

**DETERMINATION OF SOME HEAVY METALS AT LOW LEVEL USING PRECONCENTRATION AND ATOMIC ABSORPTION SPECTROMETRY**

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**ABSTRACT**

A new method for the preconcentration of some trace metal ions (Cu, Cd, and Pb) using *N*-{[phenylaminothioxomethyl]hydrazino carbonylmethyl} trimethyl ammonium chloride (PTHAC) was investigated using a mini-column filled with Amberlite IRC-50 resin. Metal contents were determined by flame atomic absorption spectrometry (FAAS). The accumulated complexes on the resin were eluted with H<sub>2</sub>SO<sub>4</sub> (2 M). The effects of the analytical parameters such as pH, amount of ligand, eluent type, resin quantity, sample volume and sample flow rate were investigated on the recovery of the metals from aqueous solutions. The relative standard deviation (R.S.D.) of the method is 2%. Characterization of the isolated solid metal complexes was also investigated.

**Keywords:** Trace heavy metals, Preconcentration, Amberlite IRC-50, Flame atomic absorption spectrometry, *N*-{[phenylaminothioxo methyl] hydrazinocarbonylmethyl} trimethylammonium chloride.

**INTRODUCTION**

The pollution of water resources due to the indiscriminate disposal of heavy metal has been causing worldwide concern for the last few decades. Pollution of the aquatic environment with heavy metals has

become a worldwide problem in recent years. The toxicity of heavy metals depends on a number of factors. Symptomology varies according to the metal in question, the total dose absorbed and whether the exposure was acute or chronic and the age of the person can also influence toxicity (**Mortada et al., 2001; Mortada, et al., 2004; Gundogan, et al., 2004; Duruibe, et al., 2007**). Among environmental pollutants' Cu, Pb and Cd are of particular concern due to their potential toxic effect and ability to bioaccumulate in aquatic ecosystem (**DE, 2010**). These metal ions when present in sufficient quantity in the aqueous media can be harmful to aquatic life, therefore water contaminated by toxic metals remains also as a serious public health problem (**Ahmed, 2004; Askun, et al., 2008; Ghaedi, et al., 2009; Duran, et al. 2009**).

The determination of trace metals by flame atomic absorption (FAAS) among the determination techniques has a number of advantages included high selectivity, speed and finally low operation coast. Despite the selectivity and sensitivity of FAAS, there crucial needs for the preconcentration of trace elements before their analysis due to frequent low concentrations in numerous samples. Solid-phase extraction (SPE) (**Candor, et al., 2005**), ion-exchange ( **Kenawy, et al., 1993; Hafez, et al., 2001**), cloud point extraction ( **Lemos, et al., 2006; Afkhami, et al., 2006**), liquid–liquid extraction (**Gupta, and Khopkas, 1996; Eskandasi, et al., 2001**), co-precipitation (**Divrikli, & Elci, 2002**) and flotation (**Cundeva, et al., 2000**), have been widely used for the preconcentration and separation of trace metal ions. The basic principle of SPE of trace metal ions is the transfer of analytes or their complexes from aqueous phase to the active sites of solid phase sorbent. Consequently, in recent years SPE has been successfully used for separation and determination of metal ions.

The aim of the present study is to introduce a novel method for separation, preconcentration and FAAS determination of metal ions as copper, lead and cadmium in water and solid samples. The results of this research will assist in acquiring information about the level of toxic metal in drinking water, fish (which is an important component of the human diet in this zone) and baby dry milk (from the market) in Mansoura city, Egypt.

## EXPERIMENTAL

### Apparatus

#### Flame atomic absorption spectrophotometer (FAAS)

A Perkin–Elmer model 2380 atomic absorption spectrophotometer (USA) equipped with single element hollow cathode lamp and air-acetylene burner used for determination of metals.

#### pH measurements

The pH values were measured using a pH-meter (Hanna-Instruments, 8519, Italy) with an expanded scale and having an accuracy of  $\pm 0.01$ .

#### UV-visible spectrophotometer

The spectra were recorded using a spectrophotometer model UNICAM 2001, UV-Vis using a 1 cm quartz cell, in the range 200-800 nm.

#### Infrared spectra

The IR spectra were carried out using Mattson 5000 FTIR spectrometer in the range  $4000\text{-}400\text{ cm}^{-1}$ .

#### $^1\text{H-NMR}$ spectra

$^1\text{H-NMR}$  measurements were obtained on a JEOL JNM LA 300 spectrometer (300 MHz). Chemical shifts are given in ppm relative to the internal TMS at Cairo University, Egypt.

#### Gas chromatography- mass spectra (GC-Mass)

Gas chromatography-mass spectra of ligand was carried out on DI analysis Shimadzu QP-2010 plus with ion source temperature  $200\text{ }^\circ\text{C}$ , scan speed 526, start-end (m/z) (50-300), electron voltage 70 eV and ionization mode (EI) at the Microanalytical Unit, Cairo University, Egypt.

#### Chemical reagents

All chemicals used are of analytical grade (BDH and Merk). Deionized distilled water is used for throughout experimental study.

Solutions of Cu(II), Cd(II) and Pb(II) salts were prepared by appropriate dilution from 1 mg.ml<sup>-1</sup> stock (BDH) solution for AAS.

### **Preparation of *N*-{[phenylaminothioxomethyl]hydrazinocarbonyl methyl} trimethyl ammonium chloride**

The ligand was synthesized by boiling under reflux a solution of Girard's T (16.8 g, 0.1 M) with phenyl isothiocyanate (12 ml, 0.1M) in absolute ethyl alcohol (100 ml) for 2 h. The white product was filtered off while hot, washed thoroughly with cold solution of absolute EtOH and dry diethyl ether, respectively, and finally dried in vacuum desiccator over silica gel. The purity of the ligand was checked by its melting point (209 °C), TLC and elemental analyses.

### **Preparation of the metal complexes**

The metal complexes were prepared by adding equivalent amount (1 mmol) of the metal (II) chloride (Cu and Cd) and Pb(II) nitrate in 25 ml deionized water to the ligand (1 mmol) in 25 ml. Sodium acetate was added in case of Cd and Pb till the pH reaches 5-6. The mixture was refluxed on a hot plate for 3 h. The isolated solid complexes were filtered off immediately, washed several time with hot water and EtOH, respectively, and finally dried in a vacuum desiccators over fused CaCl<sub>2</sub>.

### **Column preparation**

A glass column (10 cm length and 1.0 cm diameter) with a porous disk and a stopcock has been used for preconcentration of the metals. Amberlite (solid sorbent, IRC-50) was ground and sieved (150–200 μm), placed in the column and then washed successively with 1 mol L<sup>-1</sup> NaOH, water, 1 mol L<sup>-1</sup> HNO<sub>3</sub>, water, acetone and water, and finally kept in a desiccator, after drying.

### **Sampling**

Water samples were kept in polyethylene bottles, which were thoroughly washed with detergent, tap water, HNO<sub>3</sub> and deionized water, respectively, prior to collection. The samples were collected from tap water, Nile River, fish, dry milk and effluent from the Talkha fertilizer company, Mansoura, Egypt.

For fish and dry milk samples, a sample (0.25 g) was heated at 100 °C in a beaker containing a mixture of concentrated HNO<sub>3</sub> (5 ml) and H<sub>2</sub>O<sub>2</sub> (5 ml) for 15 min and then 2 ml concentrated HClO<sub>4</sub> acid was

added. The mixture was heated with stirring for 1 h till a clear solution was obtained and then evaporated near dryness on a hot plate and finally diluted to 50 ml with distilled-deionized water.

### **Preconcentration procedure**

The proposed method was tested with standard solutions prior to the determination of the trace metals in the real samples. A solution containing 50 µg of Cu(II), Cd(II) and Pb(II) salts were prepared. The pHs of the solutions were adjusted to the desired values in the range 5-6 by adding 0.5 g sodium acetate for Pb and Cu and 0.1 g for Cd and then 5.0 ml of the ligand ( $2 \times 10^{-3}$  Mol.L<sup>-1</sup>). The solution was completed with redistilled water and adjusted to 50 ml. The resultant solution was passed through the column containing 50 mg Amberlite IRC-50 with flow rate 3 ml min<sup>-1</sup> and then the column was rinsed with 10 ml of water. The retained species (metal-PTHAC) on the resin was eluted with 10 ml 2M H<sub>2</sub>SO<sub>4</sub>. Finally, the solution was analyzed by FAAS. It must be noted that the ligand and H<sub>2</sub>SO<sub>4</sub> have no affect on the AAS signal.

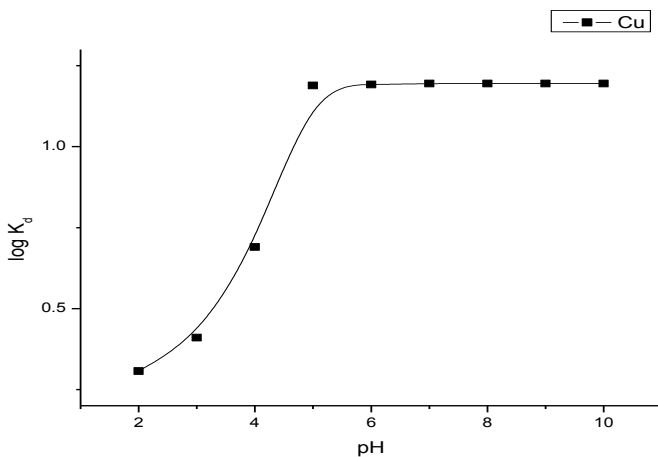
## **RESULTS AND DISCUSSION**

### **Effect of pH**

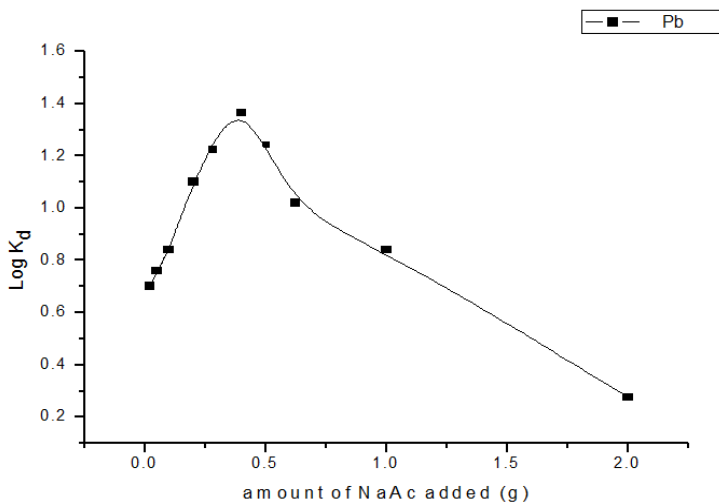
The effect of pH plays a major role in the preconcentration studies. Cu(II), Pb(II) and Cd(II) ions were tested in different pH values at pH range from 2-9. The recovery of the metal ions on the resin (IRC-50) is quantitative in pH range 5-6. The change of recovery of the metals is investigated by the distribution ( $K_d$ ) and determined using the following equation:

$$K_d \text{ (ml/g)} = C_{i,\text{ex}} \text{ (}\mu\text{g/g)} / C_{\text{sol}} \text{ (}\mu\text{g/ml)}$$

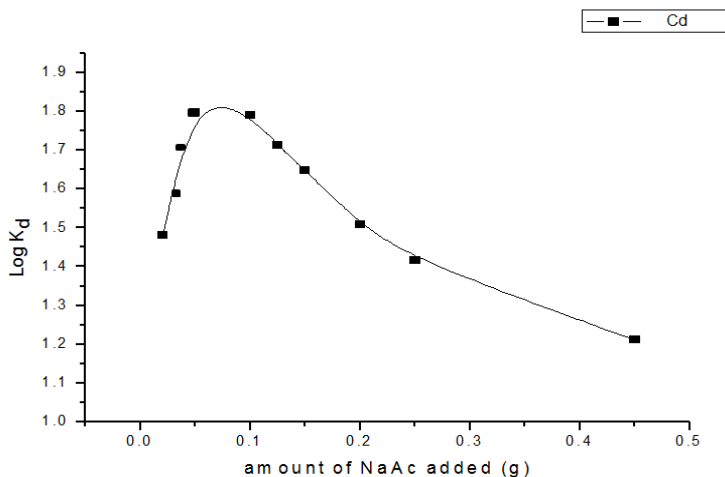
Where  $C_{i,\text{ex}}$  is the metal ion concentration on solid phase and  $C_{\text{sol}}$  is the metal ion concentration in the solution. From the later optimization study, 0.5 g sodium acetate is chosen for adjusting the pH for Pb and Cu and 0.1 g for Cd and the data are shown in Figs. 1-3.



**Fig. (1):** The variation of pH with  $\log K_d$  of the Cu ions.



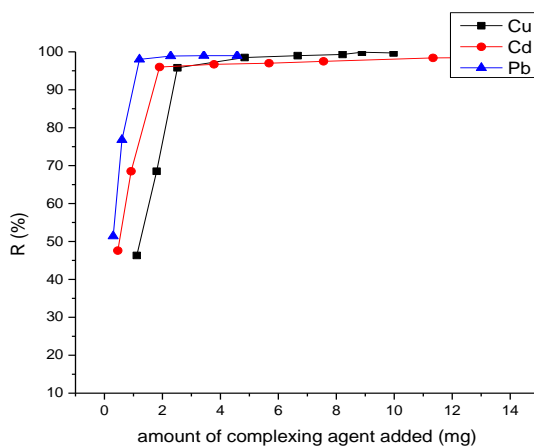
**Fig. (2):** The variation of the amount of sod. acetate added with  $\log K_d$  of the Pb ions.



**Fig. (3):** The variation of the amount of sod. acetate added with log K<sub>d</sub> of the Cd ions.

### Effect of quantity of the complexing agent

The effect of the ligand (PTHAC) concentration as a complexing agent on the retention of Cu(II), Pb(II) and Cd(II) ions are studied. Various amounts of the ligand (1-14 mg) are investigated at pH 5 and in the range of flow rate 2-5 ml/min. The quantitative recoveries of the metal ions with 2 ml.min<sup>-1</sup>. and 2 mg ligand are observed. The data are shown in Fig. 4.



**Fig. (4):** Effect of the complexing agent quantity (pH=5-6).

## Characterization of solid complexes

### Elemental analysis and physical data

All the complexes are stable in prolonged exposure in air. Elemental analyses and other physical data are shown in Table (1).

**Table (1):** Analytical and physical data of the ligand and the isolated metal complexes.

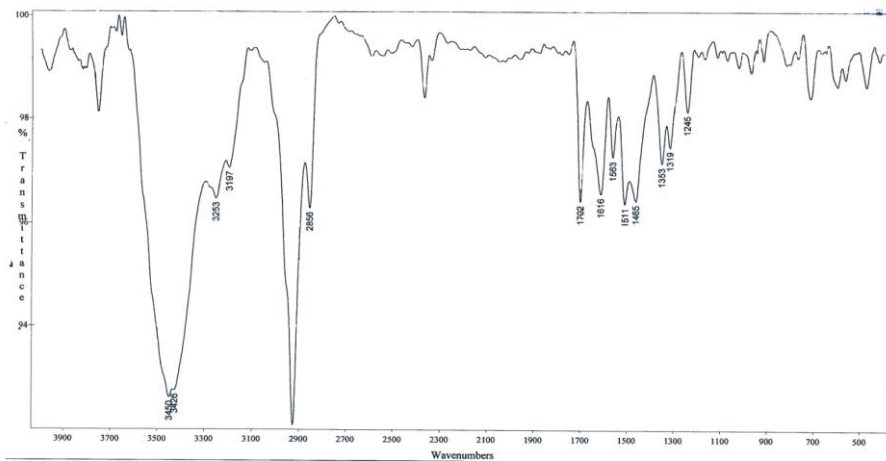
Compound	Color	M.p.; (°C)	% Found (Calcd.)			
			C	H	Cl	M
H <sub>2</sub> L	white	209	47.4 (47.6)	6.0 (6.3)	-	-
[Cu(H <sub>2</sub> L-H) <sub>2</sub> ].2.5H <sub>2</sub> O	green	160	40.4 (41.0)	4.7 (5.9)	10.3 (10.1)	8.5 (9.0)
[Cd(H <sub>2</sub> L-H) <sub>2</sub> ].4.5H <sub>2</sub> O.0.5EtOH	white	>300	35.6 (35.8)	6.1 (5.8)	7.9 (8.8)	14.3 (13.9)
[Pb(L-H)NO <sub>3</sub> .1/2H <sub>2</sub> O.1/2EtOH]	yellow	125	25.4 (25.9)	3.0 (3.7)	6.2 (5.9)	35.4 (34.4)

### <sup>1</sup>H-NMR spectra

The <sup>1</sup>H-NMR spectrum of the ligand in d<sub>6</sub>-DMSO shows three singlet signals at 11.02, 10.5 and 9.9 ppm, downfield with respect to TMS, assigned to the protons of the three NH groups. The presence of these signals indicates that the ligand exists in thione and keto forms. The multiple signals in the 7.1-7.7 ppm region are assignable to the protons of phenyl ring. The two signals at 3.25 and 4.3 ppm are assigned to the protons of CH<sub>3</sub> and CH<sub>2</sub>, respectively (Fig. 5).

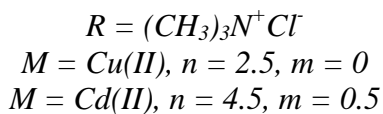
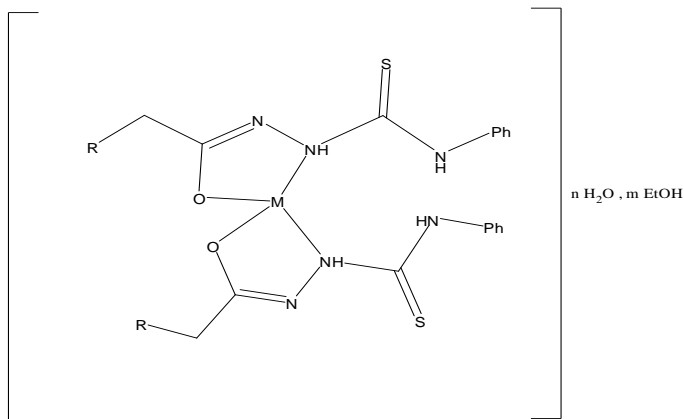






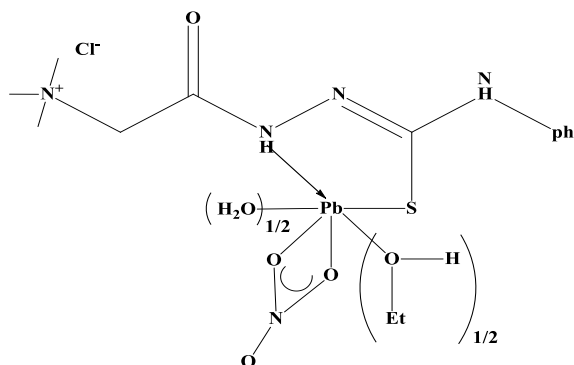
**Fig. (6):** IR of ligand.

The IR spectra of the Cu(II) (Structure 2) and Cd(II) (Structure 3) complexes show the disappearance of the carbonyl group (C=O) together with the appearance of new band at  $1598\text{ cm}^{-1}$  assigned to the (C=N) group. This suggests that the ligand coordinates in the enol form (Figs. 7-8).

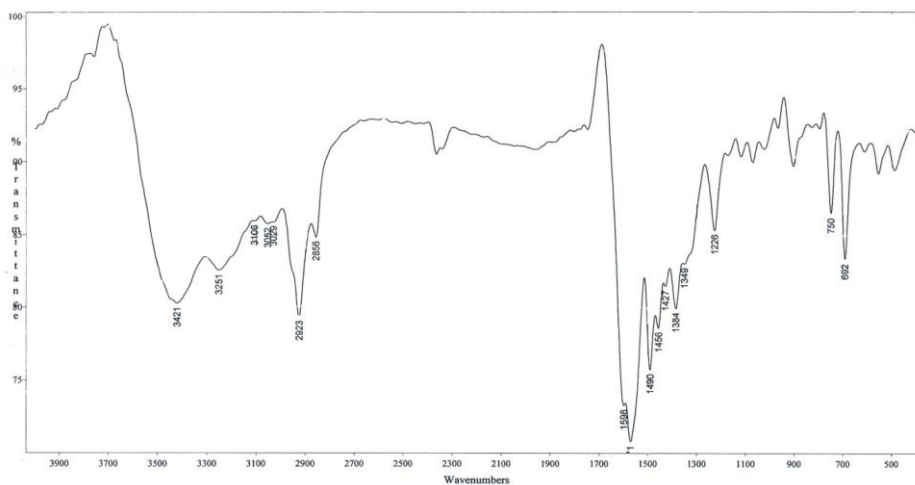


**Structure 2.**

The IR spectrum of the Pb(II) complex shows that the ligand coordinates in the keto form which is supported by the observation of the carbonyl band at  $1702\text{ cm}^{-1}$  (Fig. 9).



**Structure 3.**



**Fig. (7): IR of Cu complex.**

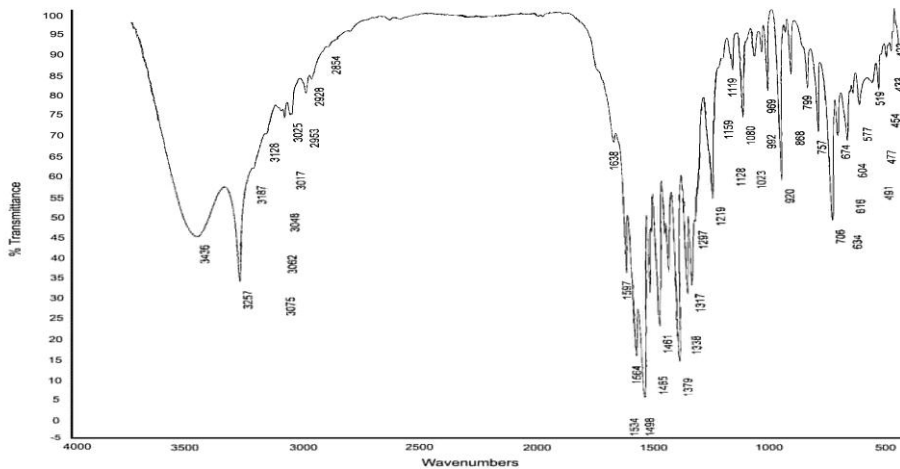


Fig. (8): IR of Cd complex.

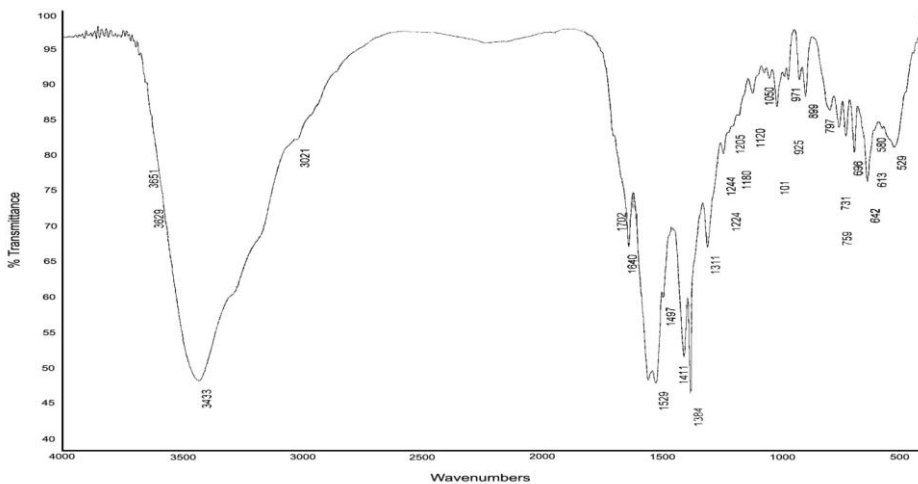


Fig. (9): IR of Pb complex.

**Mass spectra**

The mass spectra of the complexes show the presence of a signal peak at 711, 818 and 602 for Cu(II), Cd(II) and Pb(II) complexes, respectively.

**Application****Application of preconcentration method on real samples**

The preconcentration method is applied to real samples; the concentration of the tested metal ions was prepared by appropriate dilutions from 1mg ml<sup>-1</sup> (BDH) solutions for AAS. The pH's of all the prepared samples were adjusted to 5. The trace metal contents of the samples are coordinated with the ligand and passed through the mini-column filled with IRC-50 resin. The metal complexes retained in the column were then eluted with 2M H<sub>2</sub>SO<sub>4</sub>. Analytical recoveries for the investigated metal ions were assessed for various concentration levels from 8 ppb to 10 ppm for each metal. The initial sample volumes were 50 or 250 ml and the final eluted volume was 10 ml. The studied metals were analyzed by FAAS with analytical separation factor 5 or 25. The results of FAAS determination obtained for Cu, Pb and Cd are collected in Table 2. The experimental results indicated that good recoveries were reached for all studied metals from 8 ppb to 3 ppm, while low recoveries are observed at higher metal concentration above 3 ppm, this may be due to the saturation of the active sites of the resin under this condition.

**Application of preconcentration method on the investigated samples**

The proposed preconcentration method was applied to water samples, fish and baby dry milk. The pH's of all the samples were adjusted. The trace metal contents of the samples were complexed with PTHAC and passed through the mini-column filled with IRC-50 resin. The metal complexes retained in the column were then eluted with 2M H<sub>2</sub>SO<sub>4</sub>. Final volumes were made 10 ml and the studied metals were analyzed by FAAS. The results of FAAS determinations obtained for Cu, Cd and Pb are presented in table 3.

**Table (2):** Accuracy test for spiked metal ions recovery.

No.	ppm	Recovery, %							Vi	Vf
		Calculated (final)	Cu		Cd		Pb			
			Fou nd	R%	Fou nd	R%	Fou nd	R%		
1	0.008	0.20	0.21	105	0.21	105	0.20	100	250 ml	10 ml
2	0.015	0.38	0.38	100	0.40	105	0.39	103		
3	0.025	0.63	0.62	98.4	0.64	102	0.63	100		
4	0.05	1.25	1.22	97.6	1.30	104	1.28	102		
5	0.1	2.50	2.46	98.4	2.81	104	2.54	102		
6	0.5	12.5	12.3	98.4	12.7	102	12.6	101		
7	1	25.0	24.7	98.8	25.2	101	24.9	99.6		
8	3	15.0	14.8	98.6	14.9	99.3	15.0	100	50 ml	
9	5	25.0	23.1	92.4	23.7	94.8	23.5	94.0		
10	7	35.0	28.5	81.4	31.3	89.4	29.5	84.3		
11	10	50.0	34.2	68.4	38.4	76.8	36.3	72.6		

**Table (3):** The metal contents determined by method (Amberlite IRC-50/ PTHAC) of the water samples taken from various locations at Mansoura city (Sample volume: 250 ml, final volume: 10.0 ml, N=4).

No.	Sample locations	Concentration, $\mu\text{gL}^{-1}$ , $\bar{x} \pm s$		
		Cu (P.L.=1000)	Cd (P.L.=3)	Pb (P.L.= 100)
1	Tap water (Mansoura city)	6.7 $\pm$ 2	4.8 $\pm$ 2	3.5 $\pm$ 2
2	Nile water (Mansoura city)	11 $\pm$ 2	7.3 $\pm$ 2	5.0 $\pm$ 2
3	Waste water (Talkha Fertilizer plant)	22 $\pm$ 2	8.8 $\pm$ 2	9.4 $\pm$ 2

P.L.: Egyptian stunder permissible limit (2001).

**Table (4):**The metal contents determined by method (Amberlite IRC-50 PTHAC) of the fish and baby dry milk samples taken from various locations at Mansoura (Sample volume: 50 ml, final volume: 10.0 ml, N=4).

Metal	Conc (wt/wt) $\mu\text{g}/\text{kg} \pm 2$			
	Fish		Dry milk	
	Nile	Manzala lake	Conc.	P.L.
<b>Cu</b>	<b>532</b>	<b>460</b>	<b>27.0</b>	<b>-</b>
<b>Cd</b>	<b>62.0</b>	<b>21.0</b>	<b>33.0</b>	<b>50.0</b>
<b>Pb</b>	<b>186</b>	<b>173</b>	<b>167</b>	<b>300</b>

### CONCLUSIONS

A new method was developed for the determination of trace metals in various environmental liquid and solid samples. The method was found to be applicable to surface waters, industrial waste, fish and dry milk. The system was also successful in preconcentration metal ions from sample volume such as 50 or 250 ml. In conclusion, the metal contents at  $\mu\text{gL}^{-1}$  levels for copper, lead and cadmium were determined easily and with high accuracy. The obtained results provide new information of heavy metals as copper, lead and cadmium in drinking water, fish and dry milk from Mansoura city, Egypt. Based on sample analysis of the investigated metal ions, the concentration found does not exceed the permissible limits as WHO (World health organization).

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تعيين بعض العناصر الثقيلة عند مستوى منخفض باستخدام التركيز  
المسبق والامتصاص الذرى

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يهدف هذا البحث الى تقديم طريقة جديدة للتركيز المسبق لبعض المعادن ضئيلة التركيز مثل النحاس والرصاص والكاديوم بإمتزاز متراكباتها مع N- [فينيل أمينوثياوكسوميثيل] هيدرازينو كربونيل ميثيل { تراي ميثيل أمونيوم كلوريد (PTHAC) على سطح راتنج أمبرليت IRC-50 المحمل على عمود الفصل. تمت دراسة الشكل التركيبى للمرتبط ومتراكباته مع العناصر المختارة بالتحليل العنصرى والرنين المغناطيسى والأشعة تحت الحمراء. وتم كذلك دراسة تأثير العوامل المؤثرة على كفاءة التركيز المسبق مثل الرقم الهيدروجينى وكمية المرتبط والراتنج ومحاليل استرجاع العناصر. طبقت الطريقة المقترحة بنجاح لتعيين العناصر قيد الدراسة فى مياه الشرب ومياه النيل والاسماك واللبن المجفف والصرف الصناعى لمصنع سماد طلخا بمدينة المنصورة. وأثبتت الدراسة ان تركيز العناصر فى العينات المستخدمة فى حدود المسموح بها عالميا. وكان الانحراف المعيارى النسبى (RSD) للنتائج فى حدود ٢%.