



ISSN NO. 2320-5407

Journal homepage: <http://www.journalijar.com>

INTERNATIONAL JOURNAL
OF ADVANCED RESEARCH

RESEARCH ARTICLE

Separation /preconcentration and Atomic Absorption Spectrometric Determinations of Cobalt, Cadmium and Lead in aqueous and biological Samples using selective solid phase sorbent

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Manuscript Info

Manuscript History:

Received: 17 September 2015

Final Accepted: 22 October 2015

Published Online: November 2015

Key words:

Water, trace metals, pre-concentration, Amberlite IR-120, Ammonium pyrrolidine di thiocarbamate, flame atomic absorption spectrometry.

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Abstract

A method for the pre-concentration of some trace metals (Co (II), Pb (II) and Cd (II)) as complexes with ammonium pyrrolidine dithio-carbamate (APDTC) was proposed using a mini – column filled with Amberlite IR- 120 resin. Metal ions were adsorbed on IR-120 as their pyrrolidine di thiocarbamate complexes, then analytes retained on the resin were eluted by 1mol L⁻¹ nitric acid in acetone and determined by flame atomic absorption spectrometry (FAAS). The effects of the analytical parameters such as sample pH, ligand amount, eluent type, resin quantity, sample volume, sample flow rate and matrix ions were investigated on the recovery of the metals from aqueous solutions. The relative standard deviation (RSD) of the method was <3%. The validation of the procedure was carried out by analysis of certified reference materials. The proposed method was applied to natural waters, wastewater, fish, canned tuna, powder milk and rice.

INTRODUCTION

Many toxic heavy metals have discharged into the environment as industrial wastes, causing serious water and soil pollution. Co, Cd and Pb are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders [1,2]. Pollution by heavy metals is currently of great concern, due to increased awareness of the potentially hazardous effects of elevated levels of these materials in the environment [3]. The heavy metal levels in waste water, drinking water and other water sources that used for agriculture must be reduced to the maximum permissible concentration [4,5]. The removal of pollutants from water and environmental samples is an important process and is becoming more important with increasing of industrial activities. It is possible to clean polluted environment only with long study requiring expensive and complex plants. Therefore, the effective precautions must be taken to prevent water, air and soil pollution[6].

Toxicological effects of large amount of cobalt (II) may damage human health. When we breathe in too high concentrations of cobalt through air we suffer from lung problems, such as asthma and pneumonia. This mainly occurs with people whose work with cobalt. Investigations have been extended to the biochemistry of cobalt(II) in animals, microorganisms and enzymes[7]. The maximum recommended concentration of toxic ions such as cobalt (II) in drinking water for livestock is 1.0 mg L⁻¹[8]. The United States environmental protection agency (U.S.E PA) has set a limit of 2 µg L⁻¹ for drinking water. Soils near mining and melting facilities may contain very high amounts of cobalt. Cadmium is also released into water from metal plating, mining, pigments and alloy industries as well as tobacco smoke. Cadmium (II) compounds are often found in or attached to small particles present in the air, but it is difficult to smell or taste, as it doesn't have recognizable taste or odor. Breathing air with very high levels of cadmium can severely damage the lungs by tobacco smoke and may cause death[9]. Cadmium is transported to the liver through the blood. There, it is bound to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. The United States Environmental Protection Agency

(U.S.EPA) has set a limit of $5\mu\text{gL}^{-1}$ for drinking water [10]. Lead (II) pollution also has been recognized as a potential threat to air, water, and soil[11,12]. Lead (II) has been found to be toxic to human beings when present in high amount, Lead can cause several unwanted effects, such as: Disruption of the biosynthesis of hemoglobin and anemia, Kidney damage, Brain damage and Diminished learning abilities of children. The average concentration of lead(II) in earth's crust is around $13\mu\text{g/g}$. In natural water its typical concentration lies between 2 and $10\mu\text{g L}^{-1}$ [13-14].

The determination of trace elements in environmental solid/ liquid samples is nowadays made more demanding because of the large number of metal ions that have to be monitored for the quality and quantity of various samples. Various techniques have been applied for the determination of trace heavy metals over a large range of concentration in environmental samples [15-16]. The determination of trace metals by FAAS among the determination techniques has a number of advantages including high selectivity, speed and fairly low operational cost. However, preconcentration is usually required for the determination of trace metals in various samples by FAAS because of complex matrices of samples and low concentration of some metals, which are near or below the limit of detection of the instrument[17-19].

Currently, the used techniques for preconcentration and separation of trace metals include liquid- liquid extraction [20-21] , electrochemical deposition[22-23], co-precipitation[24-26], flotation[27], ion-exchange[28-29], cloud point extraction[30-32], and solid phase extraction[33,36]. Solid phase extraction (SPE) offers a number of important benefits. It reduces usage and exposure, disposal costs and extraction time for sample preparation. It has become more popular in compared with liquid- liquid extraction method because of its advantages of high recovery , high preconcentration factor, low cost, simplicity, rapid phase separation, low consumption of organic solvents and better efficiency. Several parameters determine the type of SPE sorbent that can be applied during the adsorption of metal [37]. The basic principle of SPE of trace metal ions is the transfer of analytes from aqueous phase to the active sites of solid phase. For this purpose, many adsorbents including activated carbon [38]. Alumina [39], silica gel [40], chelex 100 [41], and amberlite resins [42-43] have been used.

Various support materials are used in SPE [44-45]. Amberlite resins having most of properties above have been used with success as adsorbent or support for various chelating agents such as calmagite [46], dithiocarbamate [47], 2,6- dihydroxyphenyldiazoaminoazobenzen [48], and sulfinylicalex[4]arene [49].

Ammonium pyrrolidinedithiocarbamate (APDC) is the most common chelating agents for preconcentration and separation of trace metals from aqueous solutions in the FAAS techniques [44]. APDC forms much more stable complexes with some metals such as Co (II), Cd (II) and Pb (II) in a wide range of pH. Because of the strong complexation ability of APDC, these metals can be successfully extracted in the pH range of 2-8 [50].

The aim of this work is to show the analytical potentiality of amberlite IR-120/ APDC system for preconcentration/ separation of Co (II), Cd (II) and Pb (II) from aqueous solutions following FAAS determinations. For this purpose, effects of some analytical conditions such as sample pH, quantity of APDC, eluent type, sample flow rate and matrix interferences were examined.

2. Experimental

2.1. Instrumentation.

The concentration of different metal ions were analyzed by GBC, Sensaa Series Atomic Absorption Spectrometry (computerized AAS) with air-acetylene flame under the optimum instrumental conditions as shown in Table 1.

Table 1: Optimum instrumental conditions of the investigated metals by AAS:

	Co	Cd	Pb
Wave length, nm	240.7	228.8	217
Working calibrating range, ppm	2.5-9	0.2-1.8	2.5-10
Sensitivity, $\mu\text{g/ml}$	0.05	0.009	0.06

,respectively.Hanna-Instruments, 8519, Italy was used for pH adjustments.

2.2 Reagents and solutions

All the chemicals used were of analytical-grade and purchased from *BDH, UK*. Distilled-deionized water was used in all determinations. Stock solutions of Co(II), Cd(II) and Pb(II) at 1000 mg L^{-1} . Concentration prepared in 0.5M HNO_3 was used. The model and standard solutions of the metals were prepared by the stock solutions in appropriate ratios. 0.1 % (W/V) solution of APDC in ethanol was used as the complexing agent. the adsorbent resin amberlite IR-120 is used for preconcentration and has properties are given in table 2.

Table 2: Properties of Amberlite IR 120

Data	Amberlite IR-120
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Matrix	Styrene
Functional group	Sulphonic acid
Divinylbenzene	8%
Mesh size	16-45
Particle size (mm)	0.3–1.2
Ionic form as shipped	H⁺
Maximum temperature(C ⁰)	120
range pH	0–14
Total capacity (equiv./L)	1.9
Swelling	5-7%
exchange capacity	1.9 mequiv./g wet resin
	4.4 mequiv./g dry resin
	4.5 mmol/ml
Moisture content	45%

The buffer solutions were prepared by the following: For the pH 2 buffer solution, it was prepared by mixing of proper volume of 1M sodium sulfate and 1M sodium hydrogen sulfate solutions. Acetate buffers prepared by mixing different amounts of 1M sodium acetate and 1M acetic acid to obtain the pH values of 3-6 range. 0.1M potassium dihydrogen phosphate and 0.1M Disodium hydrogen phosphate were used for pH7 buffer preparation. 0.1M ammonium chloride buffer solutions were prepared by adding an appropriate amount of ammonia to it to obtain solutions of pH 8-11 range. pH 12 was prepared by adding amount of 0.1M sodium dihydrogen phosphate to 0.1M sodium hydroxide solution.

2.3 preparation of the mini-column

The glass mini-column (10 Cm length and 0.5 Cm diameter), having a stopcock, used for preconcentration of the metals. The resin was first washed with 1M NaOH, water, 1M HNO₃, water, acetone, and water and kept in a desiccator after drying until filled into the column.

2.4 Sampling and pre-treatments

Amberlite IR-120 was used to preconcentrate Co(II), Cd(II) and Pb(II) ions in water samples collected from taps (Mansoura university), Nile river (Mansoura city), Mineral water (Dasani) in polyethylene bottles. The polyethylene bottles were consecutively washed with detergent, tap water, HNO₃, and distilled-deionized water before to use. The water samples were acidified to pH~2.0 with HNO₃ after collection and filtered through a filter paper with 0.45µm pore size.

A sample of powdered milk (.25g) was heated at 100⁰C in a beaker containing a mixture of concentrated HNO₃ (5 mL) and H₂O₂ (5 mL) for 15 minutes and then 2mL concentrated perchloric acid was added to solution by raising of temperature to 150⁰C with stirring for 1 hour till a clear solution was obtained, was evaporated to near dryness on a hot plate, and then diluted to 50 mL with distilled-deionized water.

A quantitative 2.00g of dried fish (from the Manzala Lake) or canned tuna was placed in crucible and transferred to a cold, temperature – controlled furnace. The temperature of the furnace was raised slowly in 50⁰C/h to 450⁰C and this temperature was maintained for 3 h. The sample was then cooled, dissolved in 20 mL HNO₃ (1:1) and analyzed the proposed metal under the optimized conditions.

In order to microwave digestion of rice sample, 1.0 g of sample was digested with 6 ml of concentrated HNO₃ and 2 ml of H₂O₂ in microwave system. After digestion the samples, the volume of digested sample was made up to 50 ml with deionized water.

2.5 preconcentration procedures

The proposed method was tested first with model solutions prior to the determination of the trace metals in the real samples. The model solutions containing 5ppm of Co (II) and Pb (II) and 1ppm of Cd (II) were prepared. The pH of the model solutions was adjusted to the desired values (in the range 2-12) by the addition of 2-5mL of respective buffer solution, and 5mL of 0.1% of solution complexing agent was added. The mini-column was preconditioned with the buffer solution at the working pH. The solution containing metal complexes was passed through the column with a flow rate of 1mL min⁻¹. After the metal complexes retained on the resin in the column were washed with 10mL of distilled-deionized water they were recovered into a beaker 10mL of eluent solution, 1M HNO₃ in acetone. The beaker content was evaporated to near dryness on a hot plate at 40-50⁰C, and the residue was diluted to 5.0mL with 1M HNO₃. The metals in this solution were determined by FAAS. These procedures were repeated separately for all optimization parameters.

3. Results and discussion

3.1. Characterization of solid complexes

The structural formulae of the complexes are shown in Scheme (1, 2, and 3). The prepared compounds are listed in Tables (2, 3) and the formulae given are in agreement with the elemental analyses and IR data.

3.1.1. Elemental analysis and physical data

The complexes of Co (II), Cd (II), and Pb (II) are stable in prolonged exposure in air. Elemental analyses and other physical data are shown in Table (3).

Table 3: The elemental analysis of the ligand and its complex

Compound	Color	M.p. (°C)	% Found (Calcd.)			
			C	H	N	M
[Co(C ₅ H ₈ NS ₂) ₂].EtOH	Dark Green	>300	37.4 (36.2)	5.7 (5.5)	6.2 (7.0)	15.2 (14.8)
Cd(C ₅ H ₈ NS ₂) ₂	Off-white	>300	30.2 (29.7)	4.1 (4.0)	7.9 (6.9)	26.0 (27.8)
Pb(C ₅ H ₈ NS ₂) ₂	white	>300	25.4 (24.0)	2.7 (3.2)	5.0 (5.6)	40.2 (41.5)

3.1.2. Infrared spectra (IR)

The important IR bands of the complexes are listed in Table (4). The stretching frequency of the $\nu(\text{C} - \text{N})$ band for the dithiocarbamates was intermediate between the stretching frequencies associated with typical single and double-bonded carbon and nitrogen atoms. The $\nu(\text{C} - \text{N})$ and $\nu(\text{C} - \text{S})$ were observed in the ranges of (1580-1450) cm^{-1} and (1060- 940) cm^{-1} . The presence of only one band in the later region reports the bidentate coordination of the dithio ligand. IR spectra showed a new band at (418-445) cm^{-1} which is the evidence for the coordination of metal to sulfur $\nu(\text{M-S})$. shown in Figure (1, 2, 3, 4)

Table 4: IR spectral data (cm^{-1}) for the ligand and its complexes

Compound	IR (cm^{-1})		
	$\nu(\text{C}=\text{S})$	$\nu(\text{N}-\text{C})$	$\nu(\text{M}-\text{S})$
C ₅ H ₈ NS ₂ .NH ₄	948,997	1429	—
[Co(C ₅ H ₈ NS ₂) ₂]. C ₂ H ₅ OH	945	1437	414
Cd (C ₅ H ₈ NS ₂) ₂	941	1434	420
Pb (C ₅ H ₈ NS ₂) ₂	940	1432	422

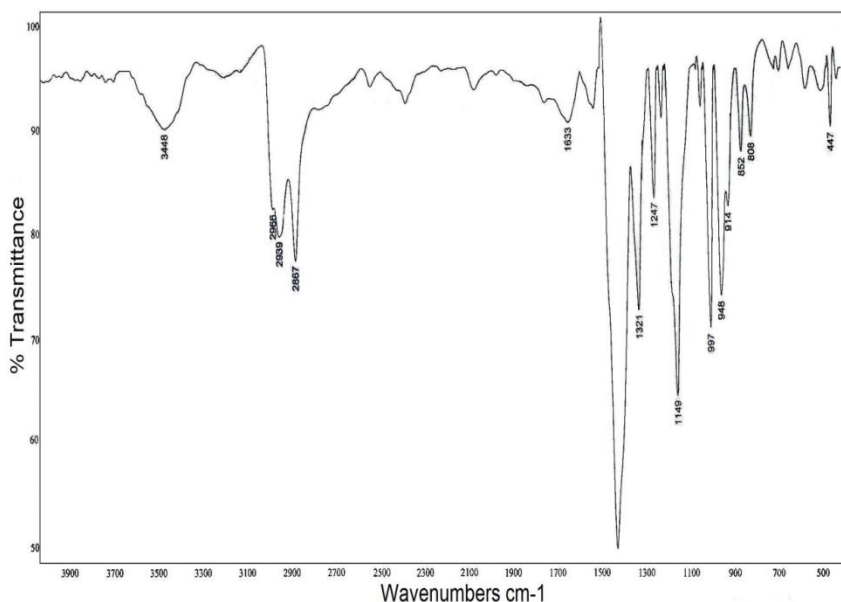


Figure 1: The IR spectrum of the ligand

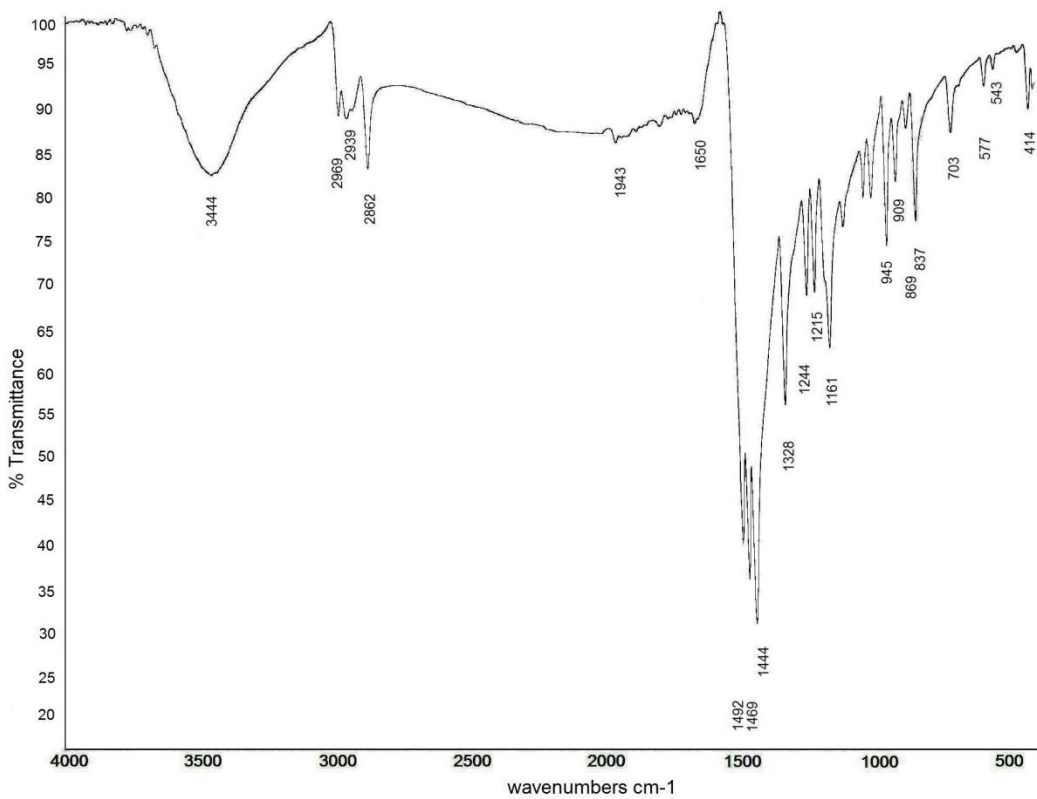


Figure 2: IR of Co⁺² complex

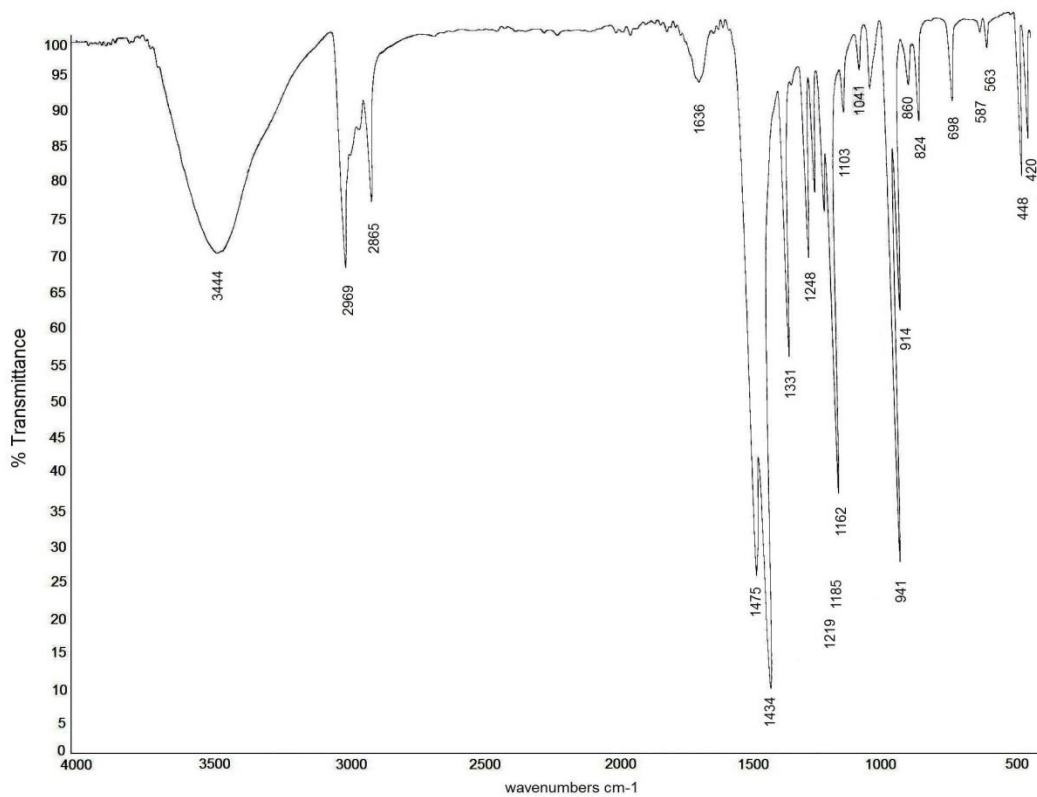
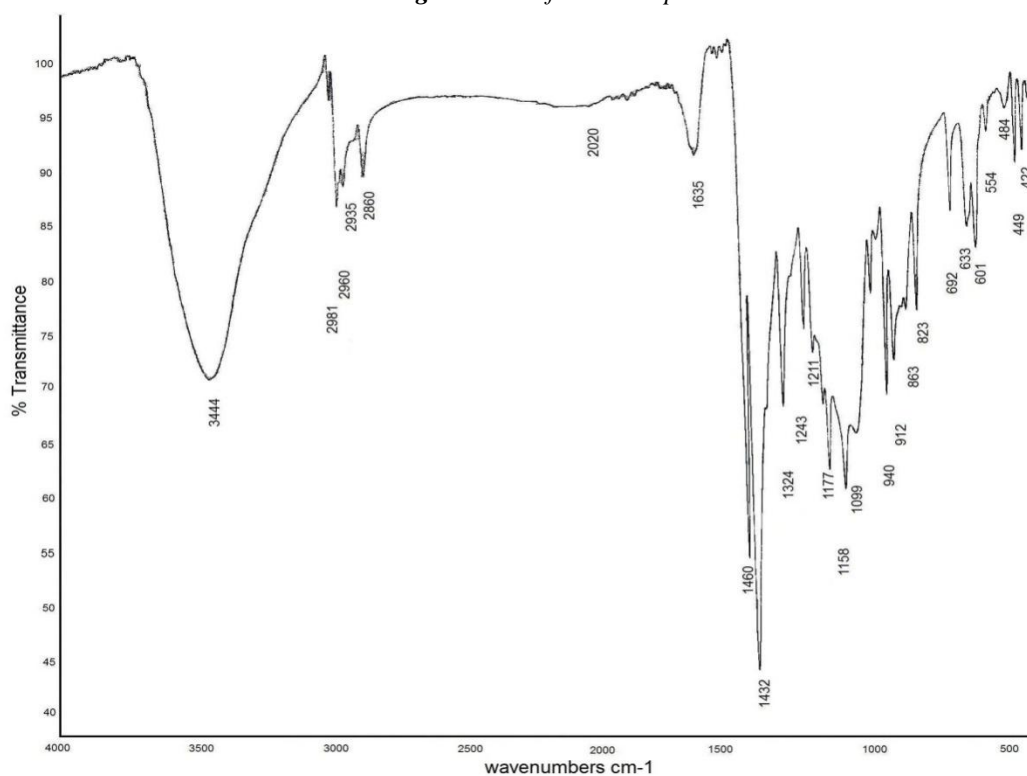


Figure 3: IR of Cd²⁺ complex.*Figure 4: IR of Pb²⁺ complex.*

3.2. Analytical discussion

3.2.1 Effect of pH on the recovery of the trace metals

The recovery efficiencies of each metal were investigated in the pH range 2-12 by use of relevant buffer solution given before. The recovery of Cd (II) was founded quantitative in pH 2-9. The recoveries of Co (II), Pb (II) were quantitative in the pH range of 4-8(Fig.5). From these results, the optimized sample pH is become as 6. Therefore, pH 6 was selected as the pH of the sample solution for the preconcentration of multi-elements in the solutions.

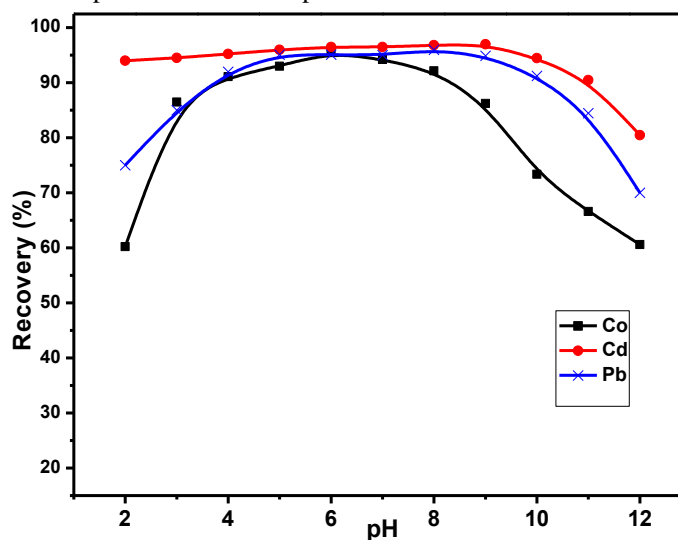


Figure 5:Effect of pH on the recovery of the trace metals (resin quantity: 200 mg, eluent: 10mL of 1M HNO₃ in acetone, complexing agent: 5mL of 0.1% APDTC, sample volume: 50mL, N=3).

3.2.2. Effect of quantity of complexing agent

APDC quantity is the most important chemical variables affecting the preconcentration of the examined analytes. So, the effect of APCD quantity on the retention was examined from 1.0 to 15mg. The results in (Figure 6) shows that the change in the concentration of APDC did not affect recovery much in the range of 1-3 mg and the recovery was slightly reduced at 15 mg of APDC. Accordingly, 5 mg of APDC (5.0 mL 0.1%, W/V) was used for further experiments. The considerable increase on the recoveries obtained by changing of APDC concentration from 3.0 to 9.0 mg indicates that the use of APDC is necessary for recovery.

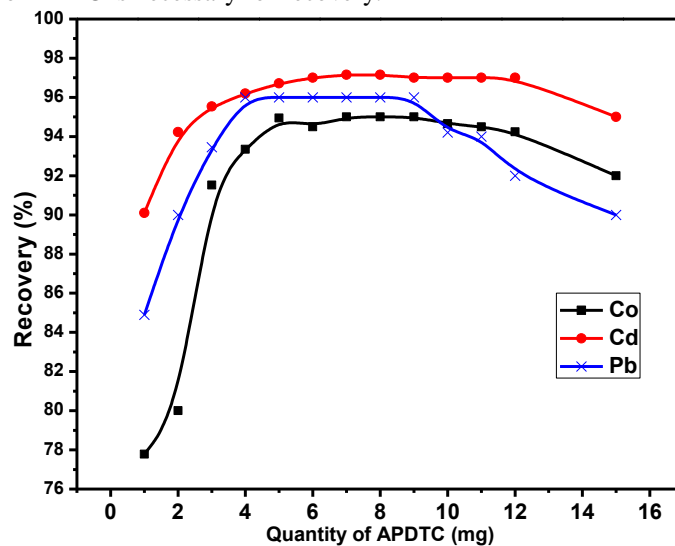


Figure 6: Effect of complexing agent quantity (pH=5, N=3)

3.2.3 Effect of resin quantity

In order to estimate the optimum resin quantity, the recoveries of the metals were examined by use of the resin quantities between 50 and 1000 mg, and the best recoveries were achieved between 200 and 400 mg (Figure 7).the optimum resin quantity was 300 mg for the later tests.

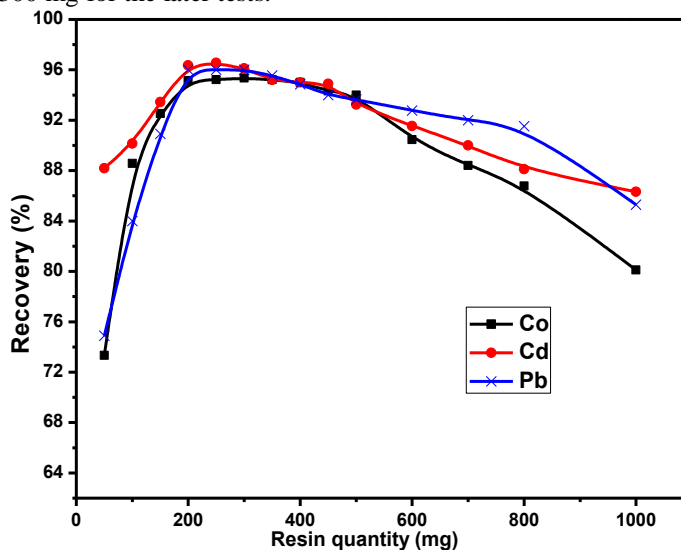


Figure 7: Effect of resin quantity on the recovery of the trace metals (N=3)

3.2.4 Effect of eluent type, concentration and volume

The following thoughtfulness should be taken into account to select a suitable eluent for effective desorption of metal complexes; (I) the eluent should desorb the metals complexes; (II) the eluent should not destroy the sorbent; and (III) the eluent should be appropriate for the subsequent determination technique_[46]. Various acids and organic solvents were used to choose the best one for the elution of the metal-APDC complexes accumulated on Amberlite IR-120 resin, and the percentage recovery for each eluent type was determined. With using different solvent

solutions especially the acids with acetone and acetonitrile provided higher recovery efficiency compared to the acids in the aqueous and alcoholic solutions, and the highest recoveries were obtained with either HNO₃ or HCl in acetone or acetonitrile. At the end, the acetone-HNO₃ or acetonitrile-HNO₃ mixture is specified as the eluent of choice for the later determinations and for optimization of the other parameters (Table 5).

After finding the type of eluent, the experiments were carried out for selecting the concentration of nitric acid solution in acetone. HNO₃ solutions in acetone at concentrations of 0.1- 4.0 M were studied for this purpose. The recoveries were increased with adding HNO₃ to acetone as shown in (Figure 8). After 1M HNO₃, the recoveries were quantitative for all conditions. Thus, the optimum concentration determined as 1 M HNO₃ in acetone used in later experiment.

The effect of volume of 1M HNO₃ in acetone solution on the recovery was investigated in (Figure 9). The quantitative recoveries were found after 8 mL of eluent. The optimum volume was as 10 mL and used in later experiments.

Table 5:Effect of eluent type on the recovery of trace metals (N=3)

Eluent solution	Recovery (%)		
	Co	Cd	Pb
HCl(1M) in water	<10	36±2	79±2
HNO ₃ (1M) in water	<10	38±2	75±2
Ethanol	19±2	28±3	30±2
HCl(1M) in ethanol	22±2	90±2	90±1
HNO ₃ (1M) in ethanol	30±2	73±2	92±1
Acetone	81±2	86±2	87±2
HCl(1M) in acetone	94±1	95±3	95±2
HNO ₃ (1M) in acetone	95±1	97±3	96±2
Acetonitrile	80±2	86±2	88±1
HCl(1M) in acetonitrile	93±2	95±2	95±2
HNO ₃ (1M) in acetonitrile	94±2	97±3	96±2

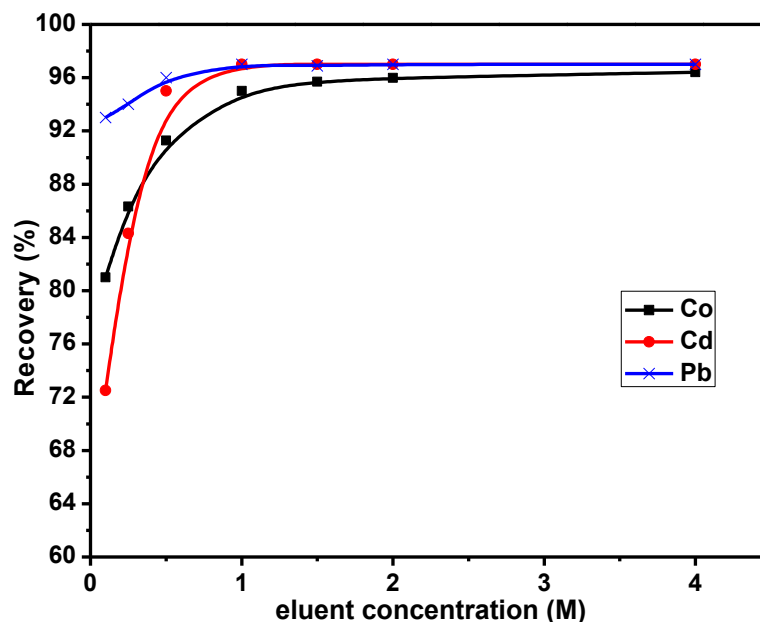


Figure 8:Effect of eluent concentration on the retention of the analyte ions (N=3)

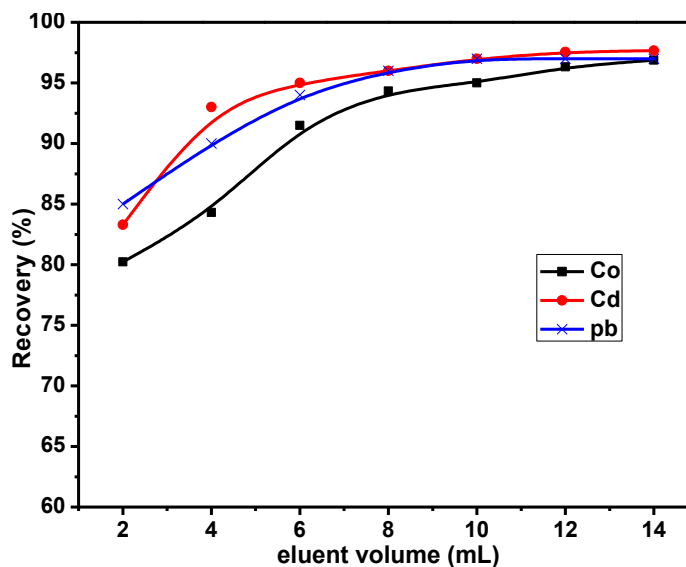


Figure 9:Effect of eluent volume on the retention of the analyte ions (N=3)

3.2.5. Effect of sample flow rate

There is contradiction between recovery and preconcentration time changing with flow rates. While the recovery increases with the decreasing flow rate, the preconcentration time increases. To obtain the quantitative recovery and to decrease the preconcentration time, the sample flow rate was investigated in the range 1-30 mL min⁻¹. The results showed in (Figure 10) that the recovery change at different flow rates studied. The recovery decreases by increasing sample flow rate. The sample flow rate was chosen as 1 mL min⁻¹ in further studies.

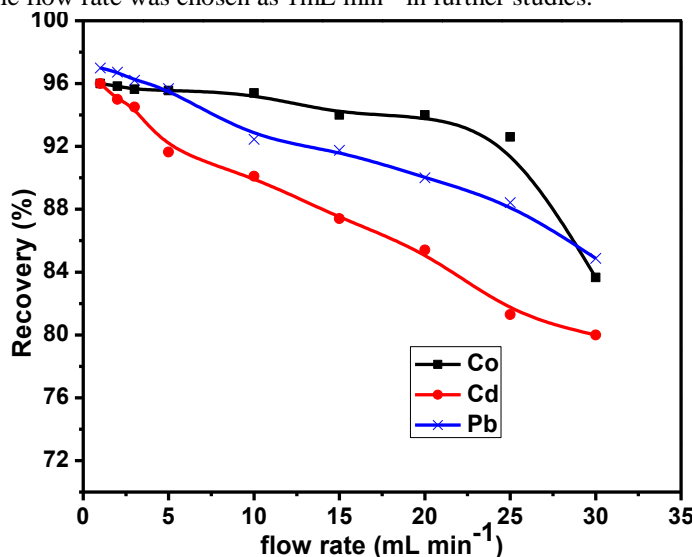


Figure 10: Effect of sample flow rate on the recovery (N=3)

3.2.6. Effect of mixed foreign ions

Water and environmental samples contain alkali, alkaline earth and some transition element salts. Therefore, the effects of some anions and cations on the recovery were evaluated. These salts are individually and then mixed together in model solution did not affect the recovery (Table 6). Matrix ions cause no interferences due to the group-specific character of APDC.

Table 6:The matrix ions and the recovery of the metal ions (N=3)

Ion	Added as	Conc.(mgL ⁻¹)	Recovery (%)		
			Co	Cd	Pb

Na ⁺	NaCl	100 1000	95±3 97±2	95±3 96±3	94±2 95±1
K ⁺	KCl	100 1000	95±3 97±2	95±3 96±3	94±2 95±1
Ca ²⁺	CaCl ₂	100	96±2	98±2	96±2
Mg ²⁺	MgCl ₂	100	92±2	97±3	94±1
Cl ⁻	NaCl	1000	97±3	96±3	95±1
NO ₃ ⁻	KNO ₃	1000	97±3	96±3	95±1
SO ₄ ²⁻	Na ₂ SO ₄	1000	96±2	97±2	96±2
PO ₄ ³⁻	Na ₃ PO ₄	1000	95±3	96±2	95±1
HCO ₃ ⁻	NaHCO ₃	1000	96±3	96±3	96±2
Fe ³⁺	Fe(NO ₃) ₃	10	97±2	95±2	95±2
Mn ²⁺	Mn(NO ₃) ₂	10	96±1	96±2	95±1
Al ³⁺	Al ₂ (SO ₄) ₃	10	96±1	96±2	95±2
Mixed*			96±3	96±2	95±2

*A sample containing 1000 mg of Na⁺, K⁺, Ca²⁺ and Mg²⁺ and 1000 mg of SO₄²⁻, Cl⁻ and NO₃⁻

3.6 Application to real samples

The water, milk, fish, tuna and rice samples were determined and the suggested procedure was applied to each sample under optimal conditions. The results for the sample are given in table 7.

Table 7: Trace metals contents of real samples with the proposed method (N=3)

Sample no.	Sample locations	Concentration, mgL ⁻¹ , $\bar{x} \pm s$		
		Co	Cd	Pb
1	Tap water (Mansoura city)	0.005±0.001	0.002±0.002	0.001±0.003
2	Nile water (Mansoura city)	0.006±0.001	0.003±0.002	0.005±0.001
3	Wastewater (Talkha Fertilizer plant)	0.01±0.003	0.026±0.002	0.019±0.003
4	Milk powder	0.004±0.001	0.086±0.036	0.056±0.017
5	Fish	0.0008±0.0001	0.03±0.002	0.176±0.001
6	Tuna sun shinecanned	0.0014±0.001	0.02±0.003	0.042±0.0012
7	Canned Tuna golden bell	0.001±0.001	0.03±0.001	0.003±0.002
8	Tuna Mariocanned	0.0007±0.001	0.028±0.002	0.005±0.001
9	Cow milk	0.002±0.001	0.042±0.002	0.033±0.01

10	Rice	0.0007±0.002	0.003±0.01	0.001±0.002
11	Mineral water	0.0027±0.017	0.004±0.002	0.002±0.005

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