

The determination of some heavy metals in food samples by flame atomic absorption spectrometry after their separation-preconcentration on bis salicyl aldehyde, 1,3 propan diimine (BSPDI) loaded on activated carbon

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Received 24 June 2007; received in revised form 30 September 2007; accepted 2 October 2007

Available online 6 October 2007

Abstract

A sensitive and simple method for the simultaneous preconcentration of Cr^{3+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} in real samples has been reported. The method is based on the adsorption of analytes on bis salicyl aldehyde, 1,3 propan diimine (BSPDI) loaded on activated carbon. The adsorbed metals on modified activated carbon were eluted using 8 mL of 2 mol L⁻¹ nitric acid in acetone or 10 mL of 4 mol L⁻¹ HNO₃. The influences of the analytical parameters including pH and sample volume were investigated. The effects of matrix ions on the retentions of the analytes were also examined. The recoveries of analytes were generally quantitative. The method has been successfully applied for these metals content evaluation in some food samples.

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Keywords: Solid phase extraction; Trace metal; Enrichment; Activated carbon; bis Salicyl aldehyde, 1,3 propan diimine (BSPDI)

1. Introduction

The determination of trace metals in the environmental samples including natural waters have been continuously performed in order to designate the level of pollution as the number of ecological and health problems associated [1–3]. The determination of elements is usually preceded by their separation from the major components of the sample, and it involves simultaneous preconcentration of the trace components. In the analysis of trace metal ions present in various samples like natural and wastewater, sediment, and tissue direct determination with some analytical techniques such as atomic absorption methods is not possible because of matrix effect of foreign ions and low concentration of metal ions in the sample and the low selectivity and sensitivity of analytical techniques. It is a necessity to preconcentrate the trace elements before their analysis to

enhance the concentration of the analyte ions to be determined [2–5].

In fact, solid phase extraction has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes [6,7]. It has several advantages over other techniques, including stability and reusability of the solid phase, reach of high preconcentration factors, easiness of separation and enrichment under dynamic conditions, no need for organic solvents and minimal costs due to low consumption of reagents. Several selective solid phase extractors have been prepared either by physical loading or chemical binding of selected chelating reagents to different solid supports such as silica gel [8,9], activated carbon, [10,11], SDS-coated alumina [12], modified chromosorb [13], ion-imprinted polymers [14], Amberlite XAD-2000 resin [15] and Sepabeads SP70 [16].

Activated carbon is widely used a trace collector for multi-element preconcentration in analysis of water, high-purity substances, vegetable sample, etc. There are general approaches to metal preconcentration using activated carbon from aqueous solutions by simply adjusting the pH to an adequate value

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and by using chelating agent [17,18]. The disadvantage of these procedures is that it requires a series of complexation steps. For this reason, the use of chelating activated carbon has been recently proposed [19–22]. Metal chelates could provide higher selectivity and high enrichment factor for such a separation and preconcentration techniques. According to our literature survey, there is no study found about bis salicyl aldehyde, 1,3 propan diimine (BSPDI) loaded on activated carbon for preconcentration and separation of trace metal ions.

The purpose of this work is preconcentration-separation of Cr^{3+} , Fe^{3+} , Cu^{2+} , Ni^{2+} , Co^{2+} and Zn^{2+} on activated carbon modified with BSPDI. The influences of the some analytical parameters including pH and sample volume on the quantitative recoveries of the analytes were investigated.

2. Experimental

2.1. Instruments

The measurements of metal ions were performed with a Perkin-Elmer 603 atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths (resonance line) using an air–acetylene flame. The instrumental parameters were those recommended by the manufacturer. A Metrohm 691 pH/Ion meter with a combined glass–calomel electrode was used for adjustment of test solution pH. The open microwave system was purchased from Daewoo company (Korea) model KOC-1BOK with following information: 220–240 V, 50 Hz. Microwave input power, 1500 W; microwave grill 1500 W; microwave convection and combination 2300 W; microwave energy input 1000 W.

2.2. Reagents

Acids and bases were of the highest purity available from Merck and were used as received. Doubly distilled deionized water was used throughout. Nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium from Merck were of the highest purity available and used without any further purification. The pH adjustment was done by addition of dilute nitric acid or sodium hydroxide to phosphate solution for preparing the desired pH buffer solution. Activated carbon (AC) (gas chromatographic grade, 40–60 mesh from Merck), were soaked in hydrochloric acid for 2 days, it was then washed with water and dried at 110 °C for 1 day.

The Schiff base ligand in this research was prepared according to the literature by condensation of 1,2-ethylene-diamine with the appropriate amount of 2-hydroxyacetophenone (1:2 mol ratio) [23,24].

2.3. Preparation of BSPDI coated on activated carbon

A Pyrex glass column containing 0.5 g of activated carbon in water suspension was 40 cm long and 0.75 cm in internal diameter. The bed height in the column was approximately 1 cm. The AC (500 mg) was impregnated with BSPDI by percolating

4 mL of 1% (w/v) BSPDI (50 mg) solution through the column packed with AC at a flow rate of 2 mL min⁻¹.

2.4. Preconcentration procedure

The pH of the solution was adjusted to 9.0 with KOH and passed through the BSPDI-loaded AC column at a flow rate of 2 mL min⁻¹ with the aid of a suction pump. The analyte was then eluted with 10 mL of 4.0 mol L⁻¹ HNO₃ or 8 mL of 2 mol L⁻¹ nitric acid in acetone. The metal ions content of the eluent was measured by FAAS.

2.5. Pretreatment of real samples

The cow meat and fish samples were digested as following. Five grams of meat or fish samples was weighted accurately in a beaker and then 20–25 mL H₂SO₄, was added. Then for the microwave digestion of cow meat and fish samples, the above mixture was digested with 4 mL of concentrated HNO₃ and 2 mL of concentrated H₂O₂ in microwave system. After digestion completed, the volume of the digested sample was made up to 250 mL with distilled water. Blanks were prepared in the same way as the sample, but omitting the sample. The preconcentration-separation procedure given above was applied to the samples.

The spinach sample was digested according to literatures [27,28]. Leaves of spinach were purchased from Firouzabad, Iran. Afterwards, they dried and were taken in small mesh. A 40 g leaves of spinach was heated in silica crucible for 3 h on a hot plate and the charred material was transferred to furnace for overnight heating at 650 °C. The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3 mL 30% H₂O₂ again kept in furnace for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated hydrochloric acid and 2–4 mL 70% perchloric acid and evaporated to fumes, so that all the metals change to respective ions. The solid residue was dissolved in water, filtered and by keeping the pH at 9.0 made up to 250 mL by addition of diluted KOH. The preconcentration-separation procedure given above was applied to the samples.

The liver sample was digested according to literatures [27,28]. A 50 g of liver were taken and dried for 48 h in an oven at 120 °C to remove the water content and to obtain constant weight (about 68% water). Dried liver sample transferred into a glass flask. For the digestion of the sample, a concentrated acid mixture of 3 mL H₂SO₄, 15 mL HClO₄, and 15 mL HNO₃ was added and left to stand over night. The solution was kept in an oil bath at 50 °C until the foaming stopped. Then the temperature was increased to 150 °C and heating was continued until the evolution of brown fumes of nitrogen oxides ceased. When a dark brown in mixture was appeared, the flask was cooled for about 2 min then a 5 mL of nitric acid had to be added. Heating was continued until nitrogen oxides fumes were longer given off. Appearance of white fume of perchloric acid in 1 mL solution is an indication of complete digestion. Then the preconcentration-separation procedure given above was applied to the samples.

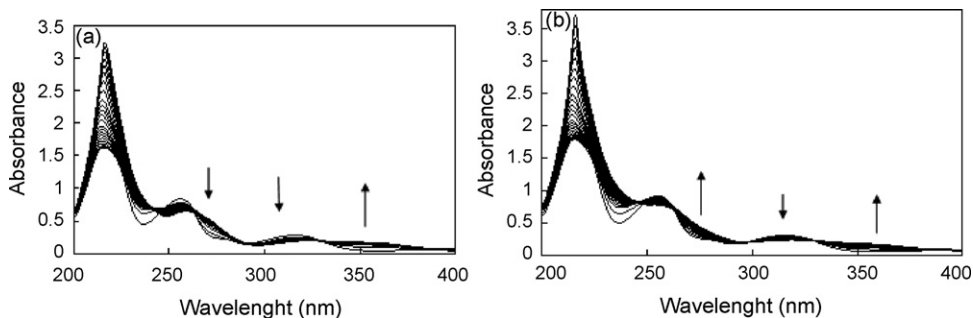


Fig. 1. Spectra of complex of BDSPI ($1 \times 10^{-3} \text{ mol L}^{-1}$) with zinc (a) and cobalt (b) ion ($1 \times 10^{-3} \text{ mol L}^{-1}$) in methanol in different mole ratio.

3. Results and discussion

In preliminary experiments, it was observed that the preconcentration of the metals with the untreated AC is not suitable for Co, Ni, Cu and Pb. Therefore, DHMP-AC seems to be a better sorbent in simultaneous sorption of the studied elements. In order to show that complexation between ions and BSPDI is responsible for selective, sensitive and reversible preconcentration of mention ions, the zinc and cobalt complexation with ligand, as model has been investigated. Since these mention ions have similar property, similar results for other can be achieved. In preliminary experiments typical complexation between zinc and cobalt ion and BDSPI was examined using spectrophotometry, and the nature of respective complex was investigated. In order to confirm this result and ascertain the nature and structure of the extracted species, to the fixed amount of BDSPI different mole ratio of zinc and cobalt ion was added and corresponding data are presented in Fig. 1. Therefore, complexation is responsible for desired ion preconcentration. The DHMP-AC can retain all the metal ions while the untreated AC cannot quantitatively retain desired ions.

3.1. Effect of pH

In the solid phase extraction studies, pH of the working solution is main factor for the quantitative adsorption of analytes on solid phase [25–29]. In order to optimize the sorption conditions for the retention of the ions on modified AC, the effects of pH was investigated in the pH range of 1–11 by using column

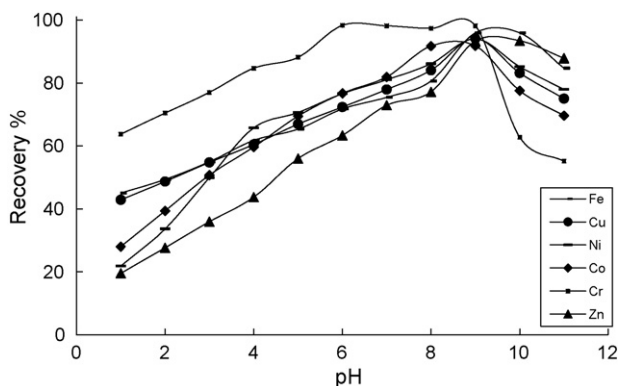


Fig. 2. Effect of pH on recovery of metal ions ($N=3$).

packed with 0.5 g modified AC. Fig. 2 shows that the optimal pH values were in 9.0. Considering these results, the pH 9.0 has been recommended for subsequent experiments.

3.2. Effect of the amount of activated carbon

In the adsorption step, an appropriate amount of activated carbon 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 amounts of activated carbon filled to the column were also investigated. The results are given in Fig. 3. The recoveries of analytes were increased with increasing amounts of AC and reach to constant and quantitative value of 0.5 g of activated carbon.

3.3. Effect of ligand concentration

The amount of ligand on the preconcentration studies is also another main factor [16,30–34]. In order to investigate the optimum amount of ligand on the quantitative extraction of these ions by the activated carbon, these ions extraction was conducted by varying the amount of ligand from 0 to 60 mg. The recoveries of analyte ions without ligand were not quantitative. The results showed that with increasing amount of ligand up to 50 mg an increase in recoveries can be achieved and further increase does not mentionable change in efficiency. Quantitative recoveries for the analytes were obtained after 50 mg of BSPDI. Subsequent

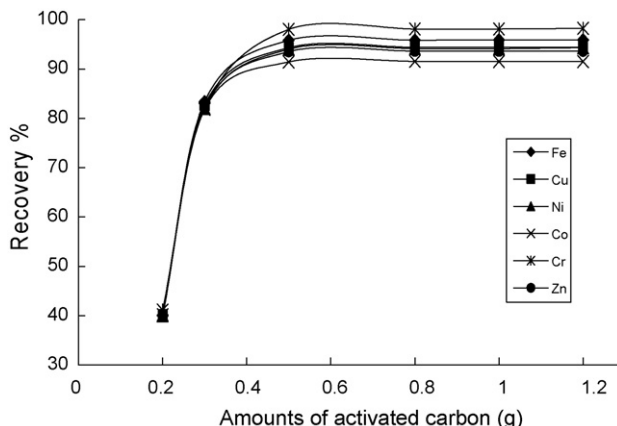


Fig. 3. Effect of amount of activated carbon on recovery of metal ions ($N=3$).

Table 1
Effect of type and concentration of eluting agent on recovery of analytes

Eluting solution	Recovery, %					
	Fe ³⁺	Cu ²⁺	Ni ²⁺	Co ²⁺	Cr ³⁺	Zn ²⁺
1 mol L ⁻¹ HNO ₃	40	40	40	40	41	40
2 mol L ⁻¹ HNO ₃	73	73	72	72	72	72
3 mol L ⁻¹ HNO ₃	86	84	84	81	88	84
4 mol L ⁻¹ HNO ₃	96	94	94	91	98	94
5 mol L ⁻¹ HNO ₃	93	94	93	92	97	94
1 mol L ⁻¹ HNO ₃ in acetone	98	98	96	99	87	98
2 mol L ⁻¹ HNO ₃ in acetone	98	98	96	98	94	97
3 mol L ⁻¹ HNO ₃ in acetone	93	93	71	93	92	93

studies for further experiments were carried out with 50 mg of ligand.

3.4. Selection of eluent and optimization of its concentration

For selection of the best eluent, various acidic solutions on the preconcentration yields of the metals were studied under the optimum conditions. Especially, the nitric acid with acetone provided higher recovery efficiency compared to the acids in aqueous solutions (Table 1). The experiments were carried out for selecting the concentration of nitric acid solution in acetone. HNO₃ solutions in acetone at the concentrations between 1.0 and 3.0 mol L⁻¹ were studied for this purpose. The recovery values were increased with adding nitric acid to acetone. After 2.0 mol L⁻¹ HNO₃, the analytes were quantitatively recovered. The optimum nitric acid concentration was determined as 2 mol L⁻¹ HNO₃ in acetone (Table 1). The optimum eluent volume is specified as 10 mL of 2 mol L⁻¹ HNO₃ in acetone for the subsequent studies.

3.5. Flow rates

The effects of the sample and eluent flow rates on the retentions and recoveries of analyte ions on the adsorbent were also examined in the flow rate range of 0.5–5 mL min⁻¹ under optimal conditions with model solutions containing analyte elements. All the analyte ions were quantitatively retained and recovered in the sample and eluent flow range of 0.5–2 mL min⁻¹. After 2 mL min⁻¹, the recoveries were not quantitative due to insufficient contact between analytes and adsorbent. In the all-further works, 2 mL min⁻¹ was selected as sample and eluent flow rate.

3.6. Interferences

In order to assess the possible analytical applications of the preconcentration procedure presented, the effect of some foreign ions which interfere with the determination of trace of these ions or/and often accompany analyte ions in various real environmental samples was examined with the optimized conditions. The results are summarized in Table 2. The tolerance limit is defined as the ion concentration causing a relative error smaller

Table 2
Effects of the matrix ions on the recoveries of the examined metal ions (N=3)

Interference ions	Tolerance limit (mg L ⁻¹)					
	Fe ³⁺	Cu ²⁺	Ni ²⁺	Co ²⁺	Cr ³⁺	Zn ²⁺
Na ⁺ , K ⁺ , Li ⁺ , Ba ²⁺ , Ca ²⁺ , Mg ²⁺ , Bi ³⁺	1000	1000	1000	1000	1000	1000
Pb ²⁺	500	1000	1000	1000	1000	1000
Cd ²⁺ , Sn ²⁺ , Hg ²⁺	750	750	750	750	750	750
Ag ⁺	800	800	800	800	800	800
Mn ²⁺	500	500	500	500	500	500

than ±5% related to the preconcentration and determination of analytes. The tolerable levels of the some heavy metal ions are suitable for the separation and preconcentration of ions in the real samples examined present study, because of the levels of transition metals in these samples are lower than their interferic level. It can be seen that the major matrix ions in the food and natural waters show no obvious interference with the preconcentration of mention ions.

3.7. Effect of the sample volume on the metal sorption

In order to obtain high preconcentration factor, volume of the sample is also an important analytical factor [35–40]. The maximum sample volume was optimized by the investigation of the recovery of trace metals in various sample volumes in the range 250–2000 mL. The recoveries of the metal ions are shown in Fig. 4. The recoveries were found to be stable until 1750 mL and were chosen as the largest sample volume to work. In this study, the final solution volume to be measured by FAAS was 10.0 mL, therefore the preconcentration factor for six metal ions is 175.

3.8. Adsorption capacity

The adsorption capacity is the maximum metal quantity taken up by 1 g of adsorbent and given by mg metal g⁻¹ adsorbent [15]. In order to determine this, test solutions of analytes weighing in the range 100–10,000 µg were loaded to the column and then

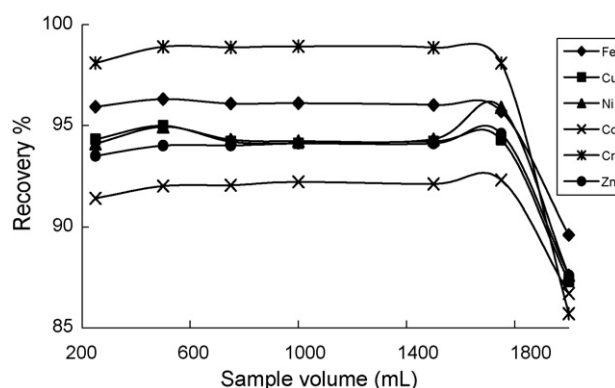


Fig. 4. Effect of sample volume on trace ion recovery.

Table 3
Specification of presented method at optimum conditions for each element ($N=10$)

Parameters	Fe ³⁺	Cu ²⁺	Ni ²⁺	Co ²⁺	Cr ³⁺	Zn ²⁺
Linear range ($\mu\text{g mL}^{-1}$)	0.02–0.8	0.02–0.8	0.02–0.8	0.02–0.8	0.02–0.8	0.02–0.8
Detection limit (ng mL^{-1})	0.28	0.27	0.29	0.30	0.28	0.33
Adsorption capacity (mg g^{-1})	2.1	2.1	2.1	2.1	2.1	2.1
R.S.D. %	0.45	0.09	0.02	0.57	0.83	0.87
Recovery %	97.5	97.0	95.9	97.5	91.5	92.9

Table 4
Recovery studies of trace metal ions in fish sample

Ion	Added (ng g^{-1})	Found (ng g^{-1})	R.S.D. %	Recovery %
Fe ³⁺	0	22.5	1.5	–
	10.0	32.26	1.1	97.5
Cu ²⁺	0	12.2	1.6	–
	10.0	21.86	1.3	96.5
Ni ²⁺	0	0.55	1.6	–
	10.0	10.3	1.2	97.5
Co ²⁺	0	0.80	1.7	–
	10.0	0.205	1.4	97.5
Cr ³⁺	0	10.25	1.6	–
	10.0	15.87	1.1	97.0
Zn ²⁺	0	4.5	1.6	–
	10.0	14.1	1.2	96.0

Table 6
Recovery studies of trace metal ions in spinach sample

Ion	Added (ng g^{-1})	Found (ng g^{-1})	R.S.D. %	Recovery %
Fe ³⁺	0	37.6	1.0	–
	1.25	38.9	0.80	104.0
Cu ²⁺	0	1.47	1.5	–
	1.25	2.70	1.1	98.4
Ni ²⁺	0	0.1	1.4	–
	1.25	1.30	1.1	96.0
Co ²⁺	0	0.1	1.6	–
	1.25	1.24	1.2	98.3
Cr ³⁺	0	1.0	1.5	–
	1.25	2.3	1.1	96.1
Zn ²⁺	0	0.1	1.6	–
	1.25	1.39	1.2	103.2

the recovery values were investigated. The adsorption capacities of sorbent were given for each metal ion in Table 3.

3.9. Investigation of method performances

By passing 250 mL solution of 0.02–2.00 $\mu\text{g mL}^{-1}$ all mention ions, the calibration curves, repeatability and reproducibility were obtained. The effluent was sent to AAS for evaluating ions content. The characteristic performances of method which presented in Table 3 show good linear range, low detection limits, high reproducibility and low relative standard deviation for all elements.

Table 5
Recovery studies of trace metal ions in meat sample

Ion	Added (ng g^{-1})	Found (ng g^{-1})	R.S.D. %	Recovery %
Fe ³⁺	0	118.7	1.4	–
	10.0	128.3	1.1	97.0
Cu ²⁺	0	10.6	1.6	–
	10.0	20.2	1.4	96.0
Ni ²⁺	0	3.1	1.7	–
	10.0	12.9	1.4	98.0
Co ²⁺	0	1.0	1.8	–
	10.0	11.6	1.4	106.0
Cr ³⁺	0	9.4	1.6	–
	10.0	19.0	1.1	96.0
Zn ²⁺	0	13.1	1.7	–
	10.0	22.8	1.2	97.0

Table 7
Recovery studies of trace metal ions in cow liver sample

Ion	Added (ng g^{-1})	Found (ng g^{-1})	R.S.D. %	Recovery %
Fe ³⁺	0	11.85	1.6	–
	1.0	12.90	1.1	105.0
Cu ²⁺	0	2.11	1.5	–
	1.0	3.12	1.2	101.0
Ni ²⁺	0	0.4	1.6	–
	1.0	1.36	1.2	98.0
Co ²⁺	0	0.11	1.5	–
	1.0	1.13	1.2	102.0
Cr ³⁺	0	1.55	1.3	–
	1.0	2.57	1.1	102.0
Zn ²⁺	0	1.10	1.4	–
	1.0	2.12	1.1	102.0

3.10. Accuracy and applications

In order to assess the applicability of the method to real samples, with different matrices containing varying amounts of a variety of diverse ions, it was applied to the separation and recovery of ions from different matrices such as vegetable, fish, meat and liver. Spiking experiments using standard addition method checked reliabilities. The percent of recoveries and relative standard deviation for each element in spiked real samples are given in Tables 4–7. As it can be seen, the results of three analyses of each sample show that, in all cases, the ions recoveries is almost quantitative with a low R.S.D.

4. Conclusion

A new method was developed for the determination of trace metals. The procedure offers a useful multi-element preconcentration technique in various samples including vegetable, fish, meat and liver samples with acceptable accuracy and precision. The other main advantages of the method include simplicity, time saving, no requirements of sophisticated instruments, and cost effectiveness. Modified activated carbon on the column could be used all through the studies without any loss of its adsorption properties. The possibilities of using the extraction system in modified AC for the preconcentration and separation of the metallic cations in solutions with relatively high contents of salts are extended.

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