78.8	95.6	98.0	101.3	99.5	102.3
Pb	91.7	99.1	97.7	98.2	99.8	99.5

Fig. 5. Effect of flow rate on analyte recovery; Cu(II), Fe(III) and Pb(II): 1.0 μg mL^{-1}; sample volume: 10 mL; pH 4; AC-AMP amount: 30 mg.

evaluated when 1 mol L^{-1} HNO$_3$ was selected. As shown in Table 1, quantitative recoveries (>95%) with 2 mL of 1 mol L^{-1} HNO$_3$ as eluent could be obtained. Therefore, 2 mL of 1 mol L^{-1} HNO$_3$ was used in this work.

3.5. Effect of the flow rate of the sample solution

In the column SPE system, the flow rate of the sample solution was one of the most important parameters, which not only affects the recovery of analyte, but also controls the time of analysis. Under the optimum conditions (pH, eluent, etc.), the flow rates were adjusted in the range of 0.5–4.0 mL min^{-1}. As shown in Fig. 5, three metal ions could be sorbed quantitatively by the adsorbent at flow rates of 0.5–2.0 mL min^{-1}. In the following experiments, the flow rate was kept constant at 2.0 mL min^{-1} in order to increase sample throughput.

3.6. Effect of column reuse

To test the stability and potential reusability of the column, several loading and elution operations cycles were carried out. The operating capacity was calculated from the loading and elution tests. The result showed that the column was relatively stable up to at least 10 extraction-elution cycles without obvious decrease of recoveries.

Table 2
Tolerance limits of electrolytes ($n = 3$).

Metal ions	Electrolytes (mmol L^{-1})							
	NaCl	NaNO$_3$	KBr	NaAc	NaH$_2$PO$_4$	Na$_2$SO$_4$	CaCl$_2$	MgCl$_2$
Cu	400	400	200	200	200	200	200	200
Fe	300	400	100	50	50	50	100	200
Pb	400	400	200	100	100	50	200	200

3.7. Adsorption capacities and distribution coefficient

The capacity study was adopted from the paper recommended by Maquieira et al. [26]. 30 mg of sorbent was equilibrated with 10 mL of various concentrations of Cu(II) and Pb(II) for 24 h at pH 4 at 25 °C. In order to reach the "saturation", the initial metal ions, concentrations were increased till the plateau values (adsorption capacity values) obtained. For Fe(III), 30 mg of sorbent was equilibrated with 20 μg mL^{-1} of various volumes of Fe(III) for 24 h at pH 4 at 25 °C to reach the "saturation". The results showed that adsorption capacity of various metal ions probably differ due to their size, degree of hydration and the value of their binding constant with the adsorbent. The adsorption of AC-AMP for Cu(II), Fe(III) and Pb(II) was found to be 12.1 mg g^{-1}, 67.1 mg g^{-1} and 16.2 mg g^{-1} at pH 4, respectively.

The distribution coefficients of the metal ion were determined by using the batch equilibration method. In the equilibration experiment, 10 mL of solution containing 100 μg Cu(II), Fe(III) and Pb(II) at pH 4 was treated with 30 mg of adsorbent and then was stirred for 2 h at 25 °C. After the solution was centrifuged, the concentrations of the metal ions in the solution were directly determined by ICP-OES. The result showed that the distribution coefficients were 21283, 13315 and 1660 for Cu(II), Fe(III) and Pb(II), respectively.

3.8. Effects of electrolytes

The effects of NaCl, NaNO$_3$, KBr, NaAc, NaH$_2$PO$_4$, Na$_2$SO$_4$, CaCl$_2$ and MgCl$_2$ on the adsorption of Cu(II), Fe(III) and Pb(II) were investigated. In these experiments, the solutions of 1.0 μg mL^{-1} of Cu(II), Fe(III), and Pb(II) containing electrolytes were analyzed following the column procedure. The reported tolerance limit was defined as the ions concentration causing a relative error <±5%. The results in Table 2 showed that the tolerance limits of electrolytes were very

Table 3
Analytical results of certified reference material and actual samples.

Ion	Added (μg g^{-1})	GBW 08501, Peach Leaf		Tuckahoe	
		Certified (μg g^{-1})	Found (μg g^{-1})[a]	Found (μg g^{-1})[a]	Recovery (%)
Cu	0	10.4 ± 0.8	9.8 ± 0.4	1.69 ± 0.05	
	5.0	–	–	6.62 ± 0.09	98.6
Fe	0	431 ± 15	442 ± 12	9.83 ± 0.21	
	5.0	–	–	14.89 ± 0.19	101.2
Pb	0	0.99 ± 0.04	1.01 ± 0.05	2.78 ± 0.09	
	5.0	–	–	7.66 ± 0.11	97.6
Ion	Added (μg L^{-1})	Tap water		Lake water	
		Found (μg L^{-1})[a]	Recovery (%)	Found (μg L^{-1})[a]	Recovery (%)
Cu	0	1.57 ± 0.06		3.98 ± 0.11	
	5.0	6.53 ± 0.08	99.2	8.79 ± 0.08	96.2
Fe	0	4.52 ± 0.12		9.91 ± 0.21	
	5.0	9.69 ± 0.16	103.4	14.83 ± 0.12	98.4
Pb	0	1.26 ± 0.04		1.79 ± 0.07	
	5.0	6.32 ± 0.13	101.2	6.68 ± 0.09	97.8

[a] $\bar{X} \pm S$ ($n = 5$). $\bar{X}$ value for five determinations, S standard deviation.

high, indicating that the present AC-AMP could be suitably used as a sorbent for analytes in high electrolytes.

3.9. Effect of the sample volume

To explore the possibility of enriching low concentrations of analytes from large volumes, the effect of sample volume on the retention of metal ions was also investigated. For this purpose, an increasing volume of sample solutions containing 5.0 μg Cu(II), Fe(III) and Pb(II) were passed through the column with the optimum flow rate. Quantitative recoveries (>95%) were obtained for sample volumes of ≤100 mL for Cu(II) and Fe(III), and ≤200 mL for Pb(II). Therefore, the concentration factors were Cu(II) and Fe(III): 50 and Pb(II): 100, respectively, since the final elution volume was 2.0 mL. 100 mL sample solution was adopted for the preconcentration of analytes from sample solutions.

3.10. The detection limits and analytical precision

According to the definition of International Union of Pure and Applied Chemistry, the detection limit of the method was calculated based on three times of the standard deviation of 11 runs of the blank solution. The detection limits of this method for Cu(II), Fe(III) and Pb(II) were 0.27, 0.41 and 0.16 $\mu g\,L^{-1}$, respectively. Under the selected conditions, 11 portions of $20\,\mu g\,L^{-1}$ standard solutions were enriched and analyzed simultaneously following the column procedure. The relative standard deviations (RSDs) was found to be lower than 3.0% (Cu(II): 1.9%; Fe(III): 2.3%; Pb(II): 2.7%), which indicated that the method had good precision for the analysis of trace Cu(II), Fe(III) and Pb(II) in solution samples.

3.11. Analysis of real samples

The proposed method has been applied to the determination of trace Cu, Fe and Pb in real samples. A reference material (GBW 08501, Peach Leaf) was used for method validation. The analytical result of certified reference material (Table 3) was in good agreement with the certified value.

In biological and water samples analysis, the standard addition method was used, and the results shown in Table 3 were satisfactory. The recoveries were reasonable for trace analysis in a range of 96.2–103.4%.

4. Conclusion

In the presented work, a new activated carbon chemically modified with 2-((2-aminoethylamino)methyl)phenol was synthesized. The preparation of AC-AMP was relatively reasonable, simple and convenient. This adsorbent showed high affinity, selectivity and good accessibility for Cu(II), Fe(III) and Pb(II) in aqueous solution. The column packed with AC-AMP was good enough for Cu(II), Fe(III) and Pb(II) separation in high electrolytes. A new method for determination of trace amount of Cu(II), Fe(III) and Pb(II) by ICP-OES after preconcentrated by AC-AMP packed column has been proposed and validated by analyzing a certified reference material. The application to a biological and two water samples was performed with satisfactory results. The precision and accuracy of the method were satisfactory.

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