



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Simultaneous detection of trace metal ions in water by solid phase extraction spectroscopy combined with multivariate calibration

Lei Wang^a, Peng Cao^b, Wei Li^a, Peijin Tong^a, Xiaofang Zhang^a, Yiping Du^a^a Shanghai Key Laboratory of Functional Materials Chemistry, and Research Center of Analysis and Test, East China University of Science and Technology, Meilong Rd 130, Shanghai 200237, China^b Yantai Entry-Exit Inspection and Quarantine Bureau, Beima Rd 66, Yantai 264000, China

ARTICLE INFO

Article history:

Received 3 June 2015

Received in revised form 15 January 2016

Accepted 23 January 2016

Available online 25 January 2016

Keywords:

SPES

UV–Visible spectroscopy

Membrane filtration

1-(2-Pyridylazo)-2-naphthol(PAN)

Simultaneous detection

ABSTRACT

Solid Phase Extraction Spectroscopy (SPES) developed in this paper is a technique to measure spectrum directly on the solid phase material where the analytes are concentrated in SPE process. Membrane enrichment and UV–Visible spectroscopy were utilized to fulfill SPES, and multivariate calibration method of partial least squares (PLS) was used to simultaneously detect the concentrations of trace cobalt (II) and zinc (II) in water samples. The proposed method is simple, sensitive and selective. The complexes of analyte ions were collected on the cellulose acetate membranes via membrane filtration after the complexation reaction with 1-2-pyridylazo 2-naphthol (PAN). The spectra of the membranes which contained the complexes of metal ions and PAN were measured directly without eluting. The analytical conditions including pH, reaction time, sample volume, the amount of PAN, and flow rates were optimized. Nonionic surfactant Brij-30 was absorbed on the membranes prior to SPES to modify the membranes for improving the enrichment and spectrum measurement. The interference from other ions to the determination was investigated. Under the optimal condition, the absorbance was linearly related to the concentration at the range of 0.1–3.0 µg/L and 0.1–2.0 µg/L, with the correlation coefficients (R^2) of 0.9977 and 0.9951 for Co (II) and Zn (II), respectively. The limits of detection were 0.066 µg/L for cobalt (II) and 0.104 µg/L for zinc (II). PLS regression with leave-one-out cross-validation was utilized to build models to detect cobalt (II) and zinc (II) in drinking water samples simultaneously. The correlation coefficient between ion concentration and spectrum of calibration set and independent prediction set were 1.0000 and 0.9974 for cobalt (II) and 1.0000 and 0.9956 for zinc (II). For cobalt (II) and zinc (II), the errors of the prediction set were in the range 0.0406–0.1353 µg/L and 0.0025–0.1884 µg/L.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

As we all know, organisms need trace amounts of many heavy metals to survive. It is however a fact that heavy metals can do harm to the natural environment even at low concentration, through their inherent toxicity and their tendency to accumulate in the food chain and/or have particularly low decomposition rates [1]. Up to now, a wide variety of methods for detection of heavy metals in different matrixes including atomic absorption spectrometry (AAS) [2–5], inductively coupled plasma atomic emission spectrometry (ICP-AES) [6,7] and inductively coupled plasma mass spectrometry (ICP-MS) [8–10] have been developed and used. Although some sophisticated instrumental techniques used as standard methods in the heavy metal detection, they often possess some drawbacks including high cost of instruments, time consuming and matrix interference that limit their applications, especially in real sample analysis. Ultraviolet–visible spectrometry

(UV–Vis spectrometry), which provides significant advantages of simplicity, rapid response, the simplicity of operation and low cost, is an alternative method for the detection of heavy metals. However, the biggest disadvantage of traditional UV–Vis spectrometry is the low sensitivity which usually detects heavy metals at ppm (mg/L) level [4,11]. Therefore, separation and pre-concentration techniques are extremely needed in the situation of detecting the ppb (µg/L) level heavy metals with complicate matrix [12].

There are various methods for separation and pre-concentration of the analytes from sample matrixes, such as liquid–liquid micro-extraction [13,14], liquid–liquid extraction [15], cloud point extraction [16] and solid phase extraction (SPE) [17,18]. SPE has become a preferred method at enrichment of many metal ions prior to their analysis by other techniques, but it is tedious and time-consuming for the elution procedure of the extracted metal ions from the adsorbing material [5,19–21].

Solid Phase Extraction Spectroscopy (SPES) developed in this paper is a technique to measure spectrum directly on the solid phase material where the analytes are concentrated in SPE process. The advantages of

E-mail address: yipingdu@ecust.edu.cn (Y. Du).

SPES are less time consuming and less organic reagent consumption because of no elution. What's more, sensitivity of SPES are higher than traditional SPE because the concentrated analytes are measured in situ but not from a solution in which the analytes must be diluted. The purpose of this paper is to improve sensitivity of UV–Vis spectrometry method in the simultaneous detection of heavy metals with SPES.

Meanwhile, the simultaneous detection of ions by the use of the traditional spectrophotometry techniques is difficult because, generally, the absorption spectra overlap in a wide region and the superimposed curves are not suitable for quantitative evaluation. Some multivariate calibration methods, such as multiple linear regression (MLR), Partial least square (PLS), principal component regression (PCR) and artificial neural networks (ANNs) have been employed for simultaneous detection of metals in different matrixes [4,11,20,22–24].

This work introduced SPES that is a simple, sensitive and low cost technique for UV–Vis spectrometric simultaneous determination of cobalt (II) and zinc (II) in water samples. Cellulose acetate membrane as the SPE material with 25 mm diameter was used to enrich the interested metal ions. 1-(2-Pyridylazo)-2-naphthol (PAN) was selected as the metal complexant, which is an important reagent for the spectrophotometric determination of metal ions [25,26]. The complexes were filtered on mixed cellulose esters under a certain vacuum degree after filtering a certain amount of Brij-30 to modify the membrane. Then the spectra of the complexes were measured directly based on SPES without eluting after the filter membrane natural drying. As a multivariate method to build a spectral calibration model, PLS was used for the simultaneous detection of cobalt (II) and zinc (II). The effects of various analytical parameters including pH, the amount of PAN, sample volume, reaction time, flow rate and interfering ions on the absorbance of Co–PAN and Zn–PAN complexes were investigated. This method was successfully used in simultaneous detection of cobalt (II) and zinc (II) in drinking water samples.

2. Experimental

2.1. Instruments

A miniature fiber optic visible spectrometer USB2000 + (Ocean Optics (Shanghai) Co., Ltd.) equipped with an integrating sphere accessory was used to collect the visible spectral data from the membrane materials. The measurements of pH were made with a model PHS-25 pH meter (Mettler Toledo instrument (Shanghai) Co., Ltd.). Ultra-pure water was obtained from an ultra-pure water purification system (SARTORIUS atrium 611DI, Germany, 18.2 M Ω *cm). SHB-III Vadose water vacuum pump (Shanghai Weikai instrument equipment Co., Ltd., China) and Filtration devices (Tianjin Xinzhou Technologies Co., Ltd., China) were used for membrane filtration-enrichment.

2.2. Reagents and materials

A complexation reagent solution of PAN was prepared by dissolving 0.0040 g PAN (Aladdin Chemistry Co. Ltd) in 250 mL acetone. The stock solutions of cobalt (II) and zinc (II) at a concentration of 1.0 g/L were prepared by dissolving 0.4771 g analytical reagent grade cobalt sulfate and 0.4398 g zinc vitriol (Sinopharm Chemical Reagent Co., Ltd., China) in 100 mL water with 0.1 mL 68%(v/v) nitric acid and kept in refrigerator at 4 °C. Buffer solution for Co–PAN and Zn–PAN complexes was Tris–HCl (pH 9.0). A nonionic surfactant solution was prepared by dissolving 3.33 g Brij-30 (Aladdin Chemistry Co. Ltd) in 100 mL water. The KI, sodium potassium tartrate tetrahydrate and thiourea were analytical reagent grade, nitric acid was guaranteed reagent grade, and all of them were dissolved by ultra-pure water to obtain their solutions. Mixed cellulose membranes (Shanghai Xingya purification material factory, P.R. China) used in this study were 25 mm in diameter with the pore size of 0.22 μ m. The mineral water was purchased from local market for

detection of cobalt (II) and zinc (II) as a real sample to evaluate the developed method.

2.3. Experimental procedure

Ultra-pure water was used throughout this work. All the glasswares in the experiments were washed and soaked with 10% HNO₃ for 15 min, and then washed with ultrapure water. The solutions of appropriate concentrations of cobalt (II) and zinc (II) ions were obtained by diluting the cobalt (II) and zinc (II) stock solutions at the concentration of 1.0 g/L with ultrapure water.

For each detection, 100 mL solution spiked with a certain concentration of cobalt (II) or/and zinc (II) was prepared. And the pH of the solution was adjusted to 8.8 with Tris–HCl. Then, 1 mL PAN–acetone solution was injected into the solution reacting for 5 min under vigorous stirring to form metal–PAN complexes. After 0.5 mL Brij-30 solution passing through the mixed cellulose ester membrane, the sample solution was filtered through the membrane under a certain suction to enrich the metal–PAN complexes. Then the membrane was air-dried and the UV–Visible diffuse reflection spectrum was measured on the membrane directly in a wavelength range of 400–800 nm.

2.4. Partial least squares model for simultaneous detection

For the detection of a metallic ion, standard curve obtained at one wavelength (single variate) is needed [12,27]. But for more than one ion, multivariate calibration methods, such as principal component regression (PCR) and partial least squares regression (PLS) are often needed for simultaneous detection. PLS regression has been found important in handling regression tasks in case there are many variables (wavelengths). The theoretical basic and applications for PLS regression can be found in many literatures [4,11,22,23]. Here it is neglected to describe.

In this work, partial least squares regression (PLS) with leave-one-out cross-validation (LOO-CV) was utilized. 24 samples were used as calibration set to build PLS model, while 6 man-made samples were used as independent prediction set to evaluate the built PLS model. The performance of the final regression model was evaluated in terms of correlation coefficient, the root mean square error of cross validation (RMSECV) and root mean square error of prediction (RMSEP). The number of latent variables in PLS multivariate calibration model should be optimized by LOO-CV with the lowest RMSECV. And the lower RMSEP means better predictive ability of the model. MATLAB Version 7.0 (Mathworks) was used to write program for data analysis.

3. Results and discussion

3.1. Optimization of detecting conditions for cobalt (II) and zinc (II)

3.1.1. UV–Visible spectra of Co–PAN and Zn–PAN complexes on membrane

The visible diffuse reflectance spectra of Co–PAN and Zn–PAN complexes on membranes were recorded in the range of 400–800 nm (shown in Fig. 1). In the spectra, the peak at 475 nm is due to PAN, and Co–PAN complex has two absorption bands around 575 nm and 625 nm (Fig. 1(a)), while the peak of Zn–PAN complex locates at 550 nm (Fig. 1(b)). In order to avoid interference from PAN, the analytical bands around 625 nm and 550 nm were selected for the detection of cobalt (II) and zinc (II), respectively.

3.1.2. Effect of pH

A critical parameter for effective formation of the metal–PAN complexes in this study is pH. Because when the pH is low, the pridyl structure of PAN is protonated and while is high, the hydroxyl ions can compete with PAN for interacting with metal ions. The results given in Fig. 2 show that the maximum absorbance of complexes are found at pH = 9.0 and pH = 8.5 for Co–PAN and Zn–PAN, respectively. In

Download English Version:

<https://daneshyari.com/en/article/1228932>

Download Persian Version:

<https://daneshyari.com/article/1228932>

[Daneshyari.com](https://daneshyari.com)