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Flame Atomic Absorption Spectrometric Determination of Iron, Copper and Zinc in leafy vegetables and medicinal plant samples after preconcentration with *p*-dimethylaminobenzyl 3, 3 dimethylbenzidene on activated carbon

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ABSTRACT

A preconcentration procedure for solid phase extraction on activated carbon as *p*-dimethylaminobenzyl 3, 3-dimethylbenzidene chelates and flame atomic absorption spectrometric determinations of iron, copper and zinc metal ions in environmental samples of leafy vegetables and medicinal plant leaf samples proposed in the present work. The influences of analytical parameters including pH of the aqueous solution, amount of activated carbon, amounts of reagents and eluent solutions, sample volume etc. on the quantitative recoveries of iron, copper and zinc ions were investigated. The effects of interference ions on the retentions of the analytes were also examined. The detection limit for Fe (II), Cu (II) and Zn (II) were found to be 0.9, 1.5, and 1.8μg. L^{-1} respectively.

Keywords: preconcentration, trace metals, FAAS, leafy vegetables and medicinal plant leaves

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INTRODUCTION

The determination of trace metal elements, particularly the heavy metal ions 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 at permissible levels. 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 are not 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 are needed for the determination of analytes by AAS [5-10].

Various methods used for the enrichment and separation of heavy metal ions including solvent extraction [11], copreciptation[12,13], cloud point extraction [14,15] and membrane filtration [16] have been carried out. Among the various preconcentration techniques solid phase extraction (SPE) techniques widely used for the determination of trace metal ions in aqueous samples, because high enrichment factors to obtain in short time and low consumption of reagent [17-21]. Various solid phase extraction materials including XAD resins [22], modified silica gel [23], microcrystalline naphthalene [24], and alumina [25,26] have been used. Activated carbon is one of the important solid support that has been used alone or modified due to its large surface area, high absorption capacity, porous stature, selective determination and high purity standards. There are several recent reports on the use of modified activated carbon for metal enrichment [27-31].

In the present work, preconcentration of Fe (II), Cu (II) and Zn (II) from aqueous solution of various samples using *p*-DMABDMB on the activated carbon adsorbent was described. The objectives of the present work *p*-dimethylaminobenzyl 3,3-dimethyl benzidene(*p*-DMABDMB) regent was prepared and used in chemical enrichment and separation of trace metal ions by preconcentration method prior to their determination. The parameters including pH of the sample, sample volume, amount of activated carbon, type and volume of eluents, effect of time of stirring and effect of foreign ions were studied. The proposed method was successfully applied for the determination of Fe (II), Cu (II) and Zn (II) in leafy vegetables and medicinal plant leaf samples.

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.

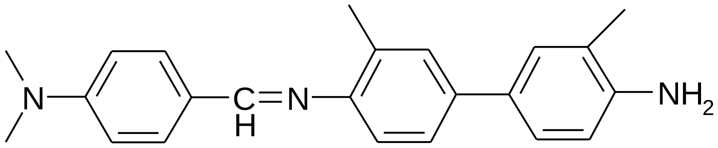
Reagents and Materials

All chemicals were used Analytical Grade (Merk India). Deionized double distilled water used for through out experimental study. Fe (II) stock solution prepared from its ammonium ferrous sulphate salt, dissolving with 5 ml of conc. H_2SO_4 and makeup with double distilled water. Cu (II) and Zn (II) stock solution prepared from copper sulphate pentahydrate and zinc sulphate was dissolved in deionized double distilled water and makeup with double distilled water. Acetate buffer solution was prepared with 0.1M sodium acetate, 0.1 M glacial acetic acid.

Synthesis of *p*-dimethylaminobenzyl 3, 3-dimethylbenzidene (*p*-DMABDMB)

1.491 g of p-dimethylaminobenzaldehyde, 2.123 g of 3, 3 dimethylbezidene dissolved in methanol. The mixture was refluxed for 30 min, pale green colour solid was formed. Then the solid was filtered and recrystalized in ethanol. The structure of the reagent is shown in Scheme 1

IR(KBR,cm^{-1}): 3300(N), 2862(CH_3), 1606(C=N)



Scheme1. *p*-dimethylaminobenzyl 3, 3-dimethylbenzidene (*p*-DMABDMB)

Preparation of Activated carbon

Activated carbons 40-60 mesh, then was stirred with concentrated HCl for 1 hour and allow to stand for 2 hours. After filtration, the activated carbon was washed with water and then dried at 120^0C for 1 hour. This purified Activated carbon was used for further work.

General procedure

A standard sample containing 1.5 μg of Fe (II), Cu (II) and Zn (II) were transferred in to 50 ml beaker, adjusted pH of 5±1.0 with acetate buffer, after 20 ml of distilled water was added. Then 2 ml of 0.005M of *p*-dimethylaminobenzyl 3, 3- dimethylbenzidene reagent solution was added. 50 mg of activated carbon was added to the above solution and the mixture was stirred on magnetic stirrer for 10 min. The preconcentrated Fe (II), Cu (II) and Zn (II) ions were eluted with 10 ml 20% HCl and determined by FAAS.

Preparation of leafy vegetables and medicinal plant leaf samples

The leafy vegetables and medicinal plant leafs were collected from Gollapalli village, near Tirupati, carefully washed with demonized 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 g leafy vegetables and medicinal plant leaves 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.

RESULT AND DISCUSSION

Effect of pH

The reaction between metal ions and reagent solution can be influenced by the pH of the solution. Therefore, in this experiment the experiment effect of pH on the preconcentration of 1.5 μg of Fe (II), Cu (II) and Zn (II) was investigated. Fig.1 shows that the absorption of metal ions increased with increasing the pH of the solution up to 5 and remained gradually decreased. Thus the pH 5 was selected as optimum value for sorption of metal ions and 2 ml of acetic acid-sodium acetate buffer solution pH-5 was used to maintain this pH.

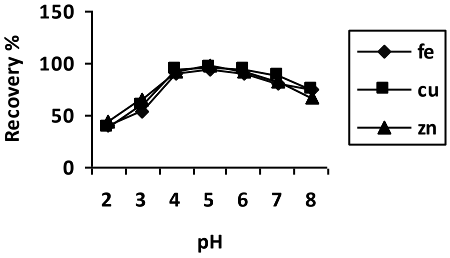


Fig: 1 Effect of pH on recovery of metal ions (amount of analytes 1.5 μg of Fe (II), Cu (II) and Zn (II) eluent: 20% HCl).

Effect of the amount of activated carbon

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 activated carbon on adsorption of metal ions at pH 5 was examined in the range of 50 - 250 mg. The results are presented in fig 2. The quantitative recoveries of the working elements were obtained by using 50 mg of activated carbon. Therefore 50 mg of adsorbent selected for further studies.

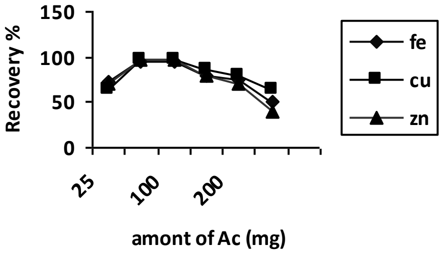


Fig: 2 Effect of amount of aviated carbon on recovery of metal ions (pH:5; amount of analytes 1.5 μg of Fe (II), Cu (II) and Zn (II) eluent: 20% HCl).

Effect of contact time

The effect of stirring time also important factor in evaluating the affinity of activated carbon to *p*-dimethylaminobenzyl 3,3-dimethylbenzidene metal chelates. To determined rate of Fe (II), Cu (II) and Zn (II) on the activate carbon, the recommended batch procedure was carried out. The contact time varied from 10-60 min during the pre-concentration and results were given fig.3 hence, 10 min of stirring was enough to reach maximum values of separation of all the metals. Therefore, it is suitable for application using the preconcentration of trace metal ions.

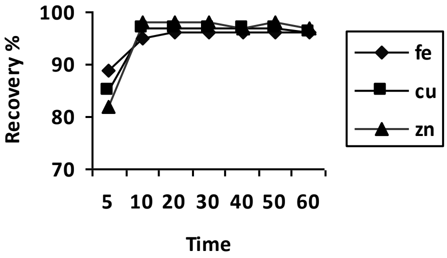


Fig: 3 Effect of time of recovery of metal ions (pH:5; amount of analytes 1.5 µg of Fe (II), Cu (II) and Zn (II) eluent: 20% HCl).

Effect of sample volume

Effect of sample volume on the preconcentration of 1.5 µg Fe (II), Cu (II) and Zn (II) metal ions was studied in the range of 10-200 ml sample volume. The amount of metal ions was adsorbed on the adsorbent was measured by using 10 ml of 20% HCl. Quantitatively recoveries were achieved for the analytes from 25 ml of sample volume. Therefore, 25 ml sample volume was selected for further studies.

Effect of the type and volume of elution solutions

The effect of the type and concentration of the eluent for elution of the analytes from activated carbon was studied. Iron, copper and zinc retained on the adsorbent were eluted using various acid solutions. For this purpose, 20 % 5 and 10mL of HCl and HNO_3 were examined as eluents. The results were given in table 1. Therefore, 10mL of 20% HCl was found to be satisfactory for metal ions (recovery > 95%).

Table.1: Effect of type and eluent concentration on the recoveries of metal ions

Eluent type	Volume (ml)	Recovery (%)		
		Fe	Cu	Zn
HNO_3	10	85	87	90
HNO_3	5	79	82	72
HCl	10	95	96	98
HCl	5	92	89	94

Detection limits

The detection limit of each element was expressed as the amount of analytes in µg. L^{-1} using blank solution. The limits based on three times of the standard deviation of blank solution were 0.9, 1.5, and 1.8 µg. L^{-1} for Fe (II), Cu (II) and Zn (II) respectively.

Effect of interference 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 Fe (II), Cu (II) and Zn (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 presented in table 2.

Table: 2: Effect of matrix ions on the recoveries of the examined metal ions

Ion	Tolerance limit (mg.L^{-1})
Na^+	1000
K^+	1000
Cl^-	1000
Mg^+	600
HCO_3^-	1000
Cd^{2+}, Ca^{2+}, Ag^+, Al^{3+}, Cr^{3+}, Hg^{2+}	100

Specification of Presented Method at Optimum Conditions

Parameter	**Optimum conditions**
pH	5
Concentration reagent solution	0.005M *p*-DMABDMB
Amount of Activated carbon (mg)	50
Eluent	10 ml of 20 % HCl
Sample volume (ml)	25
Recovery (%)	> 95%

Applications

To evaluate the applicability of the preconcentration and solid phase extraction of metal ions, it was applied to the determination of Fe (II), Cu (II) and Zn (II) in leafy vegetables and medicinal plant leaf samples. The results were summarized in table 3-7. Satisfactory recoveries were obtained for spiked analyte ions. The recoveries were higher than 95%, thus confirming the accuracy of the proposed procedure.

Leafy vegetables samples

Table:3 ***Mentha Viridis***

Analyte	Added (µg)	Found* µg.g^{-1}	Recovery (%)
Fe	-	0.96±0.23	
	10	10.92±0.72	99.63
Cu	-	2.1±0.35	
	10	10.213±1.09	100.03
Zn	-	3.96±1.56	
	10	10.383±0.45	99.86

'*' Mean value± SD (N=3).

Table:4 ***Coriyandram Sativam***

Analyte	Added (µg)	Found* µg.g^{-1}	Recovery (%)
Fe	-	0.52±0.23	
	10	10.41±0.72	98.9
	-	1.06±0.1	
Cu	10	10.9±0.56	98.6
	-	5.46±0.47	
Zn	10	14.93±0.34	96.6

'*' Mean value± SD (N=3).

Medicinal plants

Table:5 ***Strychonos Nux-vomica***

Analyte	Added (µg)	Found* µg.g^{-1}	Recovery (%)
Fe	-	N.D	
	10	9.96±1.13	99.6
Cu	-	1.08±0.22	
	10	11.1±0.89	100.18
Zn	-	4.01±0.91	
	10	13.8±0.79	98.5

'*' Mean value± SD (N=3), 'N.D' Not dectable

Table:6 *Bignonia Gracillis*

Analyte	Added (µg)	Found* µg.g^{-1}	Recovery (%)
Fe	-	1.82±0.25	
	10	11.79±0.28	99.74
Cu	-	1.02±0.2	
	10	10.76±0.45	97.64
Zn	-	5.38±0.67	
	10	14.96±0.86	97.27

'*' Mean value± SD (N=3).

Table:7 *Ocimum Canum*

Analyte	Added (µg)	Found* µg.g^{-1}	Recovery (%)
Fe	-	1.13±0.24	
	10	11.08±0.74	99.55
Cu	-	2.65±0.63	
	10	12.42±1.38	98.18
Zn	-	1.42±0.42	
	10	11.35±1.5	99.39

'*' Mean value± SD (N=3).

CONCLUSION

The proposed method was significant with respect to the development of a simple, reliable, and sensitive batch method for preconcentration and determination of trace amounts of Fe (II), Cu (II) and Zn (II). The advantages of the proposed method were high sensitivity, selectivity and low-detection limit. The conditions for pre-concentration of metal ions were selected using model solutions. The accuracy and precision of the proposed SPE method was reported in terms of recovery (%) ranging from 97.27 to 100.18 %. The proposed method could be applicable for the determination of trace metal ions in leafy vegetables and medicinal plant leaf samples.

REFERENCES

[1] Yaman M. Anal Biochem 2005; 339: 1.
[2] Mustafa Tuzen, and Mustafa Soylak. J Haz Mat 2009; 164: 1428.
[3] Guoxin Hu, and Richard L. Analytica Chimica Acta 2005; 535: 237-242.
[4] Zhifeng Tu, Qun He, Xijun Chang, Zheng Hu, Ru Gao, Lina Zhang, and Zhenhua Li. Analytica Chimica Acta 2009; 64: 252-257.
[5] Mustafa Tuzen, Mustafa Soylak, and Latif Elci. Analytica Chimica Acta 2005; 548(1-2): 101-108.

[6] Divrikli Umit, Kartal Aslihan Arslan, Soylak Mustafa and Elci Latif. J Haz Mat 2007; 145: 459-464.

[7] Purna Chandra Rao G, Kalluru Seshaiah, Yerra Koteswara Rao, and Wang MC. J Agric Food Chem 2006; 54: 2868-2872.

[8] Celal Duran, Ali Gundogdu, Volkan Numan Bulut, Mustafa Soylak, Latif Elci, Hasan Basri Sent¨urk, and Mehmet Tufekci. J Haz Mat 2007; 146(1-2): 347.

[9] Ghaedi M, Ahmadi F and Soylak M. J Haz Mat 2007; 147: 226.

[10] Ghaedi M, Shokrollahi A, Kianfar AH, Pourfarokhi A, Khanjari N, Mirsadeghi AS and Soylak M. J Haz Mat 2009; 162: 1408-1414.

[11] Abdelhamid Mellah and Djafer Benachour. Sep Pur Technol 2007; 56(2): 220-224.

[12] Prasad K, Gopikrishna P, Kala R, Prasada Rao T and Naidu GRK. Talanta 2006; 69(4): 938.

[13] Mustafa Soylak, and Hikmet Balgunes. J Haz Mat 2008; 155: 595-600.

[14] Meeravali Noorbasha N, Reddy M.kumar, and Sunil Jai. Anal Sci., 2007; 23: 351.

[15] Fathi SAM and Yaftian MR. J Coll Int Sci 2009; 334(2): 167.

[16] Umith Divrikli, Asliham Arslan Kartal, Mustafa Soylak, and Latif Elci. J Haz Mat 2007; 145: 459-464.

[17] Mehmet Sayım Karacan; Neslihan Aslantaş. J Haz Mat 2008; 155(3): 551-557

[18] Ghaedi M, Ahmadi F, Soylak M. J Haz Mat 2007, 147(1-2): 226-231.

[19] Zhenhua Li, Xijun Chang, Zheng Hu, Xinping Huang, Xiaojun Zou, Qiong Wu, Rong Nie. J Haz Mat 2009; 166(1): 133-137

[20] Ghaedi M, Montazerozohori M, Soylak M. J Haz Mat 2007; 142: 368-373.

[21] Sharma RK, Pant P. J Haz Mat 2009; 163(1): 295-301

[22] Baytak S, Balaban A, Turker AR and Erk B. J Anal Chem 2006; 61: 476-482.

[23] Xijun Chang, Haixia Luo, Yuemei Cui, Xiangbing Zhu, Yunhui Zhai, Zheng Hu Qun He. J Mol Str 2008; 891(1-3): 45-49.

[24] Gopi krishna p, Rao KS, Biju VM, Prasada Rao T, Naidu GRK. Chemia Analityczna 2004; 49: 383-393.

[25] Ghaedi M, Tavallali H, Shokrollahi A, Zahedi M, Montazerozohori M, Soylak M. J Haz Mat 2009; 166(2-3): 1441-1448.

[26] Attinti Ramesh, Bobba Aparna Devi, Hiroshi Hasegawa, Teruya Maki, Kazumasa Ueda. Microchemical J 2007; 86(1): 124-130.

[27] Ghaedi M, Shokrollahi A, Kianfar AH, Mirsadeghi AS, Pourfarokhi A, Soylak M. J Haz Mat 2008; 154(1-3): 128-134.

[28] Mehmet Sayım Karacan, Neslihan Aslantaş. J Haz Mat 2008; 155(3): 551-557.

[29] Barbara Mikuła; Bożena Puzio. Talanta 2007; 71(1): 136-140.

[30] Hasan Cesur. Turk J Chem 2003; 27: 307-314.

[31] Ayob Parchehbaf Jadid, Habibollah Eskandari. E-journal of Chemistry 2008; 5(4): 878-883.