

## Solid Phase Extraction Method for the Determination of Ni(II), Cu(II) and Zn(II) by Flame Atomic Absorption Spectrometry Using Schiff Base in Various Water Samples

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**Abstract:** A novel column solid phase extraction procedure was developed for the determination of Ni(II), Cu(II) and Zn(II) in water samples using newly synthesized reagent 1-(2-hydroxy-5-methoxybenzalidene)thiosemicarbazide for preconcentration and separation prior to FAAS using octylpolyethylene glycolphenylether (Triton x-100). The sorbed elements were subsequently eluted with 10 mL of 1 M HNO<sub>3</sub> and the acid elutes were analysed by FAAS. Various parameters such as pH, amount of adsorbent, eluent type and volume, flow-rate of the sample solution, volume of the sample solution and matrix interference effect on the retention of the metal ions have been studied. The optimum pH for the sorption of above mentioned metal ions was about 7.0±0.5. The loading capacity of adsorbent for Ni(II), Cu(II) and Zn(II) were found to 28, 26 and 20 µg mL<sup>-1</sup> respectively. The limit of detections were found to be 3.6, 3.2 and 3.6 µg mL<sup>-1</sup> for Ni(II), Cu(II) and Zn(II) respectively by applying a preconcentration factor 83. Recoveries under optimum conditions were found to be 97.6 to 104% at the 98% confident level. The proposed enrichment method was applied successfully for the determination of metal ions in various water samples. The results were obtained are good agreement with reported method.

**Keywords:** Solid phase extraction (SPE), 1-(2-Hydroxy-5-methoxybenzalidene) thiosemicarbazide, XAD-100, Flame atomic absorption spectroscopy

### Introduction

Thio substituted compounds play a vital role in analytical chemistry due to highly sensitive colour reaction, stability and selectivity towards various metal ions<sup>1-6</sup>. The compounds form water-insoluble complexes with most of the metal ions; there fore, their complexes are either dissolved in water or extracted in suitable organic solvents for their direct determination with atomic absorption spectrometry, which is quite tedious and time consuming. Therefore, there is need for preconcentration and separation technique for the analysis of metal ion prior to FAAS which gives the high extraction efficiency of metal ions.

Cobalt, nickel, copper and zinc are the most important transition metal ions in environmental samples. They are both vital and toxic to biological systems. Thus, the simultaneous determination of iron, cobalt, nickel, copper and zinc in environmental samples is very important<sup>7</sup>. Several preconcentration techniques have been reported for the determination of metal ions which includes co-precipitation, ion exchange, adsorption, solvent extraction, but they suffer from some those advantages like time consuming, more expensive, poor sensitive. To overcome the above disadvantages, solid phase extraction is the easily operatable technique for the extraction of metal ions. Solid phase extraction based on the adsorption is also one of the important preconcentration methodologies<sup>8-15</sup>. It has some advantages including short analysis time, high preconcentration factors. Several solid phase materials such as amberlite resins<sup>8,10-14</sup> molten naphthalene<sup>15</sup> chromosorb resins<sup>16,17</sup> activated carbons<sup>18-20</sup> silica gel<sup>21-24</sup> were employed for the separation and preconcentration of the metal ion in the various environmental samples. Several papers have been reported for the determination of metal ions in various environmental samples<sup>25-27</sup>. Chelating reagents like ammonium pyrrolidine dithiocarbamates (APDC) and sodium diethyl dithiocarbamates (Na-DDC) are generally used for complexation and extraction of trace metal ions into organic solvent. Use of APDC and Na-DDC has certain disadvantages like poor sensitivity, less stability and low recoveries.

In view of this authors have reported a facile, sensitive and novel analytical method was developed for the separation and preconcentration of metal ions Ni(II), Cu(II) and Zn(II) in various water samples. The column was loaded with triton x-100 support impregnated with Schiff base 4-(1-methyl-1-mesitylcyclobutane-3-yl)-2-(2-hydroxy-5-methoxy benzylidene-hydrazino) thiazole. The sorbed elements were sequently eluted with 10 mL of 1 M HNO<sub>3</sub>. The acid eluates were analysed by FAAS. Optimum experimental conditions were investigated with respect to a standard solution of the matrix, in order to examine the possibility of obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. Under these conditions the preconcentration factor was found to be 83 for 500 mL of sample solution.

## Experimental

A Perkin-Elmer ® Model 2380 Flame atomic absorption spectrometry (FAAS) with air-acetylene flame and hollow cathode lamps were used for the analysis of Ni(II), Cu(II) and Zn(II). The instrumental parameters recommended by the manufacturer were represented in Table 1. A pH meter, Elico Li-129 Model glass calomel combined-electrode was employed for measuring pH values.

**Table 1.** Recommended experimental conditions

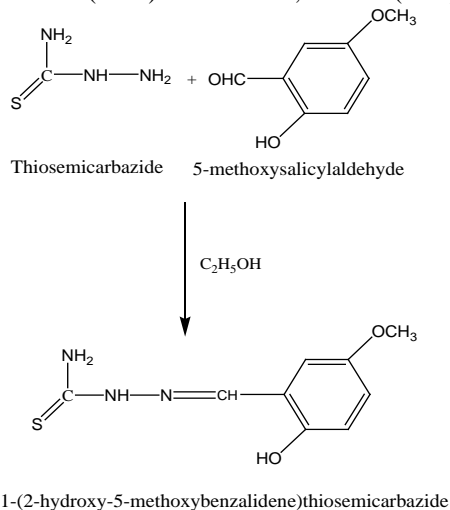
Flame: acetylene-air, L min <sup>-1</sup>	
Acetylene flow-rate	120
Air flow-rate	480
Analytical wavelength, nm	
Cu(II)	240.7
Ni(II)	232.0
Zn(II)	213.0
Lamp current (mA)	4.0
Above the burner, mm	6
Measurement mode	Background correction
Detection limits, µg mL <sup>-1</sup>	
Cu(II)	3.6

### Reagents and solutions

Reagents used were of analytical reagent grade and doubly distilled water for the preparations of stock and standard solutions. All the chemicals were purchased from Merck Chemicals, Mumbai., India. Standard stock solutions ( $1000 \text{ mg L}^{-1}$ ) of Ni(II), Cu(II) and Zn(II) were prepared by dissolving the proper amounts of analyte in doubly distilled water. Working standards of solutions were prepared by the appropriate dilution of the stock solution daily in doubly-distilled water for reference solutions. Equimolar solutions of NaOH and HCl were added appropriately to get desirable pH of  $7.0 \pm 0.5$ . The Schiff base derivative 1-(2-hydroxy-5-methoxybenzalidene) thiosemicarbazide was prepared by dissolving 6.98 g in 10 mL of ethanol and made up to the mark with doubly distilled water in 100 mL standard flask.

### Synthesis of 1-(2-hydroxy-5-methoxybenzylidene) thiosemicarbazide

The solution of thiosemicarbazide (0.9112 g, 10 mmol) in 50 mL absolute EtOH, a solution of 5-methoxysalicylaldehyde (1.52 g, 10 mmol) in 20 mL absolute EtOH were added drop wise at  $60\text{--}70^\circ\text{C}$  with continuous stirring, the solid compound started to form 5 min later. After completing the reaction, the mixture was left to stand overnight. The solid product was filtered off, washed with  $\text{H}_2\text{O}$  several times, dried in air and crystallized from aqueous EtOH (1:3) and it shown in Scheme.1, yield 94%, melting point  $231\text{--}233^\circ\text{C}$ , IR (KBr):  $3310\text{s } \nu(\text{O-H})$ ,  $1039\text{s } \nu(\text{C-O})$ ,  $1584\text{vs } \nu(\text{C=N})$  Azomethine,  $3125\text{s } \nu(\text{N-H})$ .



### Scheme 1. Synthesis of 1-(2-hydroxy-5-methoxybenzalidene) thiosemicarbazide

Characteristic  $^1\text{H}$  NMR spectra, in  $\text{DMSO-d}_6$ , showed signals at 3.73 (s, 3H)- $\text{CH}_3$ ; 6.81 (s, 2H)- $\text{NH}_2$ ; 7.49 (s, 1H) Ar-H; 8.04 (s, 1H) Ar-H; 8.16 (s, 1H) Ar-H; 8.38 (s, 1H)  $\text{N}=\text{CH}$ ; 9.49 (s, 1H)  $-\text{NH}-$ ; 11.39 (s, 1H)  $-\text{OH}$  ppm. Anal. Calcd. For  $\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2\text{S}$  (225.05) (%): C, 47.99; H, 4.92; N, 18.65; S, 14.23. Found: C, 48.11; H, 5.02; N, 18.27; S, 13.99.

### Column preparation

0.2 g of Triton x-100 loaded with 1-(2-hydroxy-5-methoxybenzalidene)thiosemicarbazide was packed in a glass column with 10 cm length and 1.0 diameter, having a porous disk and a stopcock, has been used for preconcentration of the metals. The column was condition with 1 M HCl solution and doubly distilled water then the column was conditioned to suitable pH by passing 10 mL of solution ( $\text{pH } 7.0 \pm 0.5$ ) through the column, prior to passage of the sample solution.

### Procedure

An off line column procedure was applied for the preconcentration of analyte ions in different water sample. An aliquot of the sample solution (500 mL) containing 50  $\mu\text{g}$  of Cu(II), 30  $\mu\text{g}$  Ni(II) and 25  $\mu\text{g}$  Zn(II) was taken and pH was adjusted to the  $7.0\pm 0.5$ . The resulting solution was passed through the column at flow rate of  $3 \text{ mL min}^{-1}$  experimentally. The retained metal ions were eluted from the solid phase with a suitable eluent determined experimentally. The concentration of the metal ions was determined by flame atomic absorption spectroscopy.

### Analysis of trace metal ions in water samples

The spiked water samples were prepared with 1 L of distilled water by adding known amounts of analyte ions, preconcentrated and determined by the standard procedure discussed earlier and percentage recoveries of analyte ions were summarized in Table 2.

**Table 2.** Recovery of trace metals from spiked water sample

Sample added	Proposed method			Reported method <sup>21</sup>		
	Recovery, % <sup>a</sup>			Recovery, % <sup>a</sup>		
	Ni(II)	Cu(II)	Zn(II)	Ni(II)	Cu(II)	Zn(II)
10 $\mu\text{g L}^{-1}$	98.6 $\pm$ 0.29	97.9 $\pm$ 0.04	99.7 $\pm$ 0.16	97.84 $\pm$ 0.08	97.74 $\pm$ 0.04	99.23 $\pm$ 0.08
25 $\mu\text{g L}^{-1}$	97.6 $\pm$ 0.55	98.8 $\pm$ 0.11	99.5 $\pm$ 0.36	97.92 $\pm$ 0.08	97.60 $\pm$ 0.06	99.32 $\pm$ 0.06
50 $\mu\text{g L}^{-1}$	99.3 $\pm$ 0.07	98.6 $\pm$ 0.09	98.7 $\pm$ 0.08	97.72 $\pm$ 0.17	97.42 $\pm$ 0.07	99.12 $\pm$ 0.03

<sup>a</sup>Mean  $\pm$  standard deviation ( $n=5$ )

The water samples which is collected from Swarnamukhi river belt (Srikalahasti), Sea water from Bay of Bengal near Sullurpet, Nellore dist, A.P, India was filtered through a cellulose membrane filter of pore size  $0.45 \mu\text{m}$  and the pH of the sample (500 mL) was adjusted to  $7.0\pm 0.5$  followed by the addition of Schiff base 1-(2-hydroxy-5-methoxybenzalidene) thiosemicarbazide. The sample was passed through the column at the flow rate of  $3 \text{ mL min}^{-1}$  and then washed with 5 mL of doubly distilled water. The sorbed metal ions were eluted with 10 mL of 1 M  $\text{HNO}_3$  after 2 mL of doubly distilled water added through the sorbent and determined as described in general procedure and the results were shown in the Table 3.

**Table 3.** Determination of trace metal ions in various water samples

Elements	Added, $\mu\text{g}$	River water <sup>b</sup>				Sea water <sup>c</sup>			
		Proposed method		Reported method <sup>27</sup>		Proposed method		Reported method <sup>27</sup>	
		Found,	Recovery,	Found,	Recovery,	Found,	Recovery,	Found,	Recovery,
		$\mu\text{g}$	% <sup>a</sup>	$\mu\text{g}$	%	$\mu\text{g}$	%	$\mu\text{g}$	%
Cu(II)	5	4.9	98 $\pm$ 0.2	5.1	102 $\pm$ 0.3	5.0	100 $\pm$ 0.5	4.8	96 $\pm$ 0.4
	10	10.5	105 $\pm$ 0.6	10.3	103 $\pm$ 0.5	9.9	99 $\pm$ 0.4	9.8	98 $\pm$ 0.5
	20	19.8	99 $\pm$ 0.4	19.6	98 $\pm$ 0.6	19.5	97.5 $\pm$ 0.3	19.2	96 $\pm$ 0.6
Ni(II)	5	4.95	99 $\pm$ 0.3	4.8	96 $\pm$ 0.3	5.1	102 $\pm$ 0.2	4.9	98 $\pm$ 0.4
	10	9.8	98 $\pm$ 0.4	9.8	98 $\pm$ 0.5	9.9	99 $\pm$ 0.3	9.7	97 $\pm$ 0.5
	20	20.2	101 $\pm$ 0.5	20.2	101 $\pm$ 0.6	19.5	97.5 $\pm$ 0.4	19.6	98 $\pm$ 0.6
Zn(II)	5	4.95	99 $\pm$ 0.4	-	-	4.95	99 $\pm$ 0.4	-	-
	10	9.9	99 $\pm$ 0.4	-	-	9.95	99.5 $\pm$ 0.5	-	-
	20	19.9	99.5 $\pm$ 0.3	-	-	19.9	99.5 $\pm$ 0.5	-	-

<sup>a</sup>Mean standard deviation( $n=5$ ), <sup>b</sup>Collected from Swarnamukhi river (Srikalahasti), <sup>c</sup>Collected from Bay of Bengal (Sullurpet, Nellore,A.P,India)

## Results and Discussion

1-(2-Hydroxy-5-methoxybenzalidene) thiosemicarbazide is a sensitive, selective and specific complexing ligand for analytical determination of analyte ions (Ni(II), Cu(II) and Zn(II)) at pH  $7.0 \pm 0.5$ . Crystallization of water is less in 1-(2-hydroxy-5-methoxybenzalidene) thiosemicarbazide when compared with other chelating agents, therefore the extractability of the complex become easier. The proposed method was employed for different natural water samples collected from Swarnamukhi river belt (Srikalahasti), Industrial area, Renigunta. The accuracy of the method was ascertained by comparing the results obtained from spiked water samples with reported method<sup>28</sup> and the results were shown in the Table 2.

### Effect of the pH

The pH of the sample solution plays an important role in the ability of the column containing 1-(2-hydroxy-5-methoxybenzalidene) thiosemicarbazide on triton x-100 to preconcentrate the metal ions (Ni(II), Cu(II) and Zn(II)) was studied. For this purpose, a set of solutions (500 mL) each containing one of the four metal ions (Ni(II), Cu(II) and Zn(II)) at a concentration, given in the general procedure was taken. The pH value of the sample solutions was adjusted to a range of 1-12. The obtained solutions were passed through the column at a flow-rate of  $3 \text{ mL min}^{-1}$ . The metal ions were then eluted by an appropriate eluent and determined by FAAS. In all cases, metal retention by the 1-(2-hydroxy-5-methoxybenzalidene) thiosemicarbazide increased with increasing pH and reached a maximum (pH  $7.0 \pm 0.5$ ) after which the retention decreased. So, pH  $7.0 \pm 0.5$  was the optimum pH chosen for the further studies and graphically represented in Figure 1.

### Effect of the flow rates of sample solution

The flow-rate of the sample solution affects the retention of an element on the adsorbent and the duration of complete analysis. Therefore, the effect of the flow rate of the sample solution on the recovery of the metal ions was investigated under the optimum conditions (pH, eluent type, etc.). The sample solution was passed through the column with the flow-rates adjusted in a range of  $0.5 - 5 \text{ mL min}^{-1}$  by gravity. As can be seen in Figure 2, at flow-rates greater than  $3 \text{ mL min}^{-1}$ , there was a decrease in the recovery of Ni(II), Cu(II) and Zn(II). The reason for this decrease is probably insufficient contact of the metal ions and the adsorbent to reach equilibrium. Therefore, a flow-rate of  $3 \text{ mL min}^{-1}$  was applied for Ni(II), Cu(II) and Zn(II) in throughout the experiments. Further studies were carried out at  $3 \text{ mL min}^{-1}$  flow rate of the sample.

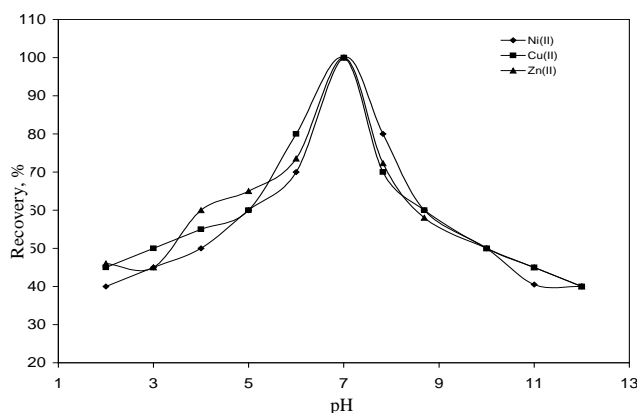
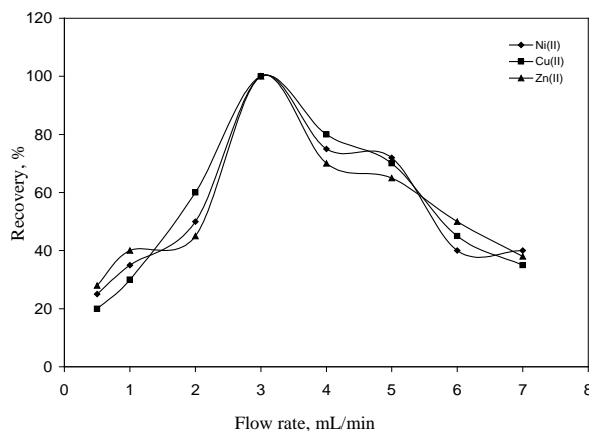


Figure 1. Effect of pH on the complexation of metal with Schiff base



**Figure 2.** Effect of flow rate sample complete retention of analyte volume

#### *Effect of the amount of adsorbent (bed height)*

The retention of the metal ions was examined in relation to the amount of adsorbent, which was varied from 100 to 600 mg. It was found that the recoveries of Ni(II), Cu(II) and Zn(II) were gradually increased up to 500 mg of the adsorbent and decreases sharply beyond 500 mg of adsorbent. Therefore, 500 mg of the adsorbent was used for the determination of Ni(II), Cu(II) and Zn(II).

#### *Effect of the type and volume of elution*

The other important factor that affects the preconcentration procedure is the type, volume and concentration of the eluent used for the removal of metal ions from the sorbent. Optimization of the elution conditions was performed in order to obtain the maximum recovery with the minimal concentration and volume of the elution solution. The different concentrations of HNO<sub>3</sub>, HCl and H<sub>2</sub>SO<sub>4</sub> were tested to remove the bound metal ions from the sorbent, 10 mL of 1 M HNO<sub>3</sub> solution was found to be satisfactory (recovery >95%) for Ni(II), Cu(II) and Zn(II) and the results were shown in Table 4.

#### *Effect of the sample volume*

The effect of sample volume on the elution of Ni(II), Cu(II) and Zn(II) was studied by taking different volumes of the water samples in the range of 100, 250, 500, 750 and 1000 mL. The extraction was carried out as described in general procedure and the results are reported in the Table 5. In all cases the recovery obtained was higher than 95.0% for these elements. However, the efficiency of the recovery slightly decreased when sample volume was more than 500 mL. Hence, 500 mL water sample was chosen for the present study.

**Table 4.** Recovery of trace metals Ni(II), Cu(II) and Zn(II) using various eluent

Eluents	Recovery, % <sup>a</sup>		
	Ni(II)	Cu(II)	Zn(II)
0.5 M HCl	96.35±0.09	95.76±0.05	95.45±0.08
1.0 M HCl	96.27±0.08	96.83±0.09	97.57±0.05
0.5 M H <sub>2</sub> SO <sub>4</sub>	96.57±0.04	96.89±0.06	97.58±0.08
1.0 M H <sub>2</sub> SO <sub>4</sub>	97.91±0.06	97.61±0.04	98.26±0.05
0.5 M HNO <sub>3</sub>	98.94±0.04	98.99±0.05	99.86±0.06
1.0 M HNO <sub>3</sub>	99.76±0.09	99.14±0.08	99.95±0.04

<sup>a</sup> Mean ± standard deviation (n=5)

**Table 5.** Effect of sample volume on elution of metal ions

Volume of sample, mL	Recovery, % <sup>a</sup>		
	Ni(II)	Cu(II)	Zn(II)
100	96.03±0.03	96.20±0.05	98.84±0.09
250	96.27±0.04	96.41±0.04	98.24±0.35
500	99.18±0.07	99.51±0.07	99.65±0.07
750	97.83±0.29	98.14±0.09	97.56±0.25
1000	98.14±0.17	99.15±0.07	98.69±0.16

<sup>a</sup>Mean ± standard deviation (n=5)*Effect of non-target species*

The interference of co-existing ions on the determination of Ni(II), Cu(II) and Zn(II) was investigated. Solution containing 50, 75, 100 and 150  $\mu\text{g mL}^{-1}$  of Ni(II), Cu(II) and Zn(II), respectively and various amounts of foreign ion solutions were prepared applied for the determination of Ni(II), Cu(II) and Zn(II) in various environmental matrices. The deviation of  $\pm 2\%$  or more from the absorbance value of the standard solution was taken as interference. Table 6 indicates that the results obtained from the present method are highly selectivity.

**Table 6.** The effect of interfering ions on 50, 100 and 150  $\mu\text{g mL}^{-1}$  of Ni(II), Cu(II) and Zn(II)

Interfering ions	Tolerance limit, $\text{mg L}^{-1}$
$\text{Cd}^{2+}, \text{Pb}^{2+}$	1100
$\text{NH}_4^+, \text{K}^+, \text{Mg}^{2+}, \text{Li}^+, \text{Cl}^-, \text{NO}_2^-, \text{SCN}^-, \text{SO}_4^{2-}$	100
$\text{Hg}^{2+}, \text{Zn}^{2+}, \text{Ca}^{2+}, \text{Se}^{+4}, \text{F}^-, \text{Al}^{3+}$	50 <sup>a</sup>

<sup>a</sup>Masked by  $\text{NaBH}_4$ *Effect of column reuse*

In order to examine the long-term stability of the reagent, it was subjected to successive adsorption and desorption cycles (5 runs in a day and the next 5 runs one-day later and so on, total 20 runs) by passing 500 mL of metal solutions through the column. The stability and potential recyclability of the column-containing reagent were assessed by monitoring the change in the recoveries of the analytes. After 10 runs, the recoveries of all of the analytes slightly decreased to below 95%.

The loading capacity of 1-(2-hydroxy-5-methoxybenzalidene)thio semicarbazide on triton x-100 was evaluated from the breakthrough curve plot by a method reported in the literature<sup>32</sup>. The capacities were found as to be 28, 26 and 20  $\mu\text{g mL}^{-1}$  for Ni(II), Cu(II) and Zn(II) when using and 18, 16 and 12  $\mu\text{g mL}^{-1}$  without using 1-(2-hydroxy-5-methoxybenzalidene)thiosemicarbazide.

*Lower limit of detection*

The detection of lower limits for any newly developed method shows the degree of sensitivity and selectivity of the analytes extraction. For the purpose were performed by passing the 500 mL sample solution through the preconditioned resin bed, containing metal ions in the range of 50-150  $\mu\text{g mL}^{-1}$  was preferred for the proposed method, a detection limit was found to be 3.6, 3.2 and 3.6  $\mu\text{g mL}^{-1}$  for analyte ions (Ni(II), Cu(II) and Zn(II)) was achieved.

### Analytical features

The analytical features of the proposed method such as precision, linear range of calibration curve, limit of detection were also examined. Precision of the method were estimated by applying successive retention and elution cycles with 500 mL of a sample solution containing 50  $\mu\text{g}$  of Ni(II), 30  $\mu\text{g}$  of Cu(II) and 20  $\mu\text{g}$  of Zn(II) under the optimum conditions, mentioned above. The recoveries of Ni(II), Cu(II) and Zn(II) were quantitative (>93%) and the precision of the method was very good (S.D<3%) for 1-(2-hydroxy-5-methoxybenzalidene)thiosemicarbazide impregnated on triton x-100. The recoveries and the precision found by using triton x-100 as adsorbent alone were very low (below 70%).

The linear calibration ranges for measurements under the optimum conditions were 1.0-8.0  $\mu\text{g mL}^{-1}$  for Ni(II), Cu(II) and Zn(II). The detection limits based on three-times the standard deviation of the blank solution were found to be 3.6, 3.2 and 3.6  $\mu\text{g mL}^{-1}$  detection limit for Ni(II), Cu(II) and Zn(II) respectively.

### Application of proposed method for the determination of trace metals with reported method

In order to check the applicability of the proposed method in various water samples containing Ni(II), Cu(II) and Zn(II) were determined in real water sample collected Swarnamukhi river belt (Srikalahati), Industrial area, Renigunta. An appropriate volume of sample solutions was adjusted to the optimum pH and subjected to the recommended column procedure for the preconcentration and determination of metal ions. The results reported in Tables 2 and 3 with a confidence interval for the 98% confidence level. The proposed method was evaluated in terms of standard deviation and relative standard deviation followed by five repetitions (n=5) which indicates the significance of proposed method over the reported method<sup>27</sup> show the applicability of the proposed method to water analysis. The analytes were determined with a relative error lower than 10% in all samples. It is evident from the data in Table 7 that the proposed method is rapid and more sensitive.

**Table 7.** Comparison of reported method with present method for determination of trace metals

Reagent	Detection limits, $\mu\text{g L}^{-1}$	Remarks	Ref
Diethyldithiocarbamates	4-23	Low detection limit, high reagent consumption	[29]
2-Aminoacetyl thiophenol	10-58	Low detection limit, less sensitivity	[30]
Ammonium pyrrolidine dithiocarbamate	0.83	Low detection limit, high reagent consumption	[31]
1-(2-Hydroxy-5-methoxy benzalidene) thiosemicarbazide	3.0 – 3.6	Sensitive, selective, facile, economical reagent, free from interference and contamination.	Present work



## Conclusion

The ability of 1-(2-hydroxy-5-methoxybenzalidene)thio semicarbazide for selective sorption of trace metals from aqueous solution was confirmed. The proposed procedure provides a simple, sensitive, precise, reliable and accurate technique for the preconcentration and separation of Ni(II), Cu(II) and Zn(II). The accuracy of the results was verified by analyzing the spiked water and natural water samples and the results were shown in the Tables 2 and 3 were compared with reported method<sup>27</sup> in literature. The recoveries for these elements were very satisfactory and it is evident for the reliability of the proposed method.

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