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Effective Enrichment and Simultaneous Quantitative Analysis of Trace Heavy Metal Ions Mixture in Aqueous Samples by the Combination of Radial Electric Focusing Solid Phase Extraction, UV-Vis Spectrophotometric Determination and Partial Least Squares Regression

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Abstract An efficient and stable preconcentration method for ionic and ionizable analytes, named radical electric focusing solid phase extraction (REFSPE), was proposed here for enriching trace Cu(II), Ni(II), and Co(II) from water samples. In REFSPE, radical electric field was introduced into solid phase extraction system to enhance the mass transfer rate of heavy metal ions in aqueous solution and shorten the extraction time obviously. The concentration of mixed heavy metal ions were predicted using partial least squares (PLS) regression by analyzing ultraviolet and visible spectrum efficiently. By optimizing chromogenic agent, pH values, extraction voltage, extraction time, and PLS parameters, the proposed method had higher figures of merit. The comparison of the determination data and the calculation results showed that the proposed method can provide a favorite quantitative precision with expanded measuring range. The limit of detection (LOD) for Cu(II), Ni(II), and Co(II) were 0.10, 0.13, and 0.15 μg L^{-1}, respectively. The reliability was confirmed by the RSD lower than 5% and the recovery of 95–102%. The novel enrichment method has a great potential for applications in detecting different ionic and ionizable analytes with the help of spectrometry determination and chemometrics calculation.

Keywords Heavy metal ions mixture · Ionizable analytes · Partial least squares · Radial electric focusing solid phase extraction · Simultaneous quantitative analysis

1 Introduction

With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries, waste disposal, and pesticides, heavy metal wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries (Fu and Wang 2011; Qiao et al. 2013; Duruibe and Ogwuegbu 2007; Bailey et al. 1999). Pollution of the natural aquatic environment by heavy metals is a problem worldwide, and heavy metals have been paid much attention due to their toxicity, persistence, non-biodegradation, and bioaccumulation in food webs (Facchinelli et al. 2001; Li et al. 2015; Ayenimo et al. 2010). Therefore, accurate detection and monitoring of heavy metal pollution in different water environments to protect the people and the environment is extremely important.

As we have seen, the methods including atomic absorption spectroscopy (Kumar et al. 2001; Trindade et al. 2015), inductively coupled plasma mass spectrometry (ICP-MS) (Silva and Curtius 2000; Nardi et al.

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2009), inductively coupled plasma optical emission spectrometer (Losev et al. 2015; Massadeh et al. 2016), ultraviolet and visible spectrophotometry (UV-Vis) (Feng et al. 2009; Zanjanchi et al. 2006), stripping voltammetry (Tukur et al. 2015), liquid chromatography (Peñalver et al. 2002), X-ray fluorescence spectrometry (Sitko 2015), and sensor (Forzani et al. 2005) are usually used to detect heavy metal ions. In spite of their widespread use, these techniques have more or less limitations including high cost, complex pre-treatment procedures, large and heavy analytical instrument requirements, skilled personnel, or expensive to run and maintain (Wei et al. 2014; Zhan et al. 2015). Accordingly, a simple, sensitive and economical method for simultaneous detection of multiple heavy metal ions is desirable (Huang et al. 2013).

In view of the abovementioned background, UV-Vis method is the most widespread and most appealing analytical technique because of its simplicity, reliability, cheap price, and ease-of-operation. However, it is difficult for the traditional UV-Vis approach in two situations: when simultaneous determination of multiple components is required and when the sample concentration is super low. As for the quantitation of different heavy metal ions simultaneously, chemometrics methods can be introduced into the data processing of spectrogram (Jia et al. 2014; Nakajima et al. 2015; Zeiner et al. 2010). In recent years, a variety of multicomponent concentration was determined with the combination method of chemometrics and spectrophotometric analysis (Juan and Tauler 2003; Jiang et al. 2002; Ni et al. 2006). The combination method can be applied to the analysis of multicomponent system quickly and accurately. As for the quantification of trace level samples accurately, new sample pre-treatment methods will achieve twice the result with half the effort. Nowadays, various techniques have been applied for the preconcentration of trace heavy metals from environmental samples, such as adsorption, liquid–liquid extraction (Anthemidis et al. 2004), cloud point extraction (Svegl and Ogorevc 2000; Talio et al. 2009), solid phase extraction (SPE) (Guo et al. 2017; Su et al. 2015), and co-precipitation (Feist and Mikula 2014). Considering the advantages and disadvantages of various methods, SPE as effective extraction technique become a preferred candidate (Mehdinia and Aziz-Zanjani 2013; Puig et al. 2008) except that it is kind of time-consuming and labor-intensive (Hennion 1999). In order to accelerate the mass transfer rate of analytes in aqueous samples and shorten the operation time, the radical electric focusing solid phase extraction (REFSPE) was proposed here. An electrostatic field, created by direct-current power supply in REFSPE, can drive charged ions to migrate orientationally. Charged ions were centralized to the membrane placed at the center of extractor and the preconcentration process of the trace heavy metals in the water completed.

Therefore, the combination of REFSPE, UV-Vis detection, and improved MATLAB® partial least squares (PLS) regression was used in the quantification of trace heavy metal ions mixture in aqueous sample. All the influence factors such as chromogenic agent, pH values, extraction voltage, extraction time, and PLS parameters were studied and optimized. The enrichment performance of various heavy metal ions was validated by the comparison of the proposed method and ICP-MS.

2 Materials and Methods

2.1 Reagents and Samples

Stock standard solutions for Ni(II), Co(II), and Cu(II) (1000 mg L^{-1}) were prepared by dissolving analytical reagent grade $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $CuSO_4 \cdot 5H_2O$ (Tianjin Kermel Co., Ltd., China) into deionized water separately. 0.05 mg L^{-1} solution of Cu(II), Ni(II), and Co(II) prepared from the abovementioned stock standard solutions was used for electric strengthen adsorption. Buffer of acetic acid-sodium acetate (CH_3COOH/CH_3COONa) was prepared by mixing appropriate volume of pure acetic and sodium acetate to pH 5–6. As chromogenic reagent, 0.3% xylenol orange (XO) was prepared by dissolving appropriate XO in deionized water. Polyvinylidene fluoride (PVDF) membranes, which are with high porosity and high surface to volume ratio, were purchased from Tianjin Motian technology Co., Ltd., China. Deionized water was used for all the dissolution and dilution process in the experiments. All the glassware were carefully cleaned with specific HNO_3 solution and rinsed with distilled water before use.

2.2 Instruments

The direct-current power supply of the preconcentration process was KIKUSUI PMC18–5 (Kikusui Electronics Corporation, Japan), and the 0.5-mm platinum electrode was from a hardware supply store. Ultrasonic cleaning machine (Shanghai Crown Ultrasonic Instrument Co., Ltd., China) was used for desorption. The EVOLUTION 300 UV-Vis spectrometer (spectra range from 200 to 800 nm), which was selected as the detection tool for all the samples, was purchased from Thermo Fisher Scientific Co., Ltd., USA. The PHS-W series laboratory pH meter was purchased from Shanghai Bante Instruments Co. Ltd., China. Agilent 7900 ICP-MS from Agilent Technologies was used for validating the proposed detection method in the paper.

REFSPE, which was carried out on a self-made instrument, adopted a radial electric field formed by a cylindrical electrode surrounding a single electrode in a central location creatively. In this structure, there is a stronger and uniform electric field force, which can drive ions to migrate faster and shorten the extraction time significantly, in the extraction system without any mixing device. At the same time, an automatic precision three-dimensional lifting platform was used in the experiments in order to ensure that each experiment operating conditions are exactly the same. As a result, the detection accuracy and repeatability increased obviously. The device diagram of REFSPE was shown in Fig. 1.

2.3 The Preparatory Work

Some hollow PVDF membrane pieces of 2.5 cm were activated by dipping them in 2.0 mol L^{-1} anhydrous ethanol for 30 min at room temperature before rinsed by distilled water. After that, the platinum electrode, which was inserted into the PVDF-activated membrane, was connect with the negative electrode of the power supply and placed on the true center of the extractor during the extraction process.

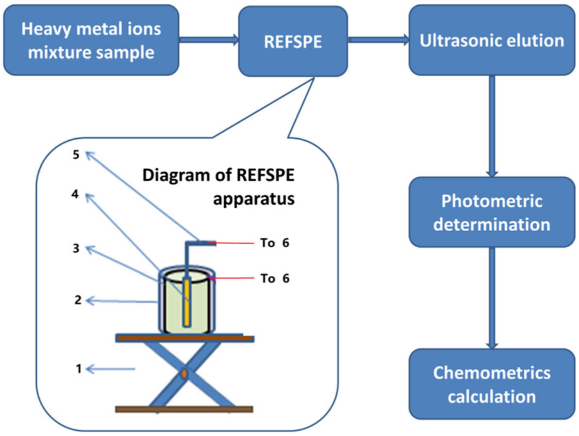

Fig. 1 Flow chart for determination of trace metal ions mixture and diagram of REFSPE system. (1) Automatic three dimensional lift platform. (2) Beaker. (3) Titanium ruthenium plating cylindrical electrode. (4) PVDF hollow fiber membrane. (5) Platinum electrode. (6) Direct-current power supply

2.4 The Preconcentration Process

At the beginning of the extraction experiment, 50 mL sample solution was enclosed into a homemade titanium plating ruthenium cylindrical container with an inner diameter of 4.8 cm and height of 8 cm, which served as a positive pole. Then, the extraction procedure was completed under the assistance of a direct current electrical field for some time. After that, the mixed ions adsorbed on hollow PVDF membrane were eluted by 2.0 mL NaAc-HAc buffer solution with the help of an ultrasonic cleaner.

2.5 Data Acquisition and Data Mining

After the desorption process, 1.0 mL color developing agent XO was added into the eluent to make UV-Vis detection much more sensitive. Then, the UV-Vis spectra data, obtained from EVOLUTION 300 UV-Vis spectrometer, were disintegrated into individual of each ion with the help of PLS. Upon the MATLAB® calculation, certain concentrations of each ion were acquired. The entire operation process was shown in Fig. 1.

3 Results and Discussion

In order to obtain an effective and sensitive detection for trace mixed heavy metal ions in aqueous sample, the conditions of enrichment and detection such as pH values, extraction time, operation voltage, elution time, and volume of XO were optimized, and the concentration of heavy metal ions was calculated from the enriched sample solution.

3.1 Effect of pH for Measured Sample

From the practical point of view, an appropriate pH can increase the sensitivity of metal ion complex and coordination agent. In order to find the optimal pH value, the absorbance values of heavy metal ions with the pH values from 5 to 6 were measured. The relationship between absorbance and pH data were displayed in

Fig. 2. It was shown that the absorbance data had the highest level at the pH of 5.6. Therefore, pH = 5.6 was chosen as the detection pH value for all the experiments.

3.2 Effect of Volume of 0.3% XO Solution for Detection

Coordination agent XO was mixed with three kinds of ions and had an occurrence of obvious chromogenic reaction. The mixture of eluent solution and different volumes of 0.3% XO were detected by UV-Vis spectrometer. The absorbance data of different additive amounts of 0.3% XO solution were illustrated in Fig. 3. It was illustrated that with the increase of reagents, absorbance tends to be stable; however, the color effect became weak due to the dilution effect of the 0.3% XO solution if excessive 0.3% XO solution is used. Therefore, 1.0 mL 0.3% XO solution was chosen for the further experiments.

3.3 Effect of Adsorption Time and Voltage

The time profiles of REFSPE were depicted in Fig. 4 at different operation voltages. It is found that the enrichment factors were constant when the adsorption equilibrium was achieved. The results are also shown in Fig. 4 that the less adsorption equilibrium time and greater enrichment factor can be reached when the higher adsorption voltage in the range of 3–9 V was adopted. On the other hand, there were some pure metals of analyte coating on the extraction material, which could reduce the preconcentration result and had an obvious effect on the subsequent experiments, when the adsorption voltage was higher than 9 V. Therefore, the optimal adsorption time was chosen at 11 min with the operation voltage of 9 V.

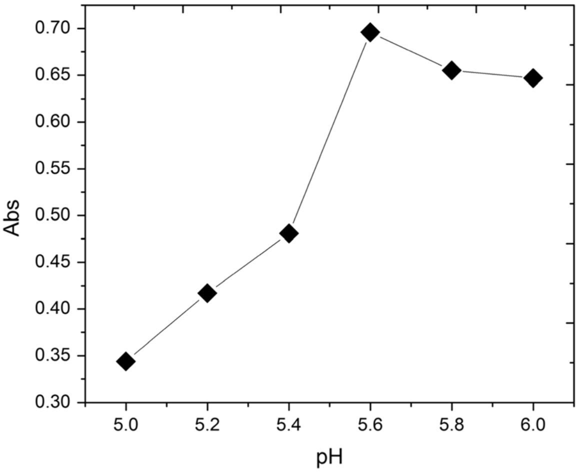

Fig. 2 Relationship between absorbance and pH data

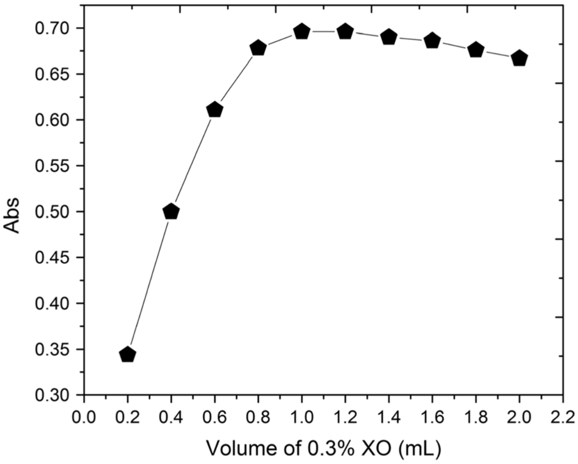

Fig. 3 Effect of volume of 0.3% XO solution for detection

3.4 Effect of Desorption Time

In order to collect the preconcentrated metal ions during the adsorption process, ultrasonic elution method was selected owing to its effective elution behavior. In the elution process, the hollow fiber membrane after adsorption was put into 2 mL buffer solution with pH = 5.6 for supersonic elution. The relationship of enrichment result and desorption time were shown in Fig. 5. According to the time profile, the stripped ion content increased until the elution content became constant after 3 min. Therefore, 3 min was chosen as the optimal desorption time in the following experiments.

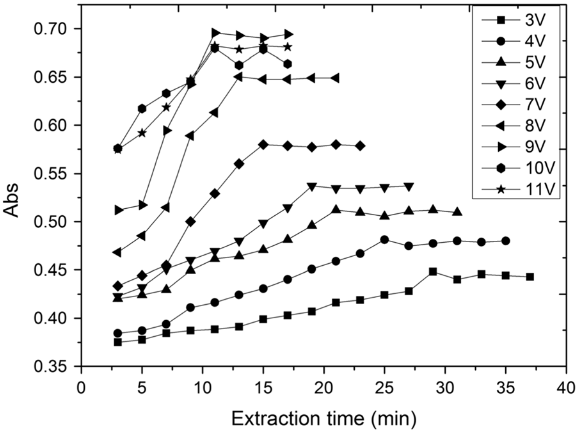

Fig. 4 The influence of extraction time and voltage on the REFSPE process

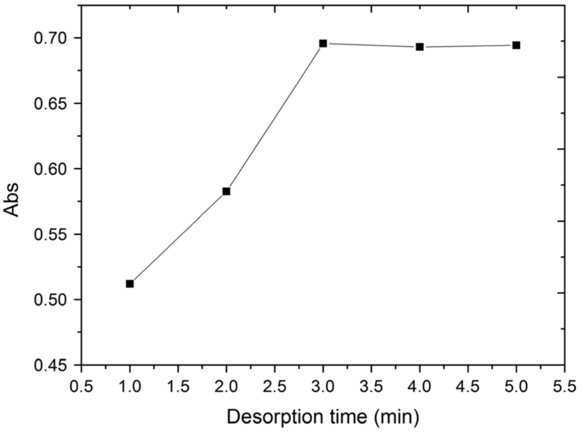

Fig. 5 Effect of desorption time on the extraction effect

3.5 Method Evaluation

In order to evaluate enrichment properties of REFSPE for heavy metal ion mixture, partial least squares of latent structure model were introduced into the calculation of mixed ions. The PLS model built for the quantification of heavy metal ions mixture was from UV-Vis spectra of 50 random samples ranged from 0.001 to 2.5 mg L^{-1}. The root-mean-square error of cross validation (RMSECV), which was an important index for predictive value through using the optimal factor number of latent variables (LV), were calculated and shown in Fig. 6. On the basis of the computed result, RMSECV were 0.1417, 0.0855, and 0.0751, when the LV for Cu(II), Co(II), and Ni(II) in sample solutions were confirmed at 5, 12, and 12, respectively. The relationships between predictive values and truth values of each ion were all higher than 0.99.

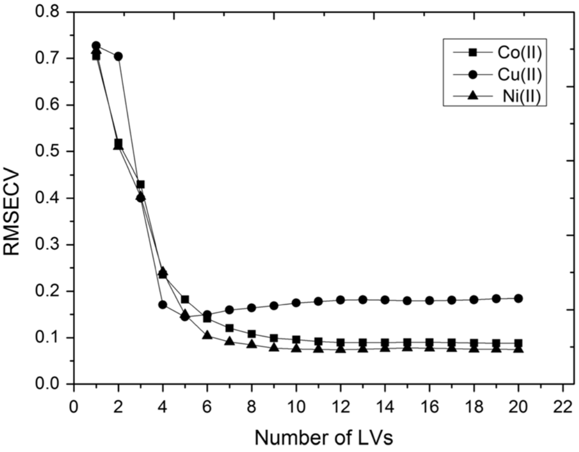

Fig. 6 The relationship of RMSECV and the number of LVs

Table 1 Comparison of the proposed method with the ICP-MS data

Detection method	$C_{\mathrm{Cu(II)}}$/mg L^{-1}	$C_{\mathrm{Co(II)}}$/mg L^{-1}	$C_{\mathrm{Ni(II)}}$/mg L^{-1}
Predictive value	1.11	1.17	1.22
ICP-MS	1.15	1.19	1.23

3.6 Analytical Performance

Under the optimal experimental conditions, the limit of detection (LOD) for Cu(II), Ni(II), and Co(II) were 0.10, 0.13, and 0.15 μg L^{-1}, respectively. In order to estimate the reliability of the proposed method, the calculation results for the enriched sample from 0.05 mg L^{-1} solution for each ion were compared with the determination values of ICP-MS. The comparison data were shown in Table 1 with RSD ($n = 5$) lower than 5% and recovery values in the range of 95–102%.

4 Conclusions

Simultaneous spectrophotometric quantization method for trace heavy metal ions in water samples using REFSPE coupled with PLS approaches was proposed here. In REFSPE, radical electric field was introduced into an SPE system to enhance the mass transfer of heavy metal ions in aqueous solution and shorten the operation time of the sample enrichment process and the experimental results proved that REFSPE can be developed as a new effective sample preparation method for ionic and ionizable analytes. The concentration of mixed heavy metal ions can be calculated through PLS approaches by analyzing UV-Vis spectrum efficiently. The LOD for Cu(II), Ni(II), and Co(II) of the proposed combination method were found at 0.10, 0.13, and 0.15 μg L^{-1}, respectively. The reliability was confirmed by the RSD lower than 5% and the recovery of 95–102%. The experimental study shows that REFSPE is a great potential for applications in detecting trace metal ion samples with the help of spectrometry determination and chemometrics calculation.

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