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Trace metal enrichment using gold nanoparticle loaded on activated carbon modified with 1-((6-(-(2,4-dihydroxybenzylideneamino))hexylimino) methyl)benzene-2, 4-diol

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Abstract

In this study, a new sorbent based on the modification of gold nanoparticle loaded on activated carbon (Au-NP-AC) with 1-((6-(-(2,4-dihydroxybenzylideneamino))hexylimino) methyl)benzene-2, 4-diol (DHBAHMB) was synthesis and its efficient application for trace metal enrichment was examined. The proposed sorbent (Au-NP-AC-DHBAHMB) has been applied for enrichment and preconcentration of trace amount of Cu^{2+}, Fe^{3+} and Zn^{2+} ions in real samples. The metal ions retained on proposed sorbent via chelation with the DHBAHMB efficiency was eluted by HNO_3 and detected by FAAS. The effect of analytical parameters including pH, amount of ligand and solid phase and the conditions (type, concentration and volume of eluent) of the eluent were optimized. Following optimization of variables, preconcentration factors of 165, 170 and 180 for Cu^{2+}, Fe^{3+} and Zn^{2+} metal ions, respectively, with detection limits of 1.4-2.6 ng mL^{-1}. The method has been applied for the extraction and determination of the ion content in same real sample with recoveries in range of 95-99.6 % and a relative standard deviation of (RSD lower than 4.0 %).

Keywords: 1-((6-(-(2,4-dihydroxybenzylideneamino))hexylimino) methyl)benzene-2, 4-diol (DHBAHMB), Gold nanoparticle, Activated carbon, Au-NP-AC.

Introduction

Generally, metals are potentially toxic to living organisms at variable concentrations. Heavy metals and metalloids (mostly not required for metabolic activities) are toxic to the cell at quite low concentrations. Heavy metals enter food chain via bioaccumulation from the contaminated water, soil and air. Therefore, their separations and determination is at great risk. Accurate determinations of trace heavy metals by atomic absorption spectrometry (AAS) methods is a difficult task for the analytical chemist because of their low concentrations in real samples and also matrix ions influence in the analysed samples (Tuzen *et al*., 2005; Yaman, 2005; Tuzen & Soylak, 2009; Hassanien, 2010). Although ICP-MS is quite sensitive analytical technique, the matrix effect may preclude direct analysis by ICP-MS or other techniques. Therefore, it is required to perform a prior separation procedure before measurement. Among the different applied separation and preconcentration techniques, chelating solid phase extraction (SPE) especially those based on nanoparticle based sorbent is preferred due to their high surface area, low risk of contamination, being environmentally safe, ability for recovery and reuse, being readily available or easily synthesized and proven good stability, high sorption capacity for metal ions, appreciable selectivity, and good flexibility in working conditions. The main requirements with respect to substances to be used as SPE adsorbents are as follows (Divrikli *et al*., 2007) possibility of extracting a large number of elements over a wide pH range, fast and quantitative sorption and elution, high capacity, regenerability and accessibility.

Nanoparticles (NPs), i.e. particles with the dimensions in the range of units to hundreds of nanometers, recently attract an extensive attention in various fields of chemistry due to their unique physical and chemical properties (Tuzen *et al*., 2005; Yaman, 2005; Divrikli *et al*., 2007; Tuzen & Soylak, 2009; Hassanien, 2010). NPs usually refer to a kind of material with a spherical-like appearance with a large surface-to-volume ratio and other fascinating properties derived from the ‘‘quantum size effect’’ (Purna *et al*., 2006). With the recent advances in nanotechnology, nanomaterials have received great interests in the field of biosensors due to their exquisite sensitivity in chemical and biological sensing (Duran *et al.,* 2007; Ghaedi *et al.,* 2007).

Experimental

Instruments

The measurements were performed with a Perkin-Elmer AA Analyst 300 (Shelton Ct, USA) atomic absorption spectrometer equipped with a hollow cathode lamp and a deuterium background corrector at respective wavelengths using an air-acetylene flame at instrumental parameters according Table 1. A Metrohm 691 pH/Ion meter with a combined glass-calomel electrode was used pH adjustment of sample solution (Ghaedi *et al*., 2009).

Table 1. Parameters of atomic absorption spectrometric study

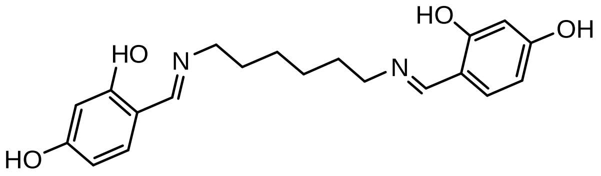
Element	Wavelength	Signal	Slite	Oxid	Energy	Fuel
Cu	324.8	AA	0.7	10	68	3
Zn	213.9		0.7	10	73	3
Fe	248.3		0.2	10	51	3

Reagents and solutions

Acids and bases were of the highest purity available from Merck (Dermasdat, Germany) was used as received. Double distilled deionized water was used throughout. Nitrate salts of lead, cadmium, mercury, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, silver, sodium and potassium as their nitrate salt were of the highest purity available and used without any further purification. The pH adjustment was done by the addition of diluted nitric acid or sodium hydroxide to sample solution. Activated carbon (AC) (gas chromatographic grade, 50-70 mesh from Merck) soaked in hydrochloric acid for 2 days and then washed with water and dried at 110°C for 1 day. At first activated carbon, powder was subjected to purification with 10% (v/v) hydrochloric acid solution for 24 h to remove adsorbed impurities and metal ions. Then, it was filtered, washed with distilled deionized water, and dried at 80 °C for 5 h (Ghaedi *et al.,* 2008).

Preparation of 1-((6-(-(2,4-dihydroxybenzylideneamino)) hexylimino) methyl)benzene-2, 4-diol

An ethanolic solution of hexane-1, 6-diamine (0.581 g, 5 mmol) was added to a solution of 2,4-dihydroxybenzaldehyde (1.38g, 10 mmol) in absolute ethanol (20 mL) and refluxed for 4 h. After several hours and evaporation of solvent, the product was obtained as yellow precipitate. The powder was filtrated and washed twice with cooled ethanol and dried under air (74 % yields). Elemental analysis, % $C_{20}H_{24}N_2O_4$: C, 67.40; H, 6.79; N, 7.86; found: C, 68.9; H, 6.7; N, 7.9. IR(KBr, cm^{-1}):3433(w, OH(H_2O)) 3300-3500(bs, v_{OH}(phenolic)), 3051(w, CH- Aromatic), 2951(w, Aliphatic), 2932(w, CH-Aliphatic), 2861(w, CH- iminic), 1640(vs, $(\text{-C=N})_{asym}$), 1603(s, $(\text{-C=N})_{sym}$), 1534(m, C=C), 1481(s, C=C), 1443(m, C=C), 1352(m, CH_2), 1271(s, C-N), 1237(s), 1171(s), 1112(m, C-O), 1011(m, C-O), 974(m), 932(w), 853(m), 792(s), 756(m).



Scheme 1-structure of ligand

Preparation of Au-NP-AC

The Au nanoparticles were synthesized according to literature (Karimipour *et al.,* 2011).

Preparation of Au-NP-AC-DHBAHMB as a new sorbent

Ligand loaded Au-NP-AC was prepared by dissolving 20 mg of DHBAHMB in 10 ml of NaOH (0.005 mol L^{-1}) and stirred at 300 rpm for 2 h. Then it was filtered and washed with deionized water become neutral and the prepared sorbent dried at 70 °C. Than 0.15 g of this solid sorbent was poured on to column (0.5 cm: diameter and 50 cm:length) that equipped with porous frits. The columned was passed with blank solution with desired pH (Mikuła & Puzio, 2007).

Test procedure

The pH of 250 ml of 0.2 µg mL^{-1} of the understudy metal ions solutions was adjusted in the range of 3-8 by dilute nitric acid or sodium hydroxide. The samples were passed through the column at a flow rate of 2 mL min^{-1}. The retained d metal ions were then eluted with 10 mL of 4 mol L^{-1} nitric acid and their concentrations in the eluent were determined by flame atomic absorption spectrometry (Cesur, 2003).

Pretreatment of real samples

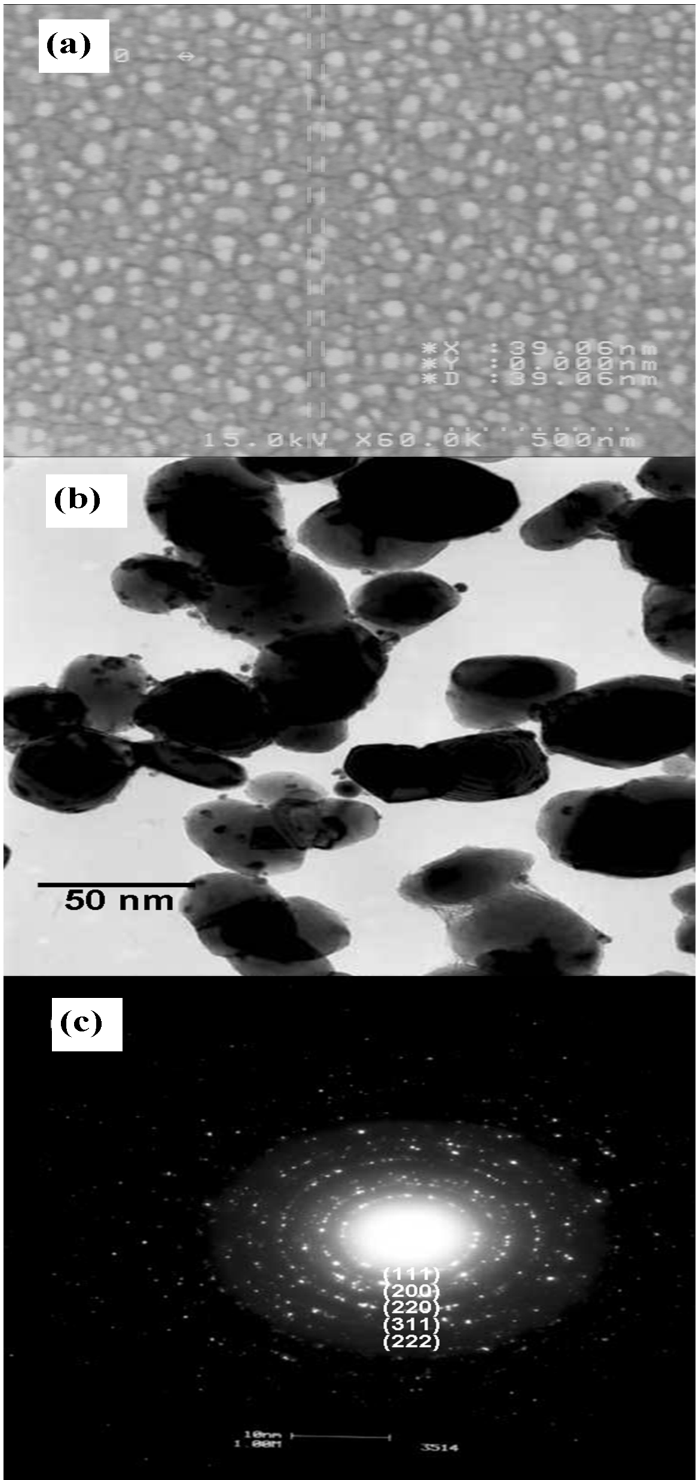
Potato, tomato and carrot fruit sample was purchased from Omidiyeh, Iran. Afterwards, they were taken in small mesh. 10.0 g of samples was heated in silica crucible for 3 h on a hot plate charring. The charred material was transferred to furnace for overnight and heated at 65 ◦C. Then, residue was cooled and treated with 10.0 mL concentrated nitric acid and 3 mL 30% (w/w) H_2O_2 again and heated for 2 h at the same temperature so that no organic compound traces are left. The final residue was treated with 3 mL concentrated HCl and 2-4 mL 70% (w/w) $HClO_4$ acid and evaporated to fumes. In these stages the metals containing compounds decompose and changed to respective metal ions. After washing the solid residue and filtering, the sample solution pH was adjusted by dilute solution of HCl and/or HNO_3 and the describe procedure has been performed.

Results and discussion

Characterization of proposed sorbents

The stability of starch caped Au nanoparticles at 70 °C for several months shows the actual role of starch as both reducing and stabilizing agent. The FESEM image of the Au nanoparticles (Fig.1a) shows their semi-spherical shape and uniform size distribution of Au nanoparticles in the range of 20-60 nm that has agreement with obtained size by the TEM image (Fig.2b) (Lemos *et al*., 2002; Chen *et al*., 2005).

Fig. 1. (a) FESEM image of the Au nanoparticles loaded onto activated carbon (b) Typical TEM image of the starch-stabilized Au nanoparticles and (c) The electron diffraction (ED) pattern of the Au nanoparticles (Ghaedi et al., 2011).



The its exact crystal structure of Au nanoparticle was drifted by electron diffraction (ED) measurements (Manzoori & Bavili-Tabrizi, 2003) and the diffraction rings of ED pattern (Fig.2c) correspond well to the crystalline planes of the cubic structured for Au nanoparticles. This observation efficiently indicates the nanocrystalline nature of Au nanoparticles. The rings in electron diffraction pattern can be assigned to the (Chen & Teo, 2001; Guo *et al*., 2004; Venkatesh *et al*., 2005) crystal planes of a face-centered-cubic (fcc) lattice structure of gold nanoparticles, respectively (Yaman, 2001).

Effect of quantity of complexing agent

The amount of chelating agent is the most important chemical variables influence the preconcentration of the understudy analytes. Therefore, the effect of the quantity of DHBAHMB on the retention and recoveries of the mention metal ions was examined from and results are shown in Fig.3. As it can been seen, change in the concentration in the range of 0.005-0.04 mg did not affect recovery so much and after that recoveries was slightly reduced at 25.0 mg of DHBAHMB. Accordingly, 2.5 mg of DHBAHMB was selected for further experiments. The considerable increase on the recoveries obtained by changing of the DHBAHMB indicates the usefulness and necessity of proposed chelating agent that this point was confirmed by caring out the preconcentration procedure without DHBAHMB addition in the pH range 3-8 (Tewari & Singh, 2001; Senkal *et al*., 2007).

Effect of pH on metal ions recoveries

The sample solutions pH significantly influences the quantity of adsorption and recovery of trace elements using hydrophobic sorbents in the presence or absence of chelating agent (Soylak *et al*., 1997; Narin *et al*., 2000; Hu *et al*., 2003). The effect of pH of test solution on the recoveries of the understudy metal ions was investigated by passing 250 ml of 0.2 µg mL $^{-1}$ of sample solution in the pH range of 3-8 thorough the column and the respective results are presented in Fig.4. As it can be seen, binding and competition of hydrogen to the DHBAHMB, at low pH leads to significant decrease in the metal ions recoveries. By further, increasing pH until 4, the potential of functional group and relative atoms of chelating agent improved and their tendency for sorption of understudy metal ions will be increased. Beyond this (Fig.4) due to possible and probable formation of insoluble precipitate of M $(OH)_n$ the recoveries decreased significantly. Therefore, the pH 4 was chosen throughout the subsequent experiments (dos Santos et *al*., 2005).

Fig. 3. Effect of amount of ligand on metal ions recoveries.

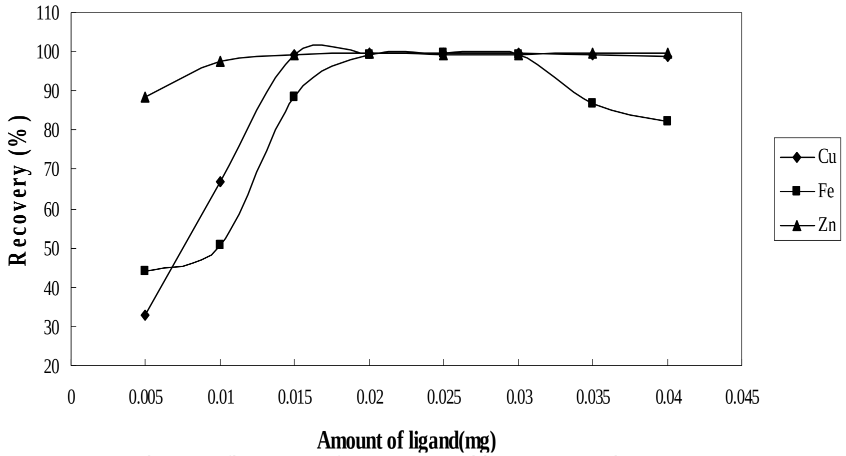


Fig. 4. Influences of pH on metal ions recoveries.

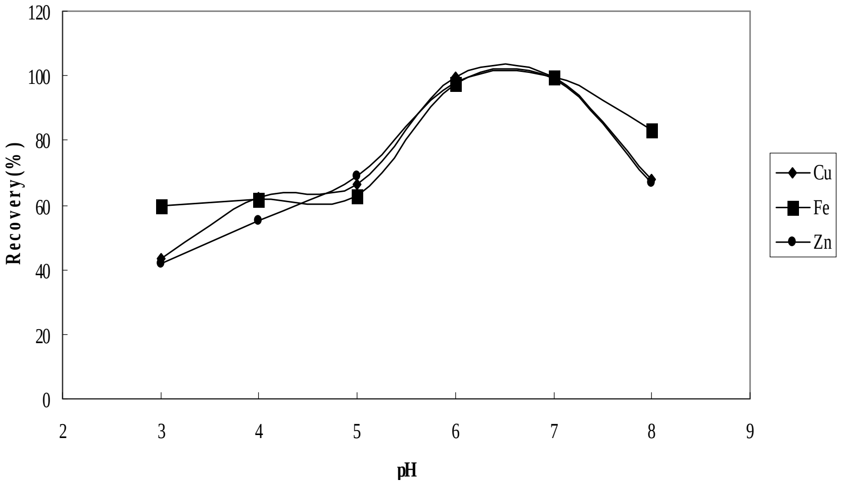
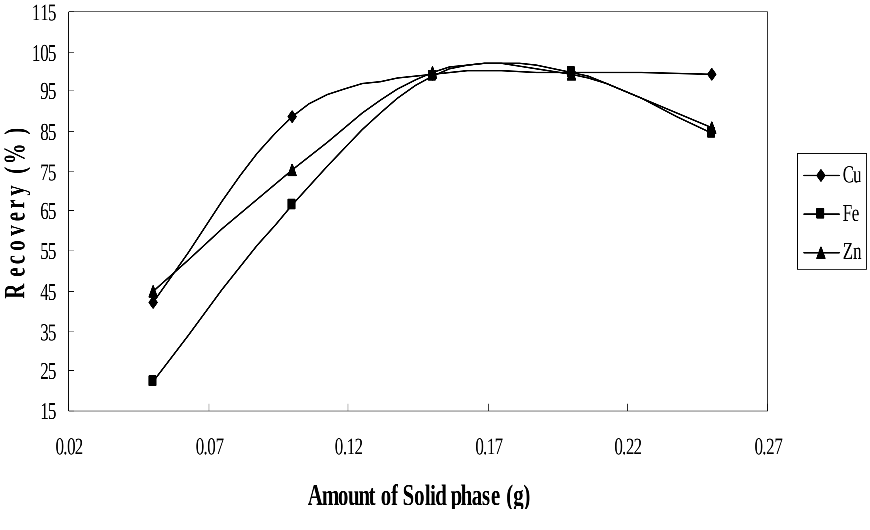


Fig. 5. Effect of amount of solid phase on metal ions recoveries.



Effects of amounts of solid phase

The influences of the amounts of solid phase with various composition and amount filled to the column in the range of were also investigated (Fig.5). The results show that up to 0.15 g of solid phase, the efficiency of extractions increased and reached a pluteu at 0.15 g. The recoveries of analytes above 0.15 g of solid phase were below 95% with 10 ml of the eluent that this value is recommended for subsequent work (Yaman, 1995; Yaman & Avic, 2006).

Effect of eluent type, concentration and volume on metal ions recoveries

Various acids including HNO_3, H_2SO_4, $HClO_4$, H_3PO_4 and HCl were tested to choose the best solution for the quantitative elution of the metal-DHBAHMB complexes accumulated on Au-NP-AC, and the percentage recoveries for each eluent was determined. Among the solvents studied, nitric acid provided higher recoveries compared to the other acids.

Finally, the HNO_3 is specified as the best eluent of choice for all the later determinations and for the optimizations of the other parameters (Table 2). After the findings above, the experiments were carried out for selecting the optimum concentration of nitric acid solution. HNO_3 solutions at the concentrations of 1.0, 2.0, 3.0, 4.0, and 5.0 mol L^{-1} were studied for this purpose and it was found that the recoveries were increased using 4 mol L^{-1} HNO_3; the recovery values were almost quantitative for all the concentrations (Yaman, 1998).

Effect of flow rate

As the retention of elements on adsorbent depends upon the flow rate of sample solutions, it becomes a significant parameter to be emphasized. Therefore, the effect of sample flow rate on metal ions recoveries in the range of 1-5 mL min^{-1} was examined under the optimum conditions (pH, eluent, etc.) by passing 250 mL. The sorption of the Cu^{2+}, Fe^{3+} and Zn^{2+} ions was practically not changed up to 3.0 mL min^{-1} flow rate and higher flow rate the recoveries of the analytes were less than 95%, as target metal ion could not equilibrate properly with the sorbent beds. Thus, the flow rate of 3.0 mL min^{-1} was selected in the column experiment (Yaman, 1999).

Sorbents properties

The reason is that the adsorption capacity of adsorbent for metal ions depends to the size of the solid support and the chelate compound. The results show this is satisfactory for the trace analysis of mentioned metal ions. To test the stability and reusability, the new sorbent was subjected to several loading and elution bath operations at sorption conditions according to the above experiments. The operating capacity and applicability were calculated from the loading and elution tests. The results from three tests yielded <5% error up to 10 cycles of repeated experiments. The sorbent showed better long-term stability and reusability towards understudy metal ions.

Table 2. Condition of eluent on metal ion recoveries.

Condition of eluent	Cu	Zn	Fe
6 mL of HNO_3 (4.0 mol L^{-1})	98.4	99.6	98.9
6 mL of H_2SO_4 (4.0 mol L^{-1})	19.8	68.4	84.8
6 mL of $HClO_4$ (4.0 mol L^{-1})	64.6	61.9	67.2
6 mL of H_3PO_4 (4.0 mol L^{-1})	24.4	48.6	66.4
6 mL of HCl (4.0 mol L^{-1})	44.6	69.6	45.0
2 mL of HNO_3 (4.0 mol L^{-1})	22.4	66.8	44.2
4 mL of HNO_3 (4.0 mol L^{-1})	59.6	88.7	55.8
6 mL of HNO_3 (4.0 mol L^{-1})	79.6	99.2	70.8
8 mL of HNO_3 (4.0 mol L^{-1})	88.4	99.0	97.9
10 mL of HNO_3 (4.0 mol L^{-1})	99.2	99.7	98.9
10 mL of HNO_3 (1.0 mol L^{-1})	66.6	79.8	44.2
10 mL of HNO_3 (2.0 mol L^{-1})	76.9	95.2	55.8
10 mL of HNO_3 (3.0 mol L^{-1})	89.0	98.6	71.3
10 mL of HNO_3 (4.0 mol L^{-1})	94.6	99.3	87.6
10 mL of HNO_3 (5.0 mol L^{-1})	99.3	98.6	98.4

Calibration curve, detection limit, determination limit and recovery

Calibration graphs were constructed with eight standard solutions containing 1-400 μg mL^{-1} of each of metal according to the general procedure. The linearly ranges, regression equation and correlation coefficient were obtained with the method of least squares. For investigation of enrichment factor and break through volume various volumes (mL) of 0.05 μg mL^{-1} of Cu^{2+}, Fe^{3+} and Zn^{2+} ions were passed through Au-NP-AC-DHBAHMB columns then the effluent was sent to FAAS for evaluating these ion content. The adsorbed ions elute were eluted using 10 mL 4.0 mol $L^{-1}$of HNO_3. The data indicate that ions content in 1650, 1700 and 1800 mL sample solutions containing 50 μg of understudy metal ions quantitatively retained on solid phase and reversibly was eluted using 10 mL 4.0 mol L^{-1} nitric acid and lead to preconcentration factors of 165, 170 and 180 for Cu^{2+}, Fe^{3+} and Zn^{2+} metal ions, respectively. Under the optimum experimental conditions, the proposed method was validated for linearity, limit of detection (LOD) and reproducibility. By employing the optimum experimental conditions, the calibration graphs obtained for Cu^{2+}, Fe^{3+} and Pb^{+2} ions, respectively, were given as, Cu^{2+}: A = 0.0018 [Cu μg L^{-1}] + .0.0055 (R^2= 0.9994, n = 7): Linear range = 2.3-550 μg L^{-1}: LOD = 0.7 μg L^{-1}: LOQ = 2.3 μg L^{-1}, Fe^{3+}: A = 0.0012 [Fe μg L^{-1}] - 0.0012 (R^2= 0.9994, n = 7): Linear range = 5.3-500 μg L^{-1}: LOD = 1.6 μg L^{-1}: LOQ = 5.3 μg L^{-1}, Pb^{+2}: A = 0.0005 [Pb μg L^{-1}] + 0.0089 (R^2= 0.9991, n = 7) Linear range = 18-600 μg L^{-1}: LOD = 2.2 μg L^{-1}: LOQ = 7.3 μg L^{-1} is linear in the interval of 5-550 μg L^{-1} for Cu^{+2} ion, 10-500 μg L^{-1} for Fe^{2+} ion and 18-600 μg L^{-1} for Pb^{2+} while R.S.D. of measurement was found to be in the range of 1.4-1.6%.

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

Interfering ions	Tolerance limit mass ratio	Cu	Fe	Zn
Ni	1000	97.6	98.2	98.9
Pb	500	99.4	96.0	98.0
Sn	600	98.0	99.0	97.6
Hg	300	96.8	98.4	97.1
C0	200	96.5	95.8	98.1
Cr	150	95.9	97.6	95.4
Mn	250	98.1	96.3	97.4
Mg	800	99.9	95.3	97.9
Na	1000	98.2	96.7	98.3
K	1000	96.1	97.8	98.6

The experimental preconcentration factors (enrichment factor: the ratio of the slope of the calibration graph with and without preconcentration) were 23 for Pb^{2+} ion, 33 for Cu^{2+} ion and 21 for Fe^{3+} ions. Effects of the matrix ions on the recoveries of the examined metal ions are given 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, three times the standard deviation (s) of the blank (n=10), were found to be 1.6, 0.7 and 2.2 μg L^{-1} for Fe^{3+}, Cu^{2+} and Pb^{2+} ions, respectively. The empirical limit of quantification (LOQ: lowest level of analyte that can be accurately and precisely measured based on 10 times blank solution standard deviation), were found to be 2.3 μg L^{-1} for Cu^{2+} , 5.3 for Fe^{+3} and 7.3 μg L^{-1} for Pb^{+2} ions. Adsorption capacity is an important factor to evaluate the sorbent (determines how much modified solid phase is required to a given solution) was investigated by bath method. In this view, 100 mL of sample solution containing 100 μg mL^{-1} of all undertaken metal ions was contacted with the solid phase at 300 rpm for 60 min and then the un-adsorbed metal ion in supernant solution was determined by FAAS. From the concentration of initial and final solution the calculated adsorption capacity were 47.7, 42.8, and 42.0 mg g^{-1} for Fe^{3+}, Cu^{2+}, and Zn^{+2} ions, respectively (Ghaedi *et al*., 2011). The reproducibility of the proposed method was calculated by analyzing replicate (N=5) from some food samples spiked at two different concentration levels (0 and 0.20 µg L^{-1}) of analyte ions (Table 4) and it was found that R.S.D. was lower than 4.4%.

Table 4. Recovery of analytes from spiked samples by using proposed method (N=5)

Samp.	Ions	Added (µg mL^{-1})	Found (µg mL^{-1})	RSD (%)	Recovery (%)
Tomato	Cu	0.00	5.33	4.30	
		0.20	5.51	3.80	102.50
	Zn	0.00	10.28	3.80	
		0.20	10.56	3.40	104.60
	Fe	0.00	15.68	3.50	
		0.20	15.89	3.00	98.70
Potato	Cu	0.00	14.25	3.30	
		0.20	14.48	3.00	103.40
	Zn	0.00	10.24	3.30	
		0.20	10.42	3.00	99.80
	Fe	0.00	8.49	3.20	
		0.20	8.71	2.90	103.50
Carrot	Cu	0.00	13.25	3.40	
		0.20	13.47	3.10	105.50
	Zn	0.00	6.26	4.00	
		0.20	6.47	3.40	104.30
	Fe	0.00	9.54	3.90	
		0.20	9.76	3.20	98.60

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