



Cloud point extraction combined with flame atomic absorption spectrometry for the determination of copper, iron and zinc using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol-tetraphenylborate ion-pairing agent

Meiyi Xie¹ · Weiting Liu¹ · Xiaotang Hao¹ · Xun Jiang¹ · Yizhou Zhong¹ · Tiantian Liu¹ · Mei Wang¹

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Abstract

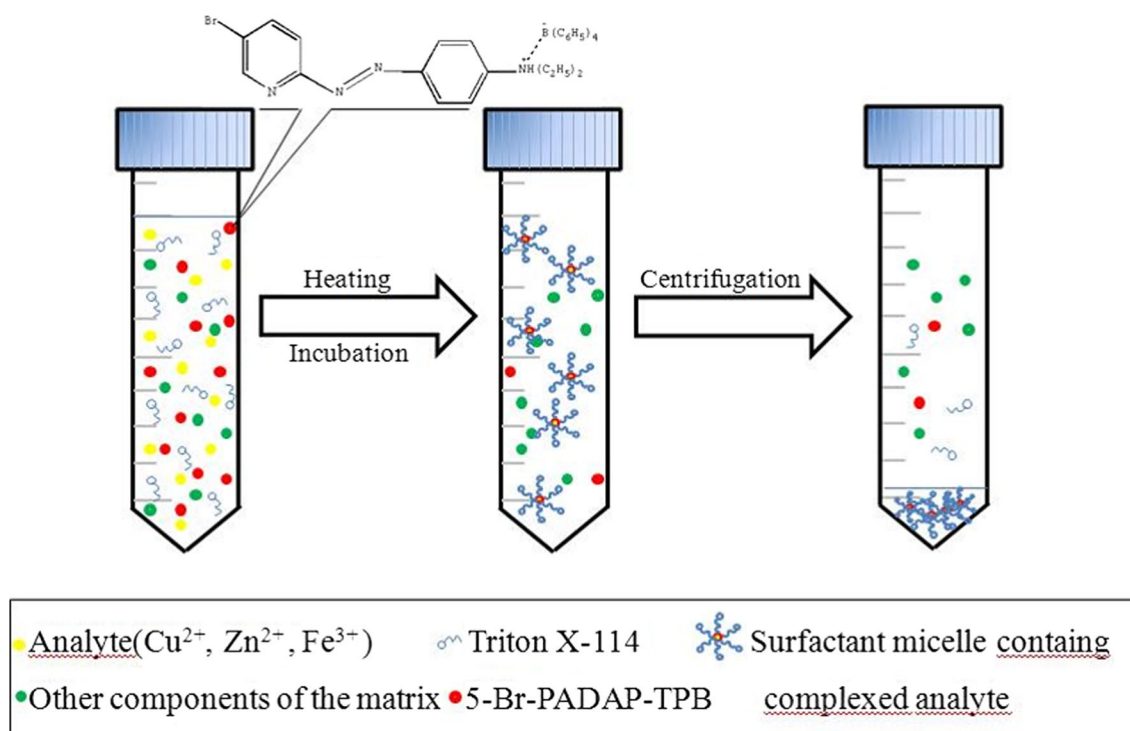
A novel cloud point extraction was developed for the pre-concentration and determination of Cu(II), Zn(II) and Fe(III) in bottled mineral water samples by flame atomic absorption spectrometry. The procedure was based on the formation of a charge transfer ion-pairing agent between the 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) and tetraphenylborate (TPB) in the presence of 0.1 mol L⁻¹ HCl, and the selective cloud point extraction was achieved after its complexation with target metals. Under the optimum conditions, good linearity was observed in the concentration ranges of 10–160 µg L⁻¹ for Cu(II), 2–30 µg L⁻¹ for Zn(II) and 20–300 µg L⁻¹ for Fe(III). In a 50 mL of sample, concentration factors of 38.4, 39.0 and 29.9 and limits of detection of 0.44, 0.14 and 0.78 µg L⁻¹ for Cu(II), Zn(II) and Fe(III) were obtained, respectively. Compared with single complexing reagent, the ion pair (5-Br-PADAP-TPB) significantly enhanced the enrichment factor of each analyte and tolerance levels of interference ions and obtained the lower detection limit. The proposed method was validated via the analysis of certified reference materials and successfully used for the determination of Cu(II), Zn(II) and Fe(III) in ten brands of bottled mineral water samples. All samples contained lower levels of Cu(II), Fe(III) and Zn(II) according to the maximum allowable concentration recommended by Chinese legislation. And recoveries for Cu(II), Zn(II) and Fe(III) were found to be between 95.0 and 105%; the relative standard deviation of this method was 0.620–1.67%

Meiyi Xie, Weiting Liu, Xiaotang Hao, Xun Jiang and Yizhou Zhong have contributed equally to this work.

✉ Mei Wang
wmei02@163.com

¹ School of Public Health, Guangdong Pharmaceutical University, Guangzhou 510310, Guangdong, China

Graphic abstract



Keywords 2-(5-bromo-2-pyridylazo)-5-diethylaminophenyl-tetrahydroborate · Cloud point extraction · Metal ions · Flame atomic absorption spectrometry · Bottled mineral water

Introduction

Trace metals refer that their amount are less than 0.01% of the total human body weight, and they are involved in nearly all types of significant life processes, such as circulation and optimal growth of the body. Iron (Fe(III)), copper (Cu(II)) and zinc (Zn(II)) as essential trace metals play a key role in cellular metabolism. The Fe(III) is an essential component of oxygen-binding molecules (hemoglobin and myoglobin) and many enzymes involved in biological oxidation (Maru 2013). The Cu(II) is necessary for the growth and formation of bone and myelin sheaths in the nervous system. The Zn(II) functions as a cofactor and is associated with more than 200 enzymatic systems (Maru 2013). These metals are critical for life processes and sustainability but are only needed at trace and the excess intake of them can also lead to adverse health effects (Liu et al. 2013; Williams 2005; Zoni and Lucchini 2013). All trace metals must have an intake range that is safe in relation to toxicity but adequate to meet nutrient requirements (Fairweather-Tait et al. 2011). Therefore, the potential human health risk from excess trace metals cannot be ignored. Various metals occur naturally in many parts of the world, and the people are unknowingly

exposed to them such as via water. For a variety of reasons, including the perception that mineral water is better than drinking water (Arve et al. 1999) or fear of contamination, many consumers now choose to drink bottled mineral water (Chiarenzelli and Pomerville 2008). However, the technological processes employed during the purification of mineral water cannot completely remove inorganic contaminants in certain cases. In addition, a lower or higher mineral content has a negative impact on human health. Hence, the determination, nutrition and risk assessment of these trace metals in mineral water are necessary.

Different approaches have been reported for the analysis of Cu(II), Zn(II) and Fe(III) using highly sensitive analytical instruments including cathodic stripping voltammetry (CSV) (Ghoneim 2010), inductively coupled plasma-optical emission spectrometry (Dogan et al. 2014; Javed et al. 2018), inductively coupled plasma-mass spectrometry (Tamburo et al. 2015), graphite furnace atomic absorption spectrometry (Ogunbileje et al. 2013) and flame atomic absorption spectrometry (Dasbasi et al. 2016; Sourouraddin et al. 2020). The flame atomic absorption spectrometry, a comparatively simple method, is cheap and available in many research laboratories. However, due to the low concentrations of target

metals in environmental samples and the complexity of the matrix, analysis requires separation and pre-concentration methods for detection of metals (Lemos and David 2010). Numerous separation/pre-concentration methods such as solid phase extraction (Chatterjee et al. 2016; Diaz-de Alba et al. 2012; Xie et al. 2008), dispersive liquid–liquid micro-extraction (El-Shahawi and Al-Saidi 2013), homogeneous liquid–liquid extraction, immersed single-drop microextraction (Pena et al. 2008) and cloud point extraction (CPE) have been developed (Pytlakowska et al. 2013). Among these, CPE based on nonionic surfactants aggregation via an increase in temperature is considered to be an efficient and environmental benign extraction technique for the extraction of hydrophobic species (Manzoori and Bavili-Tabri 2002; Rusinek et al. 2015). Until to present, the majority applications of CPE to pre-concentrate metal ions are based on the formation of hydrophobic metal complexes that are extractable by choosing effective chelating agents.

5-Br-PADAP, a ligand capable of forming complexes with various metal ions, has high sensitivity and stability. It is usually used as a chromogenic reagent for the determination of metals. Presently, the application of 5-Br-PADAP as a chelating agent in CPE is receiving more attention (Unsal et al. 2015). There are some reports of 5-Br-PADAP utilized in CPE for the determination of metal ions, including iron, cobalt, nickel, copper, vanadium, cadmium, chromium, lead, mercury and manganese with atomic spectrometry and UV–Vis spectrophotometry (Aranda et al. 2008; Bezerra et al. 2006; Borkowska-Burnecka et al. 2010; de Oliveira et al. 2018; Deng et al. 2014). The uses of 5-Br-PADAP in CPE benefit from its broad-spectrum properties, which can chelate with a variety of metal ions to form a hydrophobic compound at an appropriate pH value so that the hydrophilic metal ions in the water sample can be extracted. However, it should be noted that 5-Br-PADAP method has several drawbacks such as relatively lower extraction efficiencies and weaker tolerability of interfering ions (Saber-mahani and Taher 2014). If increasing the hydrophobicity of 5-Br-PADAP and metal complex, this method could further improve the selectivity and enrichment factor of target metals. Moreover, the detection limit could be concomitantly lowered.

The addition of the lipophilic counter anions can affect the overall hydrophobicity of the metal complex significantly, as well as their lipid/water partition coefficients. (Pytlakowska et al. 2013; Wang et al. 2017) Tetraphenylborate (TPB), which has lipophilic properties, consists of a boron anion and four phenyl groups (Fig. 1D). 5-Br-PADAP has three dissociation steps, and it can be protonated to form ion-pairing agent with TPB anion in acidic condition. The 5-Br-PADAP reacts with metal ion to form an amphiprotic complex cation, but in the presence of TPB anion it forms a water-insoluble complex. Here, TPB^- has participated in

ion-pairing complex formation as an auxiliary ligand that achieves higher hydrophobicity. Due to a more stable ternary complex formation of a metal ion with 5-Br-PADAP-TPB, the proposed method is promising for the extraction of metal ions. However, to date, there is no report on the use of 5-Br-PADAP-TPB as a chelating agent for extraction in CPE.

In this study, a CPE method using the 5-Br-PADAP-TPB ion-pairing agent was proposed for the pre-concentration of Cu(II), Zn(II) and Fe(III) prior to their determination by FAAS. The issues involved in the optimization of CPE conditions; a comparison of characteristics and results with 5-Br-PADAP were described. Ten brands of bottled mineral water samples were analyzed for these metals by the proposed method.

Materials and methods

Apparatus

An AA-6200 flame atomic absorption spectrometer (Shimadzu, Japan) with a deuterium background corrector was used in this study. All measurements were taken in an air/acetylene flame. The operating conditions were: analytical line, 324.7 nm for Cu, 248.3 nm for Fe, and 213.9 nm for Zn; slit width, 0.7 nm for Cu, 0.2 nm for Fe, 0.7 nm for Zn; lamp current, 6 mA for Cu, 12 mA for Fe, and 8 mA for Zn; air flow rate, 8 L min^{-1} ; fuel gas (acetylene) flow rate, 1.8 L min^{-1} for Cu, 2.2 L min^{-1} for Fe, and 2 L min^{-1} for Zn. A DK-600 thermostated bath (Shanghai Precision Experimental Equipment Co. Ltd., Shanghai, China) was used to maintain the desired temperature, and phase separation was assisted using a centrifuge (TG12Y; Hunan Xiangli Scientific Instrumentation Co. Ltd., Hunan, China). The pH measurements were taken with a pH meter (Shanghai Hongyi Instrumentation Co. Ltd., Shanghai, China).

Reagents and solution

All chemicals and reagents used in this study were of analytical reagent grade or higher purity. Ultrapure water was prepared using a SZ-97 automatic triple water distiller (Shanghai Yarong Biochemical Instrument Factory, Shanghai, China). The working solutions of Cu(II), Zn(II) and Fe(III) were prepared by serial dilution with ultrapure water from stock solutions (Cu(II), 1000 mg L^{-1} ; Zn(II), 1000 mg L^{-1} ; and Fe(III), 1000 mg L^{-1} , China National Center for Quality Supervision and Testing of Iron and Steel, China Iron and Steel Research Institute Group). The following solutions were prepared: 5-Br-PADAP (1×10^{-3} mol L^{-1} , Adamas Reagent Co. Ltd., Switzerland) in ethanol, a 1×10^{-3} mol L^{-1} solution of sodium tetraphenylborate (Tianjin Yongda

solution turned turbid, phase separation was achieved by centrifugation at 3500 rpm for 10 min and then the surfactant-rich phase was cooled in an ice-bath for 10 min to increase the viscosity. The supernatant aqueous phase was carefully discarded with a pipette. To decrease the viscosity and facilitate sample handling before the determination by the FAAS, the remaining surfactant-rich phase was diluted to 1.0 mL with 10% (v/v) HNO₃ in methanol. Then, the sample solution was injected into FAAS for analysis.

Real samples

Ten brands of bottled mineral water samples were purchased from supermarkets, such as Trust-Mart, Carrefour and Parkn Shop. We chose the brands of mineral water at random, mainly from Guangdong, which people regularly purchase. All the samples were filtered by 0.45- μ m-pore-size membrane filters and stored at 4 °C. Then, 30 mL of each sample was subjected to CPE.

Results and discussion

Characteristics of the ion-pairing agent

Reacting TPB with 5-Br-PADAP in the presence of hydrochloric in ethanol produced dark red precipitates at saturated condition. The ion-pair agent was soluble in CCl₄. The proton nuclear magnetic resonance (¹H NMR) was carried out to determine the structures of the complexes. Before forming ion pair, it showed two signals at 3.45 (2H) and 1.26 (3H) ppm corresponding to the methylene (CH₂) and protons of methyl (CH₃) groups, respectively. The spectrum displayed six signals at 5.88 (¹H) to 8.50 (¹H) ppm attributed to the aromatic cycloparaffin at positions, respectively. Moreover, singlet signal was observed at 15.8 ppm, as denoted by OH group (Fig. 1A). After forming ion pair, larger ¹H NMR line shifts of OH group, CH₂ group and CH₃ group to lower δ values, reflecting slightly different chemical environments around this hydrogen species. Compared with 5-Br-PADAP, the NH⁺ group in 5-Br-PADAP-TPB, has electron receptor effect can increase shielding effect to H in CH₂ and CH₃ group because of a high charged density. This phenomenon is explained by the TPB of the B⁻ ligands to the 5-Br-PADAP protonated in the H⁺, and the effect of electronic is decreased (Fig. 1B, C). The ¹H NMR spectra for compounds were considered to be consistent with the proposed structures (Fig. 1D). Table 1 shows the ¹H NMR spectra for 5-Br-PADAP before and after forming ion pairs with TPB.

Table 1 The ¹H NMR assignment of 5-Br-PADAP and 5-Br-PADAP-TPB

Compound	δ (ppm)		
	–OH	–CH ₂	–CH ₃
5-Br-PADAP	15.79	3.45	1.26
5-Br-PADAP-TPB	15.07	3.30	1.11

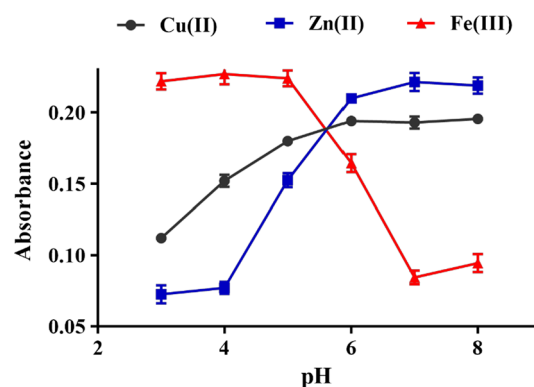


Fig. 2 Effect of pH on cloud point extraction ($n=3$)

Effect of pH

The metal complex formation and its chemical stability are two significant parameters in CPE. The pH plays a distinct role in the metal complex formation and subsequent extraction. The effect of pH ranging from 3 to 10 on the extraction efficiency of Cu(II), Zn(II) and Fe(III) was separately analyzed, and the results are shown in Fig. 2. The maximum absorbance of Fe(III) was around at pH 4, while the absorbances of Cu(II) and Zn(II) increased with increasing pH and reached plateau values in the pH range of 6–8. At pH > 5, a low extraction efficiency of Fe(III) was observed, which was attributed to the formation of hydroxide precipitate. Consequently, pH 4 was used for as the optimum pH values for maximum extraction of Fe(III), and pH 7 was selected for Cu(II) and Zn(II).

In addition, the influence of buffer volume on the absorbance was assayed at the optimum pH 4 and 7. The results showed that the maximum absorbance of metal ions was achieved at 2 mL of buffer solution. Therefore, 2 mL of the buffer solution was used in subsequent experiments.

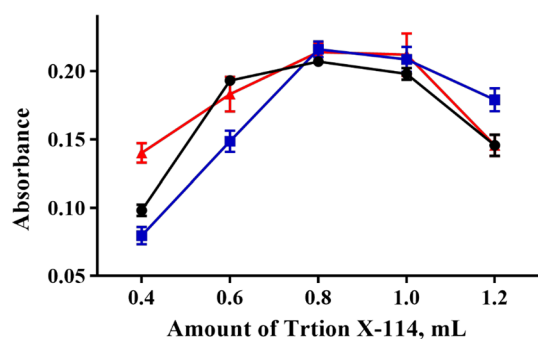


Fig. 3 Effect of Triton X-114 (5%, w/v) volume on cloud point extraction ($n=3$)

Effect of Triton X-114 concentration

Surfactant concentration is an important parameter for effective extraction and should be sufficient to quantitatively determine the target analyses. Triton X-114 is a non-ionic surfactant extensively used in CPE. Triton X-114 was chosen because of its low cloud point temperature, which is close to the ambient temperature (22–25 °C), and its high density, which can enhance the phase separation. The effect of Triton X-114 concentration on extraction efficiency was investigated in a volume range of Triton X-114 (5% w/v) from 0.4 to 1.2 mL (Fig. 3). Triton X-114 was found to be quantitatively extracted the target metal complexes from aqueous sample at surfactant volume above 0.8 mL. Beyond this optimal range, lower concentration of Triton X-114 led to the decrease of extraction efficiency. This is because the surfactant was not sufficient to entrap the metal complexes quantitatively. However, the consequence employing more surfactant volume (higher than 1.0 mL) was that the absorbance signals of these metal ions decreased. This can be interpreted that the volume and viscosity of the surfactant-rich phase increased in this situation/condition. Therefore, more solvent was needed to dilute the surfactant-rich phase, thus resulting in a loss of sensitivity. The optimal volume of 5% (w/v) Triton X-114, 0.8 mL, was chosen in the following experiments.

Effect of 5-Br-PADAP-TPB concentration

The CPE can be used for the pre-concentration of metal ions after the formation of hydrophobic complexes. The extraction efficiency strongly depends on the hydrophobicity of the chelating agent and the formed metal ion complex. The variations of the analytical signal as a function of the added 5-Br-PADAP-TPB (5×10^{-4} mol L⁻¹) volume between 0.05 and 1.0 mL were optimized. As illustrated in Fig. 4, the analytical signals of Cu(II), Zn(II) and Fe(III) had positive

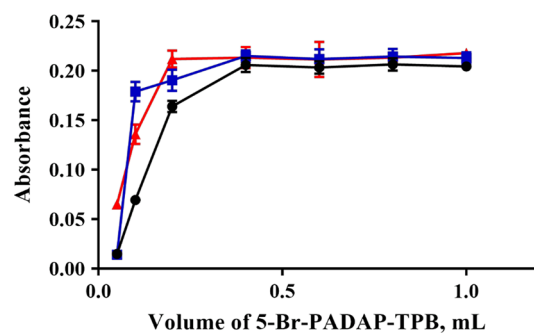


Fig. 4 Effect of 5-Br-PADAP-TPB (5×10^{-4} mol L⁻¹) volume on cloud point extraction ($n=3$)

relationships with the 5-Br-PADAP-TPB quantity. With an increasing volume of 5×10^{-4} mol L⁻¹ 5-Br-PADAP-TPB, the absorbance signals of these metal ions increased initially, reached the maximums at 0.4 mL and then remained constant until the highest volume tested. To ensure complete chelation of target metal ions, 0.8 mL of 5×10^{-4} mol L⁻¹ 5-Br-PADAP-TPB was selected for subsequent experiments.

Effect of equilibration temperature and time

The optimal equilibration temperature and the incubation time are necessary for complete reactions. The desirable condition was the most suitable equilibration temperature and shortest time to achieve efficient pre-concentration and complete phase separation. The equilibration temperature ranging from 30 to 50 °C was investigated. The higher extraction efficiency was observed at 40 °C for each analyte that remained stable at 50 °C. The incubation time was studied during a time interval of 5–30 min. The maximum absorbance signals for all metal ions were obtained after 15 min. Hence, temperature of 40 °C and 15 min time were selected for further experiments.

Effect of interference ions

In consideration of the high selectivity of FAAS, the interferences may come from the extraction step. The foreign ions in mineral water samples may react with chelating agent and decrease the extraction efficiency of target analytes. The effects of common foreign ions were investigated using 5-Br-PADAP and 5-Br-PADAP-TPB as the chelating agent, respectively. In this analysis, aqueous solutions containing either 50 µg L⁻¹ of Cu(II), 10 µg L⁻¹ of Zn(II) or 100 µg L⁻¹ of Fe(III) as well as foreign ions were analyzed according to the proposed procedure. An ion was considered to interfere when its presence altered the absorbance signals of Cu(II),

Table 2 Effect of foreign ions on the determination of Cu(II), Zn(II) and Fe(III) for both CPE

Metal ion	Tolerance level (mg)					
	In the presence of 5-Br-PADAP-TPB			In the presence of 5-Br-PADAP		
	Cu(II)	Zn(II)	Fe(III)	Cu(II)	Zn(II)	Fe(III)
Na ⁺	2.5	0.5	5	2	0.4	4
K ⁺	2.5	0.5	5	2	0.4	4
Ca ²⁺	0.5	0.1	1	0.5	0.05	1
Mg ²⁺	0.5	0.1	1	0.5	0.05	1
Pb ²⁺	0.25	0.05	0.5	0.25	0.045	0.5
As ³⁺	0.25	0.05	0.5	0.25	0.045	0.5
Cr ⁶⁺	0.25	0.05	0.5	0.25	0.04	0.5
Hg ²⁺	0.25 ^a	0.05 ^a	0.5 ^a	0.2 ^a	0.01 ^a	0.4 ^a
Mn ²⁺	0.25 ^a	0.05 ^a	0.5 ^a	0.25 ^a	0.04 ^a	0.4 ^a
Al ³⁺	0.08 ^b	0.05 ^b	0.4 ^b	0.05 ^b	0.0125 ^b	0.25 ^b
Cd ²⁺	0.25 ^c	0.05 ^c	0.5 ^c	0.25 ^c	0.04 ^c	0.25 ^c
Cu ²⁺	–	0.05 ^c	0.4 ^c	–	0.025 ^c	0.2 ^c
Zn ²⁺	0.25 ^d	–	0.5 ^d	0.2 ^d	–	0.4 ^d
Fe ³⁺	0.25 ^a	0.05 ^a	–	0.125 ^a	0.04 ^a	–

– Indicates not studied

^aTriethanolamine (10%, 2 mL) was added to mask Hg²⁺, Mn²⁺ and Fe³⁺

^bNaF (0.02 g mL⁻¹, 4 mL) was added to mask Al³⁺

^cSodium thiosulfate (0.1 g mL⁻¹, 5 mL) was added to mask Cd²⁺ and Cu²⁺

^d2-Mercapto-3-propanol (0.1%, 0.2 mL) was added to mask Zn²⁺

Zn(II) or Fe(III) by more than $\pm 5.0\%$. The effects of various ions are presented in Table 2.

As summarized in Table 2, both of 5-Br-PADAP and 5-Br-PADAP-TPB can form stable complexes with various metal ions, and most of the cations examined do not interfere at the mg level. Nevertheless, some of them may lead to the decrease of extraction efficiency because of the competitive complexing between the coexisting ions and target ions. However, this effect can be eliminated by

masking agent. Hg(II), Mn(II) and Fe(II) were tolerated in all cases by using triethanolamine as a masking agent in acidic/weakly acidic conditions. NaF was used to mask Al(III), and sodium thiosulfate masked Cd(II) and Cu(II). 2,3-Dimercaptopropanol was used for the chemical masking of Zn(II) in acidic/weakly acidic conditions. Furthermore, it can be also observed that 5-Br-PADAP-TPB has higher selectivity for target analytes than 5-Br-PADAP, especially for Zn(II).

Table 3 Analytical characteristics of 5-Br-PADAP-TPB and 5-Br-PADAP methods

Analyte	Condition	Linear range ($\mu\text{g L}^{-1}$)	Regression equation	Correlation coefficient (r^2)	LOD ^a ($\mu\text{g L}^{-1}$)	EF ^b	RSD ^c (%)
Cu(II)	With 5-Br-PADAP-TPB	10–160	$A = 0.0033c + 0.0139$	0.9983	0.44	38.4	0.62
	With 5-Br-PADAP	10–160	$A = 0.0025c + 0.0099$	0.9986	0.90	28.7	0.53
Zn(II)	With 5-Br-PADAP-TPB	2–30	$A = 0.0212c - 0.0097$	0.9971	0.14	39.0	0.90
	With 5-Br-PADAP	2–30	$A = 0.013c + 0.0125$	0.9930	0.24	24.0	1.03
Fe(III)	With 5-Br-PADAP-TPB	20–300	$A = 0.0019c + 0.0109$	0.9978	0.78	29.9	1.67
	With 5-Br-PADAP	20–300	$A = 0.0015c + 0.0178$	0.9927	1.03	23.4	1.05

^aLimit of detection (LOD) is defined as the ratio of three times the standard deviation of 10 measurements of the blank signals and the slope of the calibration curve

^bEnrichment factor(EF) is defined as the ratio of the slope of pre-concentrated samples (50 ml) to that obtained without pre-concentration

^cRelative standard deviation is obtained for 6 independent samples containing 10 $\mu\text{g L}^{-1}$ for Cu(II) or Zn(II), or 100 $\mu\text{g L}^{-1}$ for Fe(III) to the complete procedure

Analytical characteristics

To evaluate the ion-pairing agent, 5-Br-PADAP-TPB influence on extraction efficiency, the extraction of the analytes was performed in the presence of 5-Br-PADAP-TPB and 5-Br-PADAP, respectively. The analytical characteristics of the two methods are summarized in Table 3, which displayed both of two methods had good analytical characteristics. Moreover, 5-Br-PADAP-TPB method was superior to 5-Br-PADAP method for limit of detection (LOD) and enrichment factor. LODs of Cu(II), Zn(II) and Fe(III) for 5-Br-PADAP-TPB were 0.44, 0.14 and 0.78 $\mu\text{g L}^{-1}$ in sequence, whereas LODs of target metal ions for 5-Br-PADAP were greater than the former. Enrichment factors for 5-Br-PADAP-TPB were 38.4, 39.0 and 29.9 for Cu(II), Zn(II) and Fe(III), all of which were enhanced in comparison with 5-Br-PADAP. These indicated that 5-Br-PADAP-TPB method had higher selectivity and sensitivity for Cu(II), Zn(II) and Fe(III) than 5-Br-PADAP method as a result of an increase of the overall hydrophobicity of metal complex with 5-Br-PADAP-TPB.

Table 4 compares the characteristic data of the proposed method with those reported in literatures. The proposed method had the lower determination limits and the higher enrichment factors than other reported methods. This method is more suitable for detecting trace metals in environmental samples.

Table 5 Analysis of mineral water samples ($n=3$)

Sample	Cu(II) Found ($\mu\text{g L}^{-1}$)	Zn(II) Found ($\mu\text{g L}^{-1}$)	Fe(III) Found ($\mu\text{g L}^{-1}$)
Sample 1	BDL	29.3	51.0
Sample 2	BDL	93.0	48.5
Sample 3	BDL	7.3	31.8
Sample 4	BDL	19.3	57.5
Sample 5	BDL	13.0	35.2
Sample 6	BDL	18.3	46.0
Sample 7	BDL	14.1	41.8
Sample 8	BDL	9.2	46.0
Sample 9	BDL	9.0	51.8
Sample 10	BDL	16.5	58.3

BDL Below detection limit

Analysis of real samples

The proposed method was employed for the determination of Cu(II), Zn(II) and Fe(III) in mineral water samples, and the results are presented in Table 5. To verify the accuracy of the proposed method, two environmental water certified reference materials (GBW08608 for Cu(II), Zn(II) and GBW(E)080,407 for Fe(III)) were analyzed. The obtained values were $49 \pm 0.5 \mu\text{g L}^{-1}$, $91 \pm 2.4 \mu\text{g L}^{-1}$, $9.9 \pm 0.11 \text{ mg}$

Table 4 Comparison of the published CPE methods for Cu, Zn and Fe with the proposed method

Analyte	Chelating agent	Analysis technique	Linear range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	RSD (%)	EF	Refs.
Cu(II)	5-Br-PADAP	FAAS	10–100	1.5	–	–	(Shoae et al. 2012)
Cu(II)	PDBDM	FAAS	10–260	0.6	1.0	41.1	(Shokrollahi et al. 2008)
Cu(II)	5-Br-PADAP	Spectrophotometry	15–700	4.5	4.04	–	(Deng et al. 2014)
Zn(II)	PAN	FAAS	5.0–8.0	2.3	2.5	43	(Galbeiro et al. 2014)
Zn(II)	Quinaldine	FAAS	5–20	1.4	2.87–3.6	30	(Kolachi 2011)
	PAN			1.52	4.59–5.4	26	
Fe(III)	5-Br-PADAP	Spectrophotometry	50–300	4	6.5	–	(de Oliveira et al. 2018)
Fe(II)	5-Br-PADAP	Spectrophotometry	5.0–112	0.8	2.0	–	(Filik and Giray 2012)
Fe(III)				1.0	2.6		
Cu(II)	PAN,	ICP-OES	10–500, 15–500;	1.9, 2.6; 2.0, 4.7	3.0, 2.4; 2.2, 5.8	13	(Borkowska-Burnecka et al. 2010)
Zn(II)	5-Br-PADAP		20–5000, 40–5000				
Cu(II)	PAR	ICP-OES	10–500	1.2	1.3	9.77	(Silva et al. 2009)
Zn(II)			10–700	1.1	1.7	10.1	
Cu(II)	APDC	Spectrophotometry	40–1300	6	4.6	–	(Meeravali 2007)
Fe(III)			60–700	1.5	2.9		
Cu(II)	ETB	Spectrophotometry	2.4–500	0.71	2.1	50.8	(Mortada et al. 2017)
Zn(II)			0.12–500	0.35	1.9	52.6	
Fe(III)			5–500	1.5	2.6	50.0	
Cu(II)	5-Br-PADAP-TPB	FAAS	10–160	0.44	0.62	38.4	This work
Zn(II)			2–30	0.14	0.90	39.0	
Fe(III)			20–300	0.78	1.67	29.9	

PDBDM: 4-(phenyl diazenyl) benzene-1,3-diamine; PAN: 1-(2-pyridylazo)-2-naphthol; Quinaldine: 2-methyl-8-hydroxyquinoline; PAR: 4-(2-pyridylazo)-resorcinol, APDC: ammonium pyrrolidine dithiocarbamate; ETB: 2-(3-ethylthioureido)benzoic acid

L^{-1} ($n=6$) for Cu(II), Zn(II) and Fe(III), respectively. These results were in good agreement with the certified values of $50 \pm 1.0 \mu\text{g L}^{-1}$, $90 \pm 3.6 \mu\text{g L}^{-1}$, and $10 \pm 0.20 \text{mg L}^{-1}$. Recoveries for Cu(II), Zn(II) and Fe(III) were found to be between 95.0% and 105%, thus confirming the application of the method to water samples without matrix effects.

All samples contained lower levels of Cu(II), Fe(III) and Zn(II) according to the maximum allowable concentration recommended by Chinese legislation (GB8537-2008 2008). In fact, every sample contained detectable quantities of Zn(II) and Fe(III), but Cu(II) was not detected in any of the bottled water samples. A comparison of these mineral water results and the current standards for drinking water showed that all samples would pass all drinking mineral water standards for the recommended allowable concentration of trace metals ($\text{Cu} < 1 \text{mg L}^{-1}$). On the basis of Baba's study (Baba et al. 2008), Cu(II) content was also below the detection level ($< 1 \mu\text{g L}^{-1}$); for Zn(II) and Fe(III), most values were found to be below 1 and $8 \mu\text{g L}^{-1}$, respectively.

Types and concentrations of metals in mineral water are associated with a geological background. Guangdong province supply was dominated by metasilicate, a function of the geology of the groundwater. Hence, Cu, Zn and Fe concentrations are proportionally low.

Drinking water is an important source for the daily intake of many of these essential and nonessential metals. Most metals with a physiological function have a proper dose, and intake above or below this level will result in health problems. The average adult intake is 2 L water per day. Compared to the tolerable upper intake level of Cu (8mg day^{-1}), Zn (40mg day^{-1}) and Fe (40mg day^{-1}), the intakes of Cu, Zn and Fe for adults via consumption of mineral water were in safe limits. However, for the recommend intake amounts (Cu, 0.8mg day^{-1} ; Zn, 12.5mg day^{-1} for man and 7.5mg day^{-1} for woman; Fe, 12mg day^{-1} for man and 20mg day^{-1} for woman) in Chinese dietary reference intakes, the intakes of these trace metals only relying on drinking mineral water are not enough. Thus, the intake of sufficient trace metals needs to focus on ingesting various types of foods which are rich in these metals, especially the special groups needing for nutrition.

Conclusions

A novel CPE was developed for the determination of Cu(II), Zn(II) and Fe(III) in mineral water samples by FAAS. To date, 5-Br-PADAP-TPB ion-pairing agent was first used as chelating agent in CPE. The 5-Br-PADAP-TPB method had better sensitivity and selectivity than 5-Br-PADAP method, which was attributed to an increase of the hydrophobicity of metal complex. Besides that, the method had good detection limits and enrichment factors for the Cu(II), Zn(II) and

Fe(III). As a result, the proposed method offered a simple, rapid, robust and sensitive alternative to other methods.

Furthermore, 10 bottle mineral water samples from Guangdong province were analyzed by the proposed method. The Cu(II), Zn(II) and Fe(III) concentrations in all bottled mineral water samples were below the maximum allowable concentration recommended by Chinese legislation, while the intakes via water were not enough to meet the daily nutritional needs. This method could be used to determine trace metals in bottled mineral water to serve as a guide to consumers with particular health needs, and enhance susceptibility, and/or preferences in drinking water selection.

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Declaration

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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