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Solid phase extraction method for the determination of lead, nickel, copper and manganese by flame atomic absorption spectrometry using sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT) in water samples

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Abstract

A novel column solid phase extraction procedure was developed for the etermination of ead, nickel, copper and manganese in various water samples by flame atomic absorption spectrometry (FAAS) after preconc ration on sod n bispiperdine-1,1'-carbotetrathioate (Na-BPCTT) supported by Amberlite XAD-7. The sorbed element was subsequently elu with 1 M n ic acid and the acid eluates are analysed by Flame f ad ent, eluent type and volume, flow-rate of the sample atomic absorption spectrometry (FAAS). Various parameters s as pH, amo solution, volume of the sample solution and matrix interference the retention of the metal ions have been studied. The optimum pH for fte the sorption of above mentioned metal ions was about 6.0 ± 0.2 . e load city of adsorbent for Pb, Cu, Ni and Mn were found to 28, 26, 22 and 20×10^{-6} g/mL, respectively. The recoveries of lead, copped nic A and manganese under optimum conditions were found to be 96.7–99.2 at the 95% confident level. The limit of detection y 2, 2.8 3.6×10^{-6} g/mL for lead, copper, nickel and manganese, respectively by applying a preconcentration factor 50. The prop ed enric hent me d was applied for metal ions in various water samples. The results were obtained are good agreement with reported m od. © 2006 Elsevier B.V. All rights reserved.

Keywords: Preconcentration; Solid phase fraction (SPE); Jum bispiperdine-1,1'-carbotetrathioate (Na-BPCTT); Amberlite XAD-7; Flame atomic absorption spectrometry (FAAS); Water samples

1. Introduction

Trace metal analys imported part of studies in anah order to prevent the interference effect of lytical chem vels of trace metal ions in the matrix ap to deter line the ame atomic absorption spectrometry usuuples by water (ally requi rficient parconcentration step in order to bring on of the analyte within the dynamic measuring the concentry range of the design limit. The separation enrichment techniques have been used to improve the sensitivity and selectivity of the trace analysis of the metal ions. Few methods including cloud point extraction [1-3] solvent extraction [4], co precipitation [5,6] membrane filtration [7], etc have been reviewed

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for the enrichment of heavy metal ions in-off line or on-line performance. The above reported methods suffer from several disadvantages like poor sensitivity, provide low detection limit and also helps to avoid matrix interference in the analysis of the real samples.

Solid phase extraction based on the adsorption is also one of the important preconcentration methodologies [8–15]. It has some advantages including short analysis time, high preconcentration factors, low consumption of the organic solvent. In the solid phase extraction of the metal ions various adsorbents such as Amberlite resins [8,10–14] molten naphthalene [15] chromos orb resins [16,17] activated carbons [18–20] silica gel [21–24] were employed for the separation and preconcentration of the metal ion in the various environmental samples.

Chelating reagents like ammonium pyrrolidine dithiocarbamates (APPC) and sodium diethyl dithiocarbamates (NaDDC) are generally used for complexiation and extraction in to organic

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solvent. Uses of APDC and NaDDC have certain disadvantages like poor sensitivity, less stability and low recoveries.

In view of this authors have reported, a facile, simple and novel method for the column separation and preconcentration technique for the determination of lead, nickel, copper and manganese from various water samples. The column loaded with Amberlite XAD-7 supported impregnated with sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT). The sorbed elements were sequently eluted with 1 M nitric acid. The acid eluates were further analysed by FAAS. Optimum experimental conditions were investigated with respect to a standard solution of the same matrix, in order to examine the possibility of obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. Under these conditions, preconcentration factor of 40–60 was achieved.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer ® Model 2380 atomic absorption spectrometry (AAS) with air-acetylene flame and hallow cathode lamps were used for the analysis of lead, copper, nickel and manganese. All instrumental settings were those recommended in the manufacturer's manual book and the instrumental conditions were shown in Table 8. A pH meter, Elico Li-129 Model glass-electrode was employed for measuring pH values.

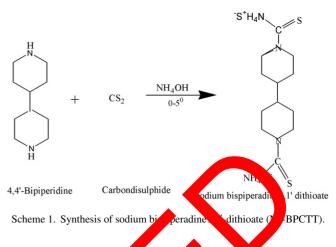
2.2. Reagents and standard solution

Doubly distilled water and highly purity recents were used for all preparations of the standard and samples solution of the the chemicals were purchased from Merri Chengener, Mumbai, India. Standard stock solutions (100% ag/L) of PerVi, Cu and Mn were prepared by dissolving the proper amounts chanalyte in doubly distilled water in a 100 mL took. Dilute solutions were prepared by the appropriate dilution of the stock solution daily in doubly distilled water for reference solutions. The pH adjustment was not e by adving 2 mL of phosphate buffer solution.

H 6.0. 1.2 was epared by adding con-Buffer soluti aric and (7.0,) 250 mL distilled water centrated su in a 500 Z flask. den monos dium dihydrogen phosphate monohydra. (20 and the flask shaken until dissolution was mpleted. The solution was then diluted to 500 mL. It was s. ed in a clean metal free polyethylene bottle. Sodium bispiperdin, 1/-carbotetrathioate (Na-BPCTT) solution (0.01%) was prepared by dissolving 0.01 g of the reagent in 100 mL of doubly deionized distilled water. Synthesis of (Na-BPCTT) is shown in Scheme 1.

2.3. Column preparation

0.2–0.6 g of Amberlite XAD-7 loaded with sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT) was packed in a glass column having stopcock and a porous disk, was 10 cm long and 1.0 cm internal diameter. A small amount of glass wool



was placed on the disk of preven disturbing of the XAD-7reagent resin beds during the scale ple loading. The bed height of the resin in column was apply trately 2 mm. The column was condition with a pl/L HCl sone on ad doubly distilled water. Then the column we conditioned of studied pH by passing an aqueous solution of Hell or NH₃ having the same pH as that of sample solution through the column, prior to passage of the sample solution.

2.4 Procedure

An off me column procedure was applied for the preconcentree An aliquot of the sample solution (500 mL) containing 15 µg of lead, 20 µg copper, 15 µg nickel and 10 µg manganese was taken and pH was adjusted to the 6.0 ± 0.2 with phosphate buffer. The resulting solution was passed through the column at flow rate of 2 mL/min experimentally. The retained metal ions were eluted from the solid phase with a suitable eluent determined experimentally. The concentrations of the metal ions were determined by flame atomic absorption spectroscopy.

2.5. Analysis of trace metal ions in water samples

The spiked water samples were prepared with 2 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 presented in Table 5.

The water samples which is collected from different places (in and around Tirupati) analysed was filtered through a cellulose membrane filter of pore size $0.45 \,\mu\text{m}$. The pH of 500 mL of the sample was adjusted to 6.0 ± 0.2 . Then the reagent solution was added. The sample was passed through the column at the flow rate of 2 mL/min. The column was then washed with 5 mL of doubly deionized distilled water. The sorbed metal ions were eluted with 10 mL of 1 M HNO₃ 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 6.

3. Result and discussion

Sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT) is a sensitive, selective and specific complexing ligand for ana-

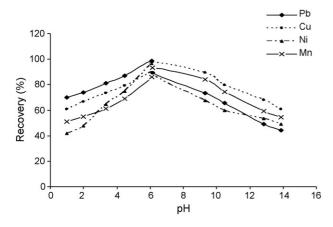


Fig. 1. Effect of pH on the complexation of metal with BPCTT.

lytical determination of analyte ions (lead, copper, nickel and manganese) at pH 6.0 ± 0.2 . Crystallization of water is less in sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT) when compared with other dithiocarbamate, therefore the extractability of the complex become easier. The metal salt of this reagent is a resonance hybrid of the structures which contributed to stability of metal complexes. This proposed method was employed for different natural water samples collected from Swarnamukhi river belt (Chandragiri), Kalyanidam reservoir and Ghajulamandayam area. The accuracy of the method was ascertained by comparing the results with reported method [26] and the number of the stability of the trade of the stability of the stability of the stability of the method [26] and the number of the stability of the method [26] and the number of the stability of the structures which contributed to stability of metal complexes. This proposed method was employed for different natural water samples collected from Swarnamukhi river belt (Chandragiri), Kalyanidam reservoir and Ghajulamandayam area. The accuracy of the method was ascertained by comparing the results with reported method [26] and the number of the stability of the stability of the stability of the stability of the number of the

3.1. Effect of the pH

The pH of the sample solution play, impor the ability of the column containing sou spiperdine-1,1'-carbotetrathioate (Na-BPCTT on Ambe XAD-7 to preconcentrate the metal ions <u>Â</u> copper, nick and manof solutions (500 mL) ganese) was studied. For that purpose, a each containing one of the our metal ion lead, copper, nickel and manganese) at a mcentration given he he general procedure, was taken the pH yr te of the sample solutions was -7 ch phosphate buffer. The obtained adjusted to a range of sed the gh the gramn at a flow rate at about solutions wer re ten eluted by an appropriate l ions 2 mL/min ne m ed by FAA. In all cases, metal retention by d determ eluent 2 the reag inc creasing pH and reached a maximum (pH o (0.2) after which the retention decreased. So pH optimum pH chosen for the further studies 6.0 ± 0.2 was and graphically resented in Fig. 1 and data was shown in Table 1.

3.2. Effect of the flow rates of sample solution

The retention of an element on an adsorbent also depends on the flow rate of the sample solution. 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 mL/min by gravity.

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Effect of pH on the complexation of metal ions with sodium bispiperdine-1,1'carbotetrathioate (Na-BPCTT)

pН	Recovery (%) ^a			
	Pb	Cu	Ni	Mn
2.0	81.8 ± 0.05	78.1 ± 0.02	81.4 ± 0.03	83.3 ± 0.04
3.0	88.5 ± 0.09	89.1 ± 0.04	88.2 ± 0.03	95.4 ± 0.05
4.0	95.3 ± 0.05	94.8 ± 0.04	92.3 ± 0.04	96.1 ± 0.09
5.0	96.1 ± 0.04	98.6 ± 0.16	98.8 ± 0.07	96.3 ± 0.11
6.0	98.1 ± 0.05	99.1 ± 0.08	99.8 ± 0.16	98.3 ± 0.04
7.0	95.2 ± 0.06	97.1 ± 0.29	o.4 I	97.2 ± 0.08
2 3 4		· · · (N 5)		

^a Mean \pm standard deviation (N=5).

n 3 mL/min, As can be seen in Fig. 2. flow rate greater 1 pper nickel and there was a decrease in e recovery of L ٦. manganese. The reast for this crease is pobably insufficient nď e adsorbet to reach equilibrium. contact of the methion. rate of 2. /min w applied for lead, copper, Therefore, a fl a the experiments. The flow nickel and nese in thro. rate of the elution. lution was 2 mL/min.

Effect of the amous of adsorbent (bed height)

The retention of the metal ions was examined in relation to a mount of a sorbent, which was varied from 200 to 600 mg. It we found that the recoveries of lead, copper, nickel and manganese were gradually increased up to 500 mg of the adsorbent. Fore, 500 mg of the adsorbent was used for lead, copper, nickel and manganese.

3.4. Effect of the type and volume of elution solutions

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 nitric acid hydrochloric acid and sulphuric acid were tested to remove the bound metal ions from the sorbent, 10 mL of 1 M HNO₃ solution was found to be satisfactory (recovery >95%) for lead,

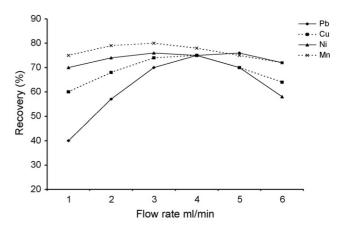


Fig. 2. Effect of flow rate of sample volume on retention of analyte ions.

Table 2Effect of sample volume on elution of metal ions

Volume of sample (mL)	Recovery (%)	a		
	Pb	Cu	Ni	Mn
100	96.0 ± 0.03	96.1 ± 0.05	96.1 ± 0.02	98.8 ± 0.09
250	96.2 ± 0.04	96.4 ± 0.04	97.1 ± 0.29	98.2 ± 0.35
500	99.1 ± 0.07	99.4 ± 0.07	98.2 ± 0.09	99.6 ± 0.07
750	97.8 ± 0.29	98.1 ± 0.09	99.1 ± 0.32	97.5 ± 0.25
1000	98.1 ± 0.17	99.1 ± 0.07	98.9 ± 0.14	98.6 ± 0.16

^a Mean \pm standard deviation (N=5).

copper, nickel and manganese and the results were shown in Table 3.

3.5. Effect of the sample volume

The effect of sample volume on the elution of lead, copper, nickel and manganese 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 3. In all cases the recovery obtained was higher than 96.0% for these elements. How ever, 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 and the results are shown in Table 2.

3.6. Effect of interfering ions

The interference of co-existing ions on the diagram in on of lead, copper, nickel and manganese was interdigated. Jultion (500 mL) containing 50, 50, 100 and 150 × 10^{10} g/s or real copper, nickel and manganese, respectively and values amounts of foreign ions were prepared and a sedure descend in the

Eluents	Recovery (%			
	Pb	Ni	2	Mn
0.5 M HCl	96 09	± 0.05	95.5 ± 0.06	95.3 ± 0.08
1.0 M HCl	$b.2 \pm 0.8$	96. 0	97.5 ± 0.08	97.5 ± 0.05
0.5 M H ₂ SQ	96.5 ± ∮ 4	96.8 🔟 .06	97.2 ± 0.08	97.2 ± 0.08
1.0 M H ₂ S	97.8 -	07.5 ± 0.04	97.9 ± 0.04	98.1 ± 0.05
0.5 M HNO3	8 £ 0.04	98.9 ± 0.05	98.8 ± 0.05	99.7 ± 0.04
1.0 M HNO ₃	± 0.09	99.1 ± 0.08	99.1 ± 0.03	99.8 ± 0.06

^a Mean \pm standard densition (N=5).

Table 4

The effect of interfering ions on the recovery of 50, 50, 100, $150 \,\mu g \,m L^{-1}$ of Pb, Cu, Ni and Mn

Interfering ions	Concentration of interfering	Recovery (%) ^a				
	ions (×10 ⁻⁶ g/L)	Pb	Cu	Ni	Mn	
Cd ²⁺	1000	99.5 ± 0.1	101.0 ± 0.2	101.0 ± 0.1	99.0 ± 0.2	
NH ₄ ⁺ , K ⁺ , Mg ²⁺ , Li ⁺ , Cl ⁻ , NO ²⁻ , SCN ⁻ , SO ₄ ²⁻	150	99.8 ± 0.2	99.5 ± 0.1	99.0 ± 0.3	99.9 ± 0.3	
Hg ²⁺ , Zn ²⁺ , Cr^{3+} , Ca ²⁺ , Se ⁺⁴ , F ^{-b} Al ³⁺	50	100.0 ± 0.1	99.8 ± 0.2	98.5 ± 0.1	100.0 ± 0.1	

^a $x \pm \text{st} \sqrt{n}$ at 95% confidence (n = 5).

^b Masked by NaBH₄.

experimental part was applied The deviation of $\pm 2\%$ or more from the absorbance value of the standard solution was taken as interference The results were shown in the Table 4. It can be seen that a very good selectivity is achieved.

3.7. Preconcentration time

The effect of preconcentration time on integrated absorbance of analyte ions (lead, copper, nickel and manganese) were investigated in the range of 200–300 s, at a security loading rate of 2 mL/min. It is the evident for the increase of preparent time causes an increase of integrater absorbance of analytes. It is very difficult for the PCC (Preconcentration column) to be eluted. There fore the loading time was nelected as 250 s for thought the experiments.

3.8. Effect of columereus

In order to examine the long open stability of the reagent, it was subjected to supersive adsorption and desorption cycles (5 runs into day and bounext 5 runs 1-day later, and so on, total to runs) by passing 50 mL of metal solutions through the comm. The stability and potential recyclability of the columncontaining reagen were assessed by monitoring the change in the assoveries of the analytes. After 10 runs, the recoveries of all of boundary slightly decreased to below 95%.

Ling capacity

The loading capacity of sodium bispiperdine-1,1'rarbotetrathioate (Na-BPCTT) immobilized on Amberlite XAD-7 was evaluated from the breakthrough curve plot by a method given by Bag et al. [30]. The capacities were found as to be 28, 26, 22 and 20×10^{-6} g/mL for lead, copper, nickel and manganese when using sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT) and 18, 16, 14 and 12×10^{-6} g/mL with out using sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT), respectively.

3.10. 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 $3-30 \times 10^{-6}$ g/mL for the

Table 5			
Recovery of trace metals	from spiked	water	sample

Elements	Proposed metho	od (conce	entration	added)						Reported metho	od [26]	
	$10 \times 10^{-6} \text{ g/L}$ $15 \times 10^{-6} \text{ g/L}$			25×10^{-6} g/L			Recovery (%) ^a					
	Recovery (%) ^a	t-Test	<i>f</i> -Test	Recovery (%) ^a	t-Test	<i>f</i> -Test	Recovery (%) ^a	t-Test	f-Test	10×10^{-6} g/L	$15 imes 10^{-6}$ g/L	$25 imes 10^{-6} \text{ g/L}$
Pb	98.3 ± 0.09	4.89	0.13	97.3 ± 0.21	1.38	0.41	98.5 ± 0.08	0.10	0.01	93.2 ± 0.03	97.1 ± 0.13	98.0 ± 0.53
Cu	97.6 ± 0.29	3.83	0.07	97.5 ± 0.55	1.49	0.11	99.2 ± 0.07	0.16	0.79	93.5 ± 0.08	96.1 ± 0.08	98.4 ± 0.17
Ni	96.9 ± 0.04	3.84	0.26	$96.7 \pm 0.0.11$	1.44	0.27	98.5 ± 0.09	1.30	0.32	92.9 ± 0.04	95.1 ± 0.06	97.0 ± 0.07
Mn	98.6 ± 0.16	4.53	0.69	98.6 ± 0.36	2.94	0.36	97.5 ± 0.08	0.10	0.83	93.9 ± 0.08	95.5 ± 0.06	98.2 ± 0.3

^a Mean \pm standard deviation (N=5).

Table 6

Determination of trace metal ions in various water samples

Elements	Proposed met	Recovery (%) ^a				
	River water		Tap water			
	Added	Found (×10 ⁻⁶ g/L)	Recovery (%) ^a	F (10 ⁻⁶ g/L)		
Pb	5	4.8	98.0 ± 0.01	4.95	99.0 ± 0.02	
	10	9.8	98.0 ± 0.02	9.9	99.0 ± 0.05	
	20	19.8	99.5 ± 0.03	19.8	99.0 ± 0.06	
Cu	5	4.95	99.0	2	104.0 ± 0.02	
	10	9.7	99 🖉 0.06		99.0 ± 0.01	
	20	19.9	99 ± 0.05	19.9	99.5 ± 0.08	
Ni	5	4.9	92 ± 0.01	5.1	102.0 ± 0.05	
	10	9.8	98. 0.07	9.95	99.5 ± 0.05	
	20	19.9	99.0 _ 94	19.6	98.5 ± 0.03	
Mn	5	4.9	0.0 ± 0.03	4.95	99.0 ± 0.04	
	10	9.9		9.95	99.5 ± 0.05	
	20	19.9	99.5 ± 0.02	19.9	99.5 ± 0.02	

^a Mean \pm standard deviation (N = 5).

proposed method, a detection limit was found to be 10, 50 and 3.6×10^{-6} g/mL for analyte ior (lead, or er, nickel and manganese) was achieved.

3.11. Analytical features

The analytical feat less of the proposed method such as precision, linear range calibre on 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 25 μ g of lead, 20 μ g of copper, 15 μ g nickel and 10 μ g of manganese under the optimum conditions, mentioned above. The recoveries of lead, copper, nickel and manganese were quantitative (>95%) and the precision of the method was very good (R.S.D. < 3%) for sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT) on Amberlite XAD-7. The

Table	7
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or present method for determination of trace metals

Complex agent	Detection limits ($\times 10^{-6}$ g/L)	Remarks	Reference
Phenylpipera. Athiocarbamate	17	Low detection limit, commercial reagent, less sensitivity	[18]
Ammonium pyrrol. Adithiocarbamate	0.83	Low detection limit, high reagent consumption, instability of the complex	[25]
Piper dine dithiocarbamate	25	It is a column technique and needs elaborated procedure, time consuming, risk of contamination	[26]
Ammonium hexamethylene dithiocarbamate	15	Low sensitivity and selectivity	[27]
Potassium propyl xanthate	10	Low detection limit, PO ₄ ³⁻ , Mn ²⁺ , and Fe ³⁺ interferes seriously	[28]
Potassium ethyl xanthate	12	Less sensitive and suffers from interference effect	[29]
Sodium bispiperdine-1,1'-carbotetrathioate (Na-BPCTT)	3.6, 3.2, 3.0, 3.6	Sensitive, selective, facile, economical reagent, free from interference and contamination	This work

Table 8
FAAS instrumental conditions employed to determination of metal ions

Flame type	Air acetylene
Air flow rate	$11.00 \mathrm{L}\mathrm{min}^{-1}$
Acetylene flow rate	$0.50 \mathrm{L}\mathrm{min}^{-1}$
Slit width	0.7 nm
Lamp current	5 mA
Burner height	13 mm
Integration time	5 S
e	

recoveries and the precision found by using Amberlite XAD-7 as adsorbent alone were very low (below 70%). The linear calibration ranges for measurements under the optimum conditions were $4.0-8.0 \times 10^{-6}$ g/mL for lead, copper, nickel and manganese. The detection limits based on three-times the standard deviation of the blank solution were found to be 3.6, 3.0, 2.8 and 3.6×10^{-6} g/mL detection limit for lead, copper, nickel and manganese, respectively.

3.12. 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, lead, copper, nickel and manganese were determined in a water sample collected in and around Tirupati an appropriate volume of sample solutions was adjusted to the optimum pH and subjected to the recommended column produce for the preconcentration and determination of metal ion. The results reported in Tables 5 and 6 with a confidence interva for the 95% confidence level show the applicability or the proposed method to water analysis. The analytest ere determined with a relative error lower than 10% in all samples.

It is evident from the data in Table 7 the the public dimethod is rapid and more sensitive.

4. Conclusion

The results presented to this paper demonstrue the usability of a sorbent sodium spiperd'te-1,1'-carbotetrathioate (Na-BPCTT), for the preconceptration of traccinetal ions. The ability of sodium bispital ine-1,1 carbotetrationate (Na-BPCTT) for selective sortion of trace meals from aqueous solution was confirmed. The proposed procedure provides a simple, sensitive, precise, reliable and accurate technique for the preconcentration and determination of lead, copper, nickel and manganese. The recoveries of analytes studied were nearly quantitative (>95%). The accuracy of the results was verified by analyzing the spiked water samples and the results were shown in the Table 5. The recoveries for these elements were very satisfactory and it is evident for the reliability of the proposed method for the analysis of water samples.

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