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Chemically modified activated carbon with ethylenediamine for selective solid -phase extraction of Cr (III) and Fe (III)

H.Tavallali*, A. Daneshyar

Department of Chemistry, Faculty of science, Islamic Azad University, Omidiyeh branch, Omidiyeh, IRAN

****Corres.author: tavallali@yahoo.com, Tel-fax: +98-711-6222284***

Abstract : Carbon active chemically bonded ethylenediamine as one sorbents successfully were applied for the enrichment of trace amount of some metal ions. The influences of the variables including pH, amount of solid phase, sample flow rate, type and condition of eluting solution and sample volume on the metal ions recoveries were investigated. The method has high sorption-preconcentration efficiency even in the presence of various other ions due to their high selectivity, while the relative standard deviation of recoveries of all understudy metal ions was found to be less than 2.8%, especially for their determination in real samples.

Keywords: Carbon active; chemically bonded; ethylene diamine ; Solid phase extraction.

1. Introduction

The toxicity and the influence of trace amount of metal ions is very important in the contex of pollution and nutritional fields view. Modern and even sensitive analytical methods especially flame atomic absorption spectroscopy (FAAS) as low cost even accessible instrument fail to directly determine trace amount of metal ions in various environmental and biological complicated matrices samples due to their inadequate detection limits and interference from various species [1-3]. These difficulties efficiently can be couple with doing a preliminary separation and/or preconcentration procedure prior to measurement to decrease the matrices interference or improve detection limit [4-7].

Solid phase extraction (SPE) which is based on selective and reversible binding of analytes to a modified solid support and their subsequent elution with a small volume of solvent, efficiently improve the selectivity and sensitivity of method. Among the various sorbents carbon active chemically bonded with various organic compounds has received great attention due to its good mechanical and thermal stability, less susceptibility to swelling and shrinking [8]. The selectivity pattern of such sorbent to words metal ions depends to size of the modifier and activity of the loaded group based on hard-soft and/or acid-base concept. Due to large number of reactive sites on carbon active, it surface can be efficiently modified by chemical reaction with various organic compounds.

In present work, Carbon active chemically bonded ethylene diamine have been used for the preconcentration and separation of Cr(III) and Fe(III) to their determination by FAAS.

2. Experimental

2.1. Apparatus

The measurements of metal ions were performed with a Perkin-Elmer AA Analyst 300 (Shelton USA) equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths 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.

2.2. Reagents and materials

All applied chemicals were of analytical reagent grade purchased from Merck, dermasdut Germany; while all experiments were conducted using double-distilled deionized water. All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1:9) and were rinsed with distilled water prior to use. Stock solutions of diverse elements were prepared from high purity compounds. The pH was adjusted by addition of dilute choleric acid or sodium hydroxide to analytes solution.

2.3. solid -phase preparation

Carbon active (10.0 g) with ethylene diamine (150 mL) under reflex 48 h at 60 ^{0}C temperature were done. Then, the mixture was filtered and washed with nitric acid (3 mol L^{-1}). After drying in vacuum oven Carbon active chemically bonded ethylene diamine (AC-EDA) was obtained as dark solid (1.1 g).

2.4. Test procedure

250 mL of 0.5 µg mL^{-1} of the understudy metal ions at pH 8.0 was passed through solid -phase containing 1.5 g of AC-EDA. After elution of retained metal ions their content was efficiently eluted and determined by FAAS.

2.5. Application

5 g of soil and 10.0 g vegetable spinach was collected from the city of Omidiyeh, IRAN. Then these real samples were through shrink and washed with nitric acid.

3. Results and Discussion

3.1. Effect of pH

The affinity and applicability of each sorbent for selective preconcentration and efficient of some metal ions in the presence of coexisting metal ions depend significantly to the nature of the surface function groups of support and solution pH [9]. The pH value significantly influence the extractability of metal ions by the proposed sorbent due to competitive reactions between chelate functional groups and hydrogen ions in solution.

The effect of sample solution's pH on the sorption recoveries of target analysts within the range of 2-10 was examined and respective results for both sorbents are presented in Fig. 1. As it can be seen at pH < 8 a weak complexation and sorption occurs; which is explained by competition between metal ions and hydrogen ions for the binding to sorbent. On the other hand by increasing the pH, the potential of active sites of sorbent functional group for binding metal ion will be increased. Therefore, the pH 8.0 was chosen throughout the subsequent experiments. At higher pH probably due to formation of insoluble $M(OH)_n$ or $M(OH)^+$ the recoveries significantly will be decreased.

3.2. Effect of amount of solid phase on metal ions recoveries

The lipophilicity of sorbent and the equilibrium constant of its complex with target analytes and the kinetics of their reaction transference between the phases are important factor which significantly influence the metal ions recoveries [10-11]. In this a set of similar experiments was conducted by passing 250 mL of 0.5 µg mL^{-1} of understudy metal ions at pH 8.0 composed of different amount of AC-EDA and finally the retained metal ions efficiently was eluted and evaluated by FAAS which respective results are in Fig. 2.

At higher amount of solid phase probably due to insufficiently of eluent or formation of charged complexes recoveries were decreased. With a lower amount, the extent of complexation and retention of metal ions on the loaded solid phase is low and hence the recoveries were decreased. Therefore 1.5 g of adsorbent was selected for further study.

3.3. Sample and eluent flow rate

The sample and eluent flow rates control the contact time between the sample solutions and the sorbent. The influences of the sample flow rates on the metal ions recovery were examined with sample flow rates in the range of 1–5 mL min^{-1} and it was seen that flow rate variations in the range of 1–4 mL min^{-1} had no significant effect on the sorption of the all metal ions and further addition lead to decrease in metal ions recoveries. All further studies were performed at 4.0 mL min^{-1} flow rates for sample solutions.

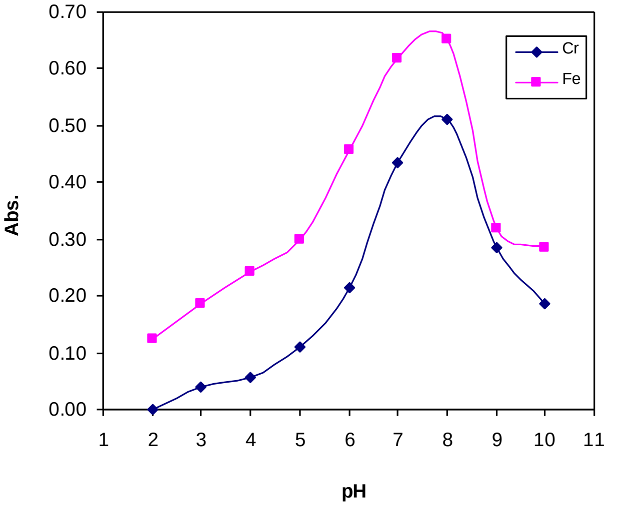

Fig.1. Effect of pH on metal ions recovery Cr^{3+}, Fe^{3+}

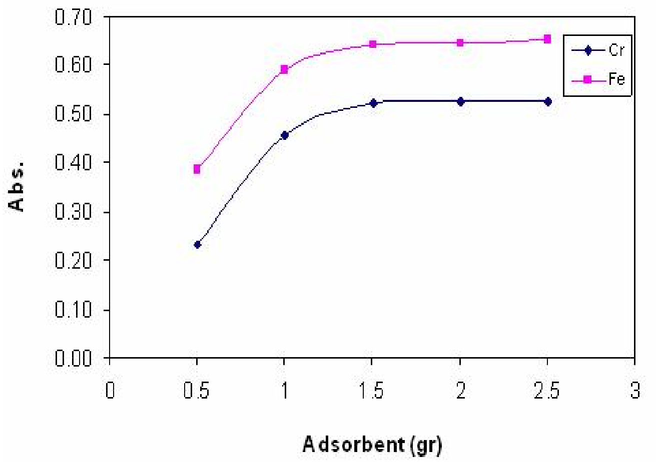

Fig.2. Effect of amount of solid phase on metal ions adsorption Cr^{3+}, Fe^{3+}

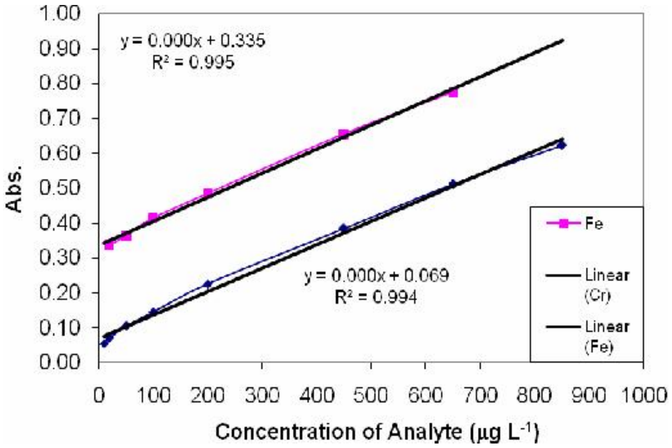

Fig.3. Effect of volume eluting solution on metal ions adsorption Cr^{3+}, Fe^{3+}

3.4. Condition of eluent

The eluent type is an important factor in solid-phase extraction studies. The effect of 5 mL of various eluents including acetic acid, phosphoric acid, sulfuric acid, nitric acid and hydrochloric acid on the recoveries of understudy metal ions was studied. The adsorbed understudy metal ions were eluted using 5 mL of 3.0 M of the above selected eluents and the amount of understudy metal ions back-extracted metal ions was measured using FAAS. The results showed that maximum recoveries were obtained using acetic acid and nitric acid for AC-EDA respectively (Table 1). The acid concentration was an important factor while high acid concentration affects the determination step due to the contamination from applied acid [12].

The influence of the concentration of nitric acid on the elution of these ions was studied. As it is shown in Table 1 with increasing nitric acid concentration till 4.0 mol L^{-1} the extraction efficiency increased recovery of understudy metal ions.

In order to achieve a high preconcentration factor, the retained metal ions in large sample volume must be quantitatively eluted by a small amount and volume of agent. This was examined using various volume of nitric acid or acetic acid in the range of 5-9 mL and respective results are presented in Table 1. As it can be seen quantitative recoveries of understudy metal ions could be obtained with 5.0 mL of 3.0 mol L^{-1} nitric acid which these eluents was used for subsequent work.

3.5. Effect of sample volume

To obtain reliable and reproducible analytical results it is very important to get satisfactory recoveries for all the compounds studied from large volume of sample solutions. To determine the maximum volume, different volumes of sample solution at pH 8.0. In order to explore the possibility of enriching low concentration of the analyte from large volume of solution, the effect of sample volume on the retention of metal ion was investigated. The results showed that the maximum sample volume could be up to 450 mL with the recovery >95%. Therefore, 450 mL of sample solution was adopted for the preconcentration of analytes from sample solutions.

Table 1: Kind of eluent on metal ion recovery.

Condition of eluent	Recovery(%)	
	Cr	Fe
CH_3COOH	65	43
H_2SO_4	78	65
H_3PO_4	85	81
HCl	85	83
HNO_3	97	98
HNO_3 2M	91	85
HNO_3 3M	96	96
HNO_3 4M	96	97
5 mL HNO_3 3M	96	95
7 mL HNO_3 3M	88	85
9 mL HNO_3 3M	74	72

3.6. Interference

To assess the possible analytical applications of the recommended procedure, the effect of some foreign ions (which interfere with the determination of metal ions) often accompany analyte ions in various real samples was examined with the optimized conditions above. For these studies, a fixed amount of metal ions was taken with different amounts of foreign ions and recommended procedure was followed. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated analyte ions by the combination of the proposed solid phase extraction and the flame atomic absorption spectrometric determination methods. The recoveries of metal ions in these studies were higher than 95% and respective results are summarized in Table 2. As it is seen, large numbers of ions used have no considerable effect on the determination of analyte ions.

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

Matrix ions	Recovery(%)
Sn^{2+}, $Na^{+,}$, K^{+}, Al^{3+}, Cu^{2+}, Zn^{2+}	700
SO_4^{2-}, PO_4^{3-}, Cl^{-}, CO_3^{2-}, Br^{-}	1000

3.7. Analytical features

By applying the optimum experimental conditions, the characteristics performance of the method is presented in Table 3.

The limit of detection (LOD) of a method is the lowest analyte concentration that produces a response detectable above the noise level of the system, Typically, the limit of detection is three times the standard deviation of the blank (n = 10), was found to be 1.5and 2.7 µg mL^{-1}for Cr^{3+} and Fe^{3+} ions respectively .

Table 3:Specification of presented method at optimum conditions for each element.

Parameters	Cr	Fe
Linear Range (µg mL^{-1})	10-850	20-650
Detection Limit (ng mL^{-1})	1.5	2.7
RSD (repeatability) (%)	2.8	1.7

3.8. Application to environmental samples

We have explored the feasibility of the methodology given in Section 2.6 using preconcentration with chemically bonded Carbon active for the determination of understudy metal ions in different environmental matrices including soil and vegetable spinach by standard addition method. Reliability was checked by spiking experiments and independent analysis and results are presented in Table 4. The recovery of spiked samples is satisfactorily reasonable and was confirmed using standard addition method, which indicates the capability of the system in the determination of the understudy metal ions. A good agreement was obtained between the added and measured analyte amounts. The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects.

Table 4: Specification of presented method at optimum conditions for each element.

Ion	soil		
	Added(µg)	Founded (µg)	% Recovery
Cr	0	---	---
	200	204	102
Fe	0	---	--
	200	205	102.5
Ion	spinach		
	Added(µg)	Founded (µg)	% Recovery
Cr	0	---	---
	100	96	96
Fe	0	170	---
	100	265	95

3.9. Comparison with literature

A comparison of the proposed system with other preconcentration procedures using several sorbents is given in Table 5 [13-16]. As Table 5 shows, the proposed method shows comparable capacity level, lower detection limit, and wider linear range and is a convenient, safe, simple, rapid and inexpensive method for the determination of trace quantities of these cations in real samples with satisfactory results. The proposed preconcentration system shows good preconcentration factors with reasonable preconcentration time over other preconcentration methods. As seen from the Table 5, the detection limit for proposed method was comparable to those given by many methods.

Table 5: Comparative from some studies for preconcentration of trace metals using SPE.

Studied metals	Sorbent	RSD	LOD(µgL^{-1})	PF	References
Cu, Cd, Pb, Zn, Ni, Co	Chromosorb 108/bathocuproine disulphonic acid	1-17	0.16-0.60	80.0	Tuzen et al.
Co, Ni	5,7-Dichloroquinolinone-8-ol embedded styrene-ethyleneglycol dimethacrylate polymer	4.7-6.3	4.10-13.60	20.9	Praveen et al.
Cd	IL-silica	3.70 <	0.60	75.0	Liang
Cu, Co, Ni, Cd	2,4,6-Trimorpholino-1,3,5-triazin bonded silicagel	1.65-2.95	0.20-0.30	50-100	Madrakian
Fe, Cr	AC-EDA	1.7-2.8	1.5-2.7		This Work

4. Conclusions

In the presented study, two new sorbents was prepared and developed for the preconcentration of metal ions including of Fe^{3+}, Ni^{2+}, Cd^{2+} and Zn^{2+} ions in environmental samples prior to their determination by FAAS. The method is simple, accurate, and economical and can be applied for the determination of these ions in environmental samples. The system showed reproducibility and reliability in analytical data, with an R.S.D. value of lower than 5% on triplicate experiment and can be used as high as greater than 10 experiments without any loss in its sorption behavior. The system was successful in preconcentration of analytes from large sample volume.

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