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Determination of Cr(III), Cu(II), Zn(II), Cd(II) and Pb(II) in food samples by FAAS after preconcentration on silica gel modified with 5-[2-hydroxybenzylideneamino]-2-hydroxy benzoic acid

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Abstract

A method was developed for preconcentration of trace Cr(III),Cu(II),Zn(II),Cd(II) and Pb(II) prior to their determination by atomic absorption spectrometry. A new adsorbent 5-[2-hydroxy benzylideneamino]-2-hydroxy benzoic acid-immobilized silica gel was prepared as a new solid-phase extractor. The recoveries of analytes at pH 4 with 100 mg solid phase were greater than 96% using 5 ml of 3N HNO_3 eluent at a flow rate of 2 mi/min. The optimal experimental conditions for the absorption of analytes were investigated, including the effect of pH, the volume of sample, flow rate, elution condition and interfering- ions. The detection limits of the method were found to be 1.02, 4.2, 1.54 5.46, 2.1 μg. L^{-1} for Cr(III),Cu(II), Cd(II),Zn(II), Pb(II) respectively. The proposed method provides quantitative recoveries of target metal ions ranging from 96.0 to 99.3%. The method was successfully applied for the preconcentration of Cr(III), Cu(II), Zn (II), Cd (II) and Pb(II) in mango pulp, leafy vegetables and fish samples.

Key words: Solid phase extraction, metals, modified silica gel, mango pulp, leafy vegetables and fish samples

Introduction

The determination of trace metal elements, particularly the heavy metals has received increasing attention in pollution studies. Heavy metals are extensively used in various industrial applications. The natural levels of these elements are usually harmless to the organisms including man. However at higher concentration they are toxic due to increasing anthropogenic activities.

Heavy metals enter in to the food chain through the bioaccumulation from the contaminated water, soil and air. They cannot be degraded and destroyed [1-4]. Therefore separations of heavy metals are at great risk. Accurate determinations of trace heavy metals by atomic absorption spectrometry (AAS) methods is not possible for the analytical chemist because of their low concentrations in real samples and also influence matrix ions in the analyzed samples. In order to achieve accurate and sensitive results, separation and preconcentraion techniques needed for the determining of analytes by AAS[5-10].

Various methods used for the enrichment and separation of heavy metal ions including solvent extraction, copreciptation[11-15], cloud point extraction[16-21] and membrane filtration[22] have been carried out. Among these techniques solid phase extraction is an attractive technique based on the use of the sorbent that retains the analytes. The retained analytes are eluted from the sorbent using relatively small volume of suitable solvent. These features provide a high preconcentration factor for large volume samples and short time extraction[23-24]. Various sorbents such as Amberlite XAD resins[25-28], activated carbon[29-30], Naphthalene[31-36] and alumina[37-38] etc, have been used for the solid phase extraction of metal ions from different matrices.

Silica gel is a very good adsorbent as it does not swell and having good mechanical strength and thermal stability. Modified silica gel is used in various areas due to its both inorganic and organic functionalities. Modified silica gels have also been used in the separation and pre-concentration of trace metal ions in aqueous samples[39-44].

Therefore in the present study 5 [2-hydroxy benzylideneamino] 2-hydroxy benzoic acid was prepared and immobilized with silica gel used as an adsorbent for the pre-concentration of Cr(III), Cu(II), Zn(II), Cd(II) and Pb(II) in mango pulp, leafy vegetables and fish samples, prior to their determination by FAAS. The parameters including pH of the sample, sample volume, amount of resin, type and volume of eluents, flow rate and effect of foreign ions were studied.

Materials and Methods

Experimental

Flame atomic absorption spectrometer {Perkin- Elmer model 2380, USA} equipped with multi-elemental hallow cathode lamp and air acetylene burner was used for the determination of metals. ELICO deluxe pH meter was used for preparation of buffer solution.

Reagents and Materials

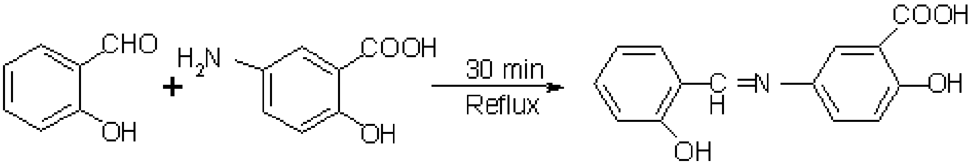
All chemicals were used analytical Grade (Merk India). Deionised double distilled water used for throughout the experimental study. Stock solutions of Cr(III), Cu(II), Zn(II), Cd(II) and Pb(II) were dissolved their nitrate salts in small amount of HNO_3 and makeup with double distilled water and Silica gel (100-200mesh) was used.

Synthesis of 5 [2-Hydroxy benzylideneamino] 2-hydroxy benzoic acid (HBAHBA)

0.122g of salicylaldehyde (0.01 moles) dissolved in methanol was added to 1.531g of 5-Amino salicylic acid (0.01 moles). The mixture was refluxed for 30 min, yellow colour solid was formed. Then solid was filtered and recrystalized in ethanol. The preparation of the reagent is shown in Scheme 1.

Elemental analysis, calculated as % of $C_{14}H_{11}NO_4$: C, 65.37; H, 4.31; N, 5.44; Found: C, 65.33; H, 4.29; N, 5.41; IR(KBR, cm^{-1}) 3419(-OH), 3063(-COOH), 2917(CH-Aliphatic), 1671(C=N), 1598(C=C),

Scheme-1



Preparation of Schiff's base coated Silica gel

3 g portion of silica gel was added to 10 ml of 0.1% 5 [2-hydroxy benzylideneamino] 2-hydroxy benzoic acid (50mg) in acetone. The mixture was stirred to complete solvent evaporation (approx 30 min) in room temperature. Then it was homonized in mortar and stored in amber glass flask.

General Procedure

100 mg of immobilized Schiff's base coated silica gel was packed into mini column (10 mm Id, and 30cm). The column was conditioned by passing through 10 ml of acetate buffer. About 10-100ml of the standard solution containing 0.2 µg of Cr, 0.1µg of Cu, 0.03µg of Zn, 0.05 µg of Cd and 0.08µg of Pb metal ions, then the pH adjusted with acetate buffer to pH 4. The sample solution passed through the mini column at a flow rate of 5ml / min. Then the column washed with 2ml of distilled water, the adsorbed metal ions were eluted by the using 5ml of 3N HNO_3 at a flow rate of 2 ml/ min. The concentration of metal ions was determined by FAAS.

Pretreatments of real Samples

Mango pulp collected from mango pulp industry in Chittoor, Andra Pradesh, India. An amount of 20g mango pulp was taken in to a 100ml of volumetric flask, add 10 ml of HCl then made up to volume with distilled water, shaked the solution and centrifuged. Then the solid particles were removed by the filtration. The pH was adjusted to 4.0 with buffer solution. The sample was passed through the mini column. The absorbed metal ions on the adsorbent in the column were eluted with 5ml of 3N HNO_3. Analytes were determined by flame atomic absorption spectrometry (FAAS).

The leafy vegetables were collected from Gollapalli village, carefully washed with deionosed water and dried in an oven at 70 ^{0}C in the laboratory then grinded in to fine powder, sieved through 1 mm nylon mesh. 1 gm plant samples were digested with 5 ml of diacid mixture, nitric acid:perchloric acid in the ratio of 3:2 at 110 ^{0}C for 8h. Then distilled water added to the digested samples to make up the volume to 50ml and then filtered by Whatmann 42 filter paper. Then above preconcentration procedure was followed for determination of analytes.

Fish sample collected at local market in Tirupati, then fish samples rinsed with deionised water and frozen at 0 ^{0}C. The sample was subsequently defrozen and rinsed with deionized water prior to sample preparation. Approximately 10 g of fresh weight was taken of fish muscle sample and homonised in a clean glass beaker and digested with 20 ml of 1:1 concentrated HNO_3 and H_2O_2 on a tharmostated hot plate maintained at 100 ^{0}C in side a fume hood until white fume emanated from the solution. The resulting digest was cooled, filtered and made up to the mark in 25 ml standard flask with deionised water. Then above preconcentration procedure was followed for the determination of analytes.

Results and Discussion

Effect of pH

The effect of pH plays as major role in the preconcentration studies, due to this the influence of pH was investigated at the pH ranges 2-9 with model solutions keeping other parameters constant. Then Cr(III), Cu(II), Zn(II), Cd(II) and Pb(II) metal ions were tested in different pH values with 10ml of model solution. The results are presented in fig 1. The results of this study showed that metal ions were completely adsorbed on the adsorbent over the pH range of 3.0-5.0. Therefore, pH 4 was selected as the optimum pH for further studies.

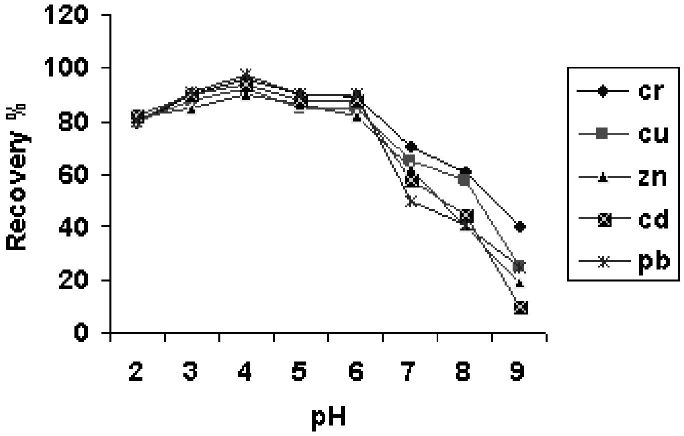


Fig:1 Effect of pH on recovery of metal ions (amount of analytes 0.2 µg Cr, 0.1µg Cu, 0.03 µg Zn 0.05µg Cd, 0.08µg and Pb; eluent:3N HNO_3)

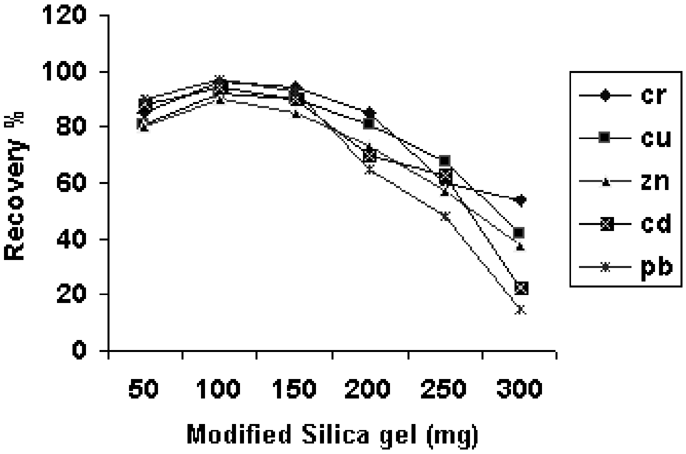


Fig:2 Effect of amount of modified silica gel on Recovery of metal ions (pH:4; amount of analytes 0.2 µg Cr, 0.1µg Cu, 0.03 µg Zn 0.05µg Cd, 0.08µg and Pb; eluent:3N HNO_3)

Effect and amount of adsorbent (modified silica gel)

The effect and amount of solid phase extractor were also important factors in the column studies in solid phase extraction method. The effect of amount of modified silica gel on adsorption of metal ions at pH4 was examined in the range of 50 - 300 mg. The results are presented in fig 2. The quantitative recoveries of the working elements were obtained by using 100mg of modified silica gel. Therefore 100 mg of modified silica gel used for further studies.

Effect of sample volume

In order to explore the possibility of low concentration of analytes from large volumes, the maximum applicable sample volume must be determined. For this purpose 10, 25, 50 100 and 200 ml volume of samples were adopted to test the effect of the sample volume. Sample solution containing 0.2µg of Cr(III), 0.1µg of Cu(II), 0.03µg of Zn(II), 0.05 µg of Cd(II) and 0.08 µg of Pb(II) metal ions were passed through the mini columns at optimum flow rate. The results are presented in fig 3. The quantitative recoveries were obtained from 10 ml of sample solution. Therefore 10ml volume of sample was selected for further studies.

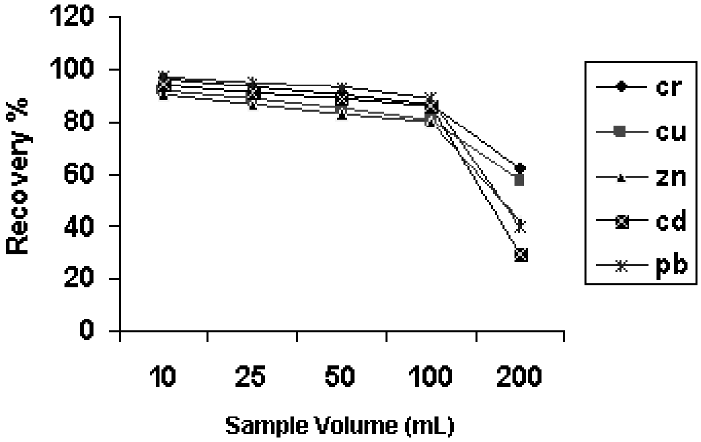


Fig:3 Effect of sample volume on recovery of metal ions (pH:4; amount of analytes 0.2 µg Cr, 0.1µg Cu,0.03 µg Zn 0.05µg Cd, 0.08µg and Pb; eluent:3N HNO_3)

Effect of flow rate

As the retention of analytes on the adsorbent is depends upon the flow rate of the samples solution. The effect of flow rate was examined under the pH 4 by passing the sample solution through the mini column with the flow rates carrying in the range of 2-5ml /min and elution flow rate in the range of 0.5-2ml/min. The quantitative recoveries of metal ions were obtained with a flow rate of 5 and 2ml/min both sample and eluent.

Choice and volume of eluent

A different concentration of eluents was tested to elute the adsorbed metal ions complex in the column. In order to choose most effective different concentrations eluents such as 3N $HNO_{3,}$ 2N $HNO_{3,}$ 1N $HNO_{3,}$ 3N HCl, 2N HCl and 1N HCl, were studied. The elution studies were carried out by maintaining the concentration of 0.2µg.ml^{-1}, 0.1 µg.ml^{-1}, 0.03 µg.ml^{-1}, 0.05 µg.ml^{-1}and 0.08 µg.ml^{-1}of Cr(III), Cu(II), Zn(II), Cd(II) and Pb(II) in 10 ml volume of sample. The quantitative recoveries were obtained by using of 5 ml of 3N HNO_3 at the flow rate of a 2 ml/min and the results are presented table 1.

Table.1 Effect of type and concentration on the recoveries of metal ions (pH: 4, flow rate 2 ml per minute)

Eluent type	**Volume (ml)**	**Recovery (%)**
3 N HNO_3	10	95
3 N HNO_3	5	96
3 N HCl	10	92
3 N HCl	5	94
1 N HNO_3	10	89
1 N HNO_3	5	90
2 N HNO_3	10	91
2 N HNO_3	5	93

Effect of Foreign Ions

Under the optimum conditions to examine the effects of various tested metal ions, extraction these metal ions in presence of some selected metal ions by and have been carried out which prompted us to perform an intensive selectivity study to evaluate the possible interference of some metal ions in the process of selective solid phase extraction of Cr(III), Cu(II), Zn(II), Cd(II) and Pb(II). Various amounts of NaCl, KCl, $Cacl_2$, $MgCl_2$, Na_2Co_3 and $NaHCo_3$ as the major components of water samples were added to solution containing fixed amount of analytes and procedure was followed. The results are given in table 2. This results show that the proposed preconcentration method could be also applied in saline samples at mgL^{-1} levels.

Table. 2: Effect of foreign ions on the recovery of metal ions

Foreign ion	Added as	Tolerance limit (mgL^{-1})
Na^+	NaCl	20,000
K^+	KCl	2,500
Ca^+	$CaCl_2$	1,000
Mg^+	$MgCl_2$	2,500
Co_3^{2-}	Na_2CO_3	2,500
SO_4^{2-}	Na_2SO_4	12,000
HCO_3^-	$NaHCO_3$	250
Cl^-	HCl	250

Table.3 Podhina (Mentha Viridis)

Analyte	Added (μgg^{-1})	Found* μgg^{-1}	Recovery (%)
Cr	-	0.84±0.11	
	2.5	3.32±0.30	99.4
Cu	-	2.53±0.37	
	2.5	4.83±0.38	96.0
Zn	-	4.06±0.18	
	2.5	6.47±0.22	98.6
Cd	-	N.D	
	2.5	2.42±0.13	96.8
Pb	-	0.18±0.12	
	2.5	2.65±0.31	98.8

Table.4 Gongura (Hybiscus Cunnabinus)

Analyte	Added ($\mu g g^{-1}$)	Found* $\mu g g^{-1}$	Recovery (%)
Cr	-	1.26±0.18	
	2.5	3.71±0.37	98.6
Cu	-	3.21±0.1	
	2.5	5.59±0.41	97.8
Zn	-	5.34±0.07	
	2.5	7.71±0.34	98.3
Cd	-	N.D	
	2.5	2.44±0.12	97.6
Pb	-	0.25±0.11	
	2.5	2.73±0.29	99.2

Table.5 Fish samples

Analyte	Added ($\mu g g^{-1}$)	Found* $\mu g g^{-1}$	Recovery (%)
Cr	-	0.29±0.08	
	2.5	2.77±0.2	99.2
Cu	-	0.826±0.03	
	2.5	3.2±0.16	96.2
Zn	-	0.45±0.07	
	2.5	2.88±0.37	97.6
Cd	-	0.024±0.01	
	2.5	2.45±0.28	98
Pb	-	0.39±0.08	
	2.5	2.87±0.64	99.3

'' Mean value± SD (N=3).*

Table.6 Mango pulp sample

Concentration of analytes in Mango pulp

Analyte	Added ($\mu g g^{-1}$)	Found* $\mu g g^{-1}$	Recovery (%)
Cr	-	0.82±0.09	
	2.5	3.29±0.12	99.1
Cu	-	0.25±0.14	
	2.5	2.65±0 .22	96.4
Zn	-	1.51±0.36	
	2.5	3.95±0.26	98.5
Cd	-	0.88±0.09	
	2.5	3.31±0.24	97.9
Pb	-	0.43±0.12	
	2.5	2.92±0.18	98.7

'' Mean value± SD (N=3).*

Analytical applications

The accuracy of results was verified by analyzing the concentration after the addition of known amount of analytes in to mango pulp, leafy vegetables and fish samples. The results are presented tables3-6. The results replicate three analyses of each sample so that the ions almost quantitatively recovered. The recovery of spiked samples is satisfactory and accurate thus confirmed using this method, which indicate the capability of proposed method for determination of analytes in different matrices.

Table.7 Some recent reported studies on silica gel adsorbent for preconcentration of metal ions

Metals	Chelating reagent	Detection Method	D.L (μg. L^{-1})	Samples	References
Cr(III),Cu(II),Ni(II), Pb(II),Zn(II)	Paradimethylamino Benzaldehyde	ICP-OES	1.10, 0.69, 0.99, 1.10, 6.50	River Sediments, water Samples	40
Pb(II),Cd(II),Ni(II), Co(II), Cu(II)	Aminothioamido-antraquinone	FAAS	22.5, 1.1, 2.9, 0.95, 1.0	Pond, tap, Drinking Water Samples	41
Co(II), Ni(II)	Polyethylene Glycol	FAAS	0.37, 0.71	Black Tea, Rice flour, Water Samples	42
Cu(II),Fe(II), Zn(II)	Aminopropyltrimethoxysilane	ICP-OES	0.12, 0.15, 0.40	Biological, Natural Water Samples	43
Cr(III),Cd(II), Pb(II)	Tris(2-aminoetyl)amine	ICP-AES	0.61, 0.41, 0.55	Water Samples	44
Cr(III),Cu(II), Cd(II),Zn(II), Pb(II)	5[2-hydroxybenzylideneamino] 2-hydroxybenzoicacid	FAAS	1.02, 4.2, 1.54, 5.46, 2.1	Leafy Vegetables, Mango Pulp, Fish Samples	Present Method

Conclusion

The Schiff's base coated silica gel preconcentration method is sensitive and accurate for the determination of trace amount of Cr(III), Cu(II), Zn(II), Cd(II) and Pb(II) ions in FAAS. 5 [2-hydroxy benzylideneamino] 2-hydroxy benzoicacid coated silica gel was used as solid phase extractor for preconcentration of analytes. This separation and preconcentration procedure is selective determination for analysis of Cr(III), Cu(II), Zn(II), Cd(II) and Pb(II) metal ions at low levels in aqueous solution. The advantages of proposed method are simple, time saving, low cost reagents and eco friendly. Some recent reported studies on silica gel adsorbent used for preconcentration of metal ions as presented in table 7. The proposed method is successfully applied for the determination of anlaytes in mango pulp, leafy vegetables and fish samples.

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