RESEARCH ARTICLE

Simple, Selective and Sensitive Spectrophotometric Method for Determination of Trace Amounts of Lead (II), Cademum (II), Cobalt (II) with Organomercury Compounds

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Abstract

A selective and sensitive reagent of 2-{[(2-mercurychlorid, 4-methylphenylImino] methyl} phenol (K) was synthesized and studied for the spectrophotometric determination of Lead, Cademum, and cobalt, in detail. At a pH value (7), which greatly increased the selectivity; lead, cademume, cobalt, reacted with (K)to form a 1:1, 1:1, and 1:1 complexes, with absorption peaks at 394, 394, 389 nm, respectively. Under the optimal conditions, Beer's law was obeyed over the ranges ($1X10^{-6}$, $1X10^{-5}$, $1X10^{-4}$, $1x10^{-3}$ $1X10^{-2}$) mg/L respectively. The apparent molar absorptivity and Sandell's sensitivities were (0.3, 0.1, 0.2) L·mol^{-1}·cm^{-1} respectively, and0.027, 0.05, 0.013) µg·cm^{-2}respectively the detection limits were found to be be0.052, 0.036, 0.039) mg/L respectively.

Introduction

Mercury is an extremely toxic metal [1] and symptoms of mercury (methyl mercury) poisoning include instantaneous neurological damages particularly irritability, paralysis, insanity, blindness, chromosome instantaneous neurological damages particularly irritability, paralysis, insanity, blindness, chromosome damage and birth defects [2].

The toxicity of mercury depends on its chemical state [3]. Some forms of mercury are relatively non-toxic and have been used as medicines, e.g., for the treatment of syphilis [4]. Speciation of mercury at trace and ultra-trace levels is a matter of current interest.

Mercury enters the environment mainly through human activities. The chief sources of mercury. Pollution is chlor-alkali plants, paper, pulp, cellulose and plastic industries, electrical, paint, pharmaceutical industries, etc. Uses of mercury as fungicides, pesticides, etc., also add mercury to the environment [5]. Mercury is also believed to be the most dangerous of all the metal contaminants which may be present in our daily foods.

Compounds of mercury consumed in fish, cereals and other food stuffs have resulted in numerous poisoning [6]. At present few analytical techniques with sufficient sensitivity and selectivity are available for the determination and speciation of trace and ultra-trace levels of mercury in environmental and biological samples.

Some form of preliminary separation, solvent extraction and pre-concentration is required to determine the low levels of individual mercury species by sensitive techniques such as cold vapour atomic absorption spectrophotometry [7] and neutron activation analysis. Although these sophisticated atomic absorption spectrphotometry and neutron activation analysis [8].

Although these sophisticated techniques are available for the determination of mercury at trace levels in numerous complex materials, factors such as the low cost of instrument, easy handling, lack of requirement for consumables and almost no maintenance have caused spectrophotometry to remain a popular technique, particularly in

laboratories of developing countries with limited budgets.

The colorimetric solvent extractive [9, 10, 11] method employing orange complex of dithizone is still a valuable method for analyzing mercury (II). However, this method is lengthy and time consuming, require large amounts of reagents, is pH. Organomercury preper in different ways like relatively few organic halides react directly with metallic mercury to afford the corresponding organomercury halides [12] organomercury halides.

$$MeI + Hg \xrightarrow[81\%]{h\nu} MeHgI$$
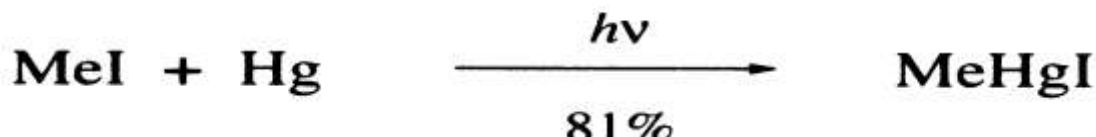
Ester - and amide-containing organomercurials can be readily prepared by reacting mercuric acetate with carbon monoxide in the presence of an alcohol or amine with carbon monoxide in the presence of an alcohol or amine [13].

$$AcOHgCOR \xleftarrow[ROH]{CO} Hg(OAc)_2 \xrightarrow[HNR_2]{CO} Hg(CNR_2)_2$$

The direct electrophilic substitution of arenes by mercuric salts is one of the most important reactions in organomercury chemistry [14].

$$ArH + HgX_2 \longrightarrow ArHgX + HX$$
$$X = Cl, OAc, O_2CCF_3, NO_3$$

Experimental

Reagents

All the chemicals used were of analytical reagent grade. Distilled water was used throughout the experiments. A standard stock solution of lead, cademume, cobalt $(1x10^{-4}$ mmol/mL) was prepared by dissolving 0.0032g of lead acetate, 0.0023g of cademume nitrate, 0.0023g of cobalt chloride in 100 mL of distilled water. A 0.0001 mmol/mL (k) solution was prepared by dissolving 0.00044 g of (k) in (10 ml) in Dmso and ethanol.

Apparatus

PerkinElmer UV-Vis Spectrophotometer Lambda 35with 1.0 cm matched quartz cells was used for all the absorbance measurement. (Shimadzu FTIR-spectrometer).Spectrophotometer and KBr discs were used for IR measurement. Nuclear Magnetic Resonance Spectra were obtained using Bruker DRX System AL500 (500MHZ).

Mass Spectra were obtained using (Work mass selective Detector) 5973. And 211 microcessor PH meter with a combined glass electrode was used for all the pH.

Synthesis of 2-{[(2-mercurychlorid, 4-methylphenylImino] methyl} phenol (K)

2- amino -5- methyl phenyl mercury chloride were prepared as in previous literature [15] (0.008 mol,2.7 gm) of 2- amino -5- methyl phenyl mercury chlorid in (10 ml) of ethanol add to (0.008 mol, 0.8 ml) of salsaldehyde with drops of glecial acetic acid.

The resulting mixture was left under reflax for (3 hr) checking by Thin layer chromatography (TLC) and the solid product formed was separated by filtration, and recrystallization it by hot ethanol (Scheme 1) (m.p.209-210 Cº) yield 71%,and color is slight yellow As shown in Fig.1 and Table 1, the band at1614 cm^{-1} is due to the CH=N [16] group and the absorption bands at3444 cm^{-1}due to the OH [17] group of the reagent.
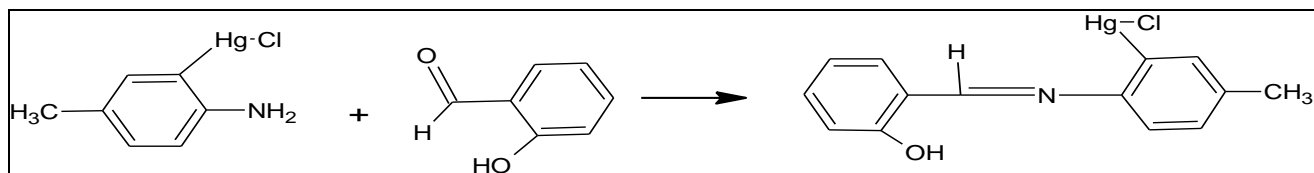
Scheme 1: Synthesis of 2-{[(2-mercurychlorid, 4-methylphenylImino] methyl} phenol (K) .... (1)

Table 1: Infrared data

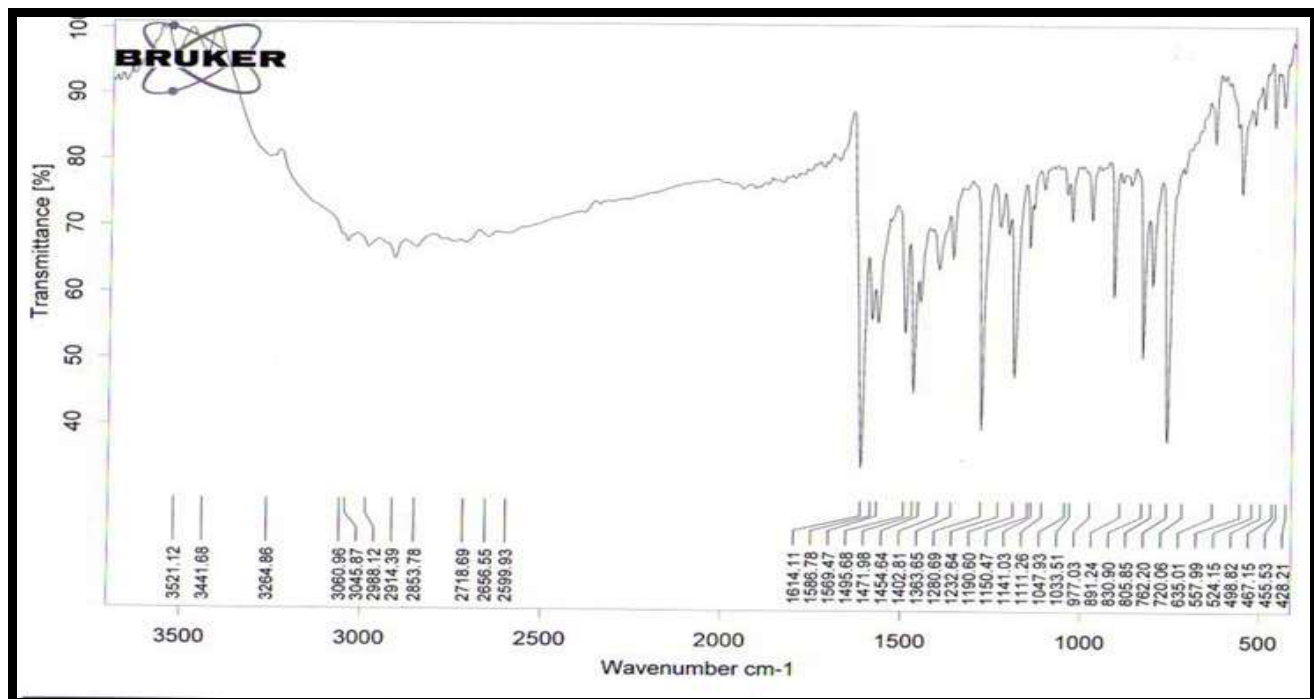| Symbol	Compound	Stractural formula	OH	CH=N	C-H$_{AR}$	C-H$_{AL}$
K	$C_{14}H_{12}ONHgcl$		3444	1614	3060	2920

Figure 1: Infrared spectrum for K

The fragment path ways of the molecular ions for K are summarized in Table (2).fragmentation at K involves (M$^{+\cdot}$) in 447 m\z the occurrence of a peaks for the ions (76, 91, 115, 237, 270, 285, 307, 313, 327, 354, 410, 413, 423, 433)

$[C_{14}H_{12}ONHg]^+$,$[C_6H_6O]^{+\cdot}$,$[C_8H_8N]^{+\cdot}$,$[Hgcl]^{+\cdot}$,$[C_6H_5Hg]^{+\cdot}$,$[C_7H_6Hgcl]^{+\cdot}$,,$[C_6H_5]^{+\cdot}$ $\cdot[C_{13}H_9NHgcl]^+$, $[C_7H_7Hgcl]^{+\cdot}$,$[C_8H_7NHgcl]$ $[C_{14}H_{12}ONHg]^+$, $[C_{13}H_{10}NHgcl]^{+\cdot}$,$[C_{14}H_{12}NHgcl]^{+\cdot}$,$[C_{13}H_9ONHgcl]^+$. Respectively.

Table 2: Most characterization ions in mass spectra of K

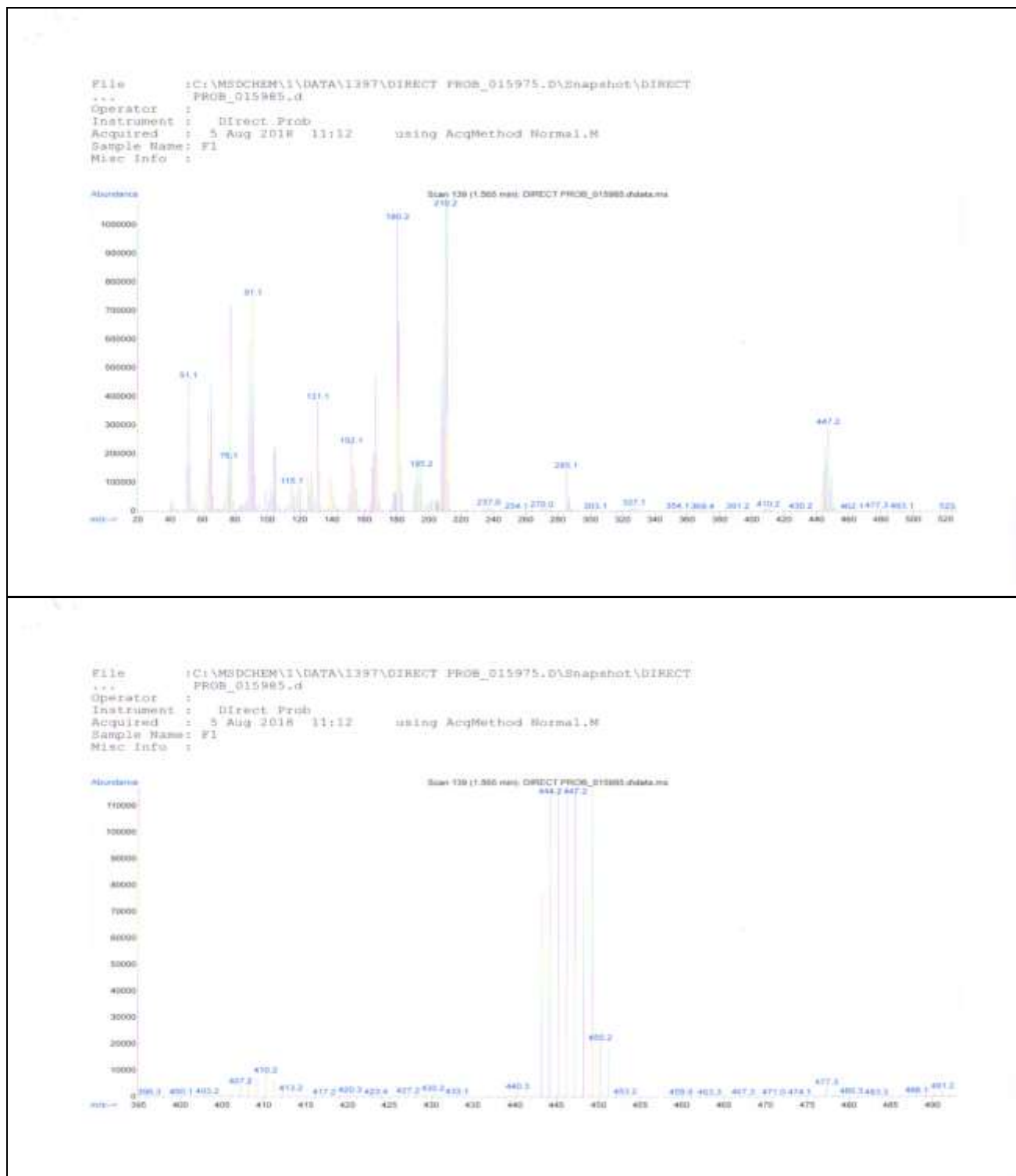| Ions	M\Z
$[C_{14}H_{12}ONHgcl]^{+\cdot}$	447
$[C_6H_5]^{+\cdot}$	76
$[C_6H_6O]^{+\cdot}$	91
$[C_8H_8N]^{+\cdot}$	115
$[Hgcl]^{+\cdot}$	237
$[C_6H_5Hg]^{+\cdot}$	270
$[C_7H_6Hgcl]^{+\cdot}$	285
$[C_{14}H_{12}ONHg]^{+\cdot}$	307
$[C_{13}H_{10}NHgcl]^{+\cdot}$	313
$[C_7H_7Hgcl]^{+\cdot}$	327
$[C_8H_7NHgcl]^{+\cdot}$	354
$[C_{14}H12ONHg]^{+\cdot}$	410
$[C_{13}H_{10}NHgcl]^{+\cdot}$	413
$[C_{14}H_{12}NHgcl]^{+\cdot}$	423
$[C_{13}H_9NHgcl]^{+\cdot}$	433

Figure 2: mass spectra for K

^{1}H NMR spectral data in depurated DMSO solution of the synthesized compounds are given in Table (3) and Figure (3) a multiple signal appeared at (7.0-7.8) [18] ppm referred to aromatic rings protons. The protons of (CH=N) group was obtained as a single at (8.9) [19] with phenolic (OH) protons has been appeared at (12.6) [20] ppm as a single the methyl protons give a singlet signal at (2.3) [21].

Table 3: ^{1}H NMR data compound K

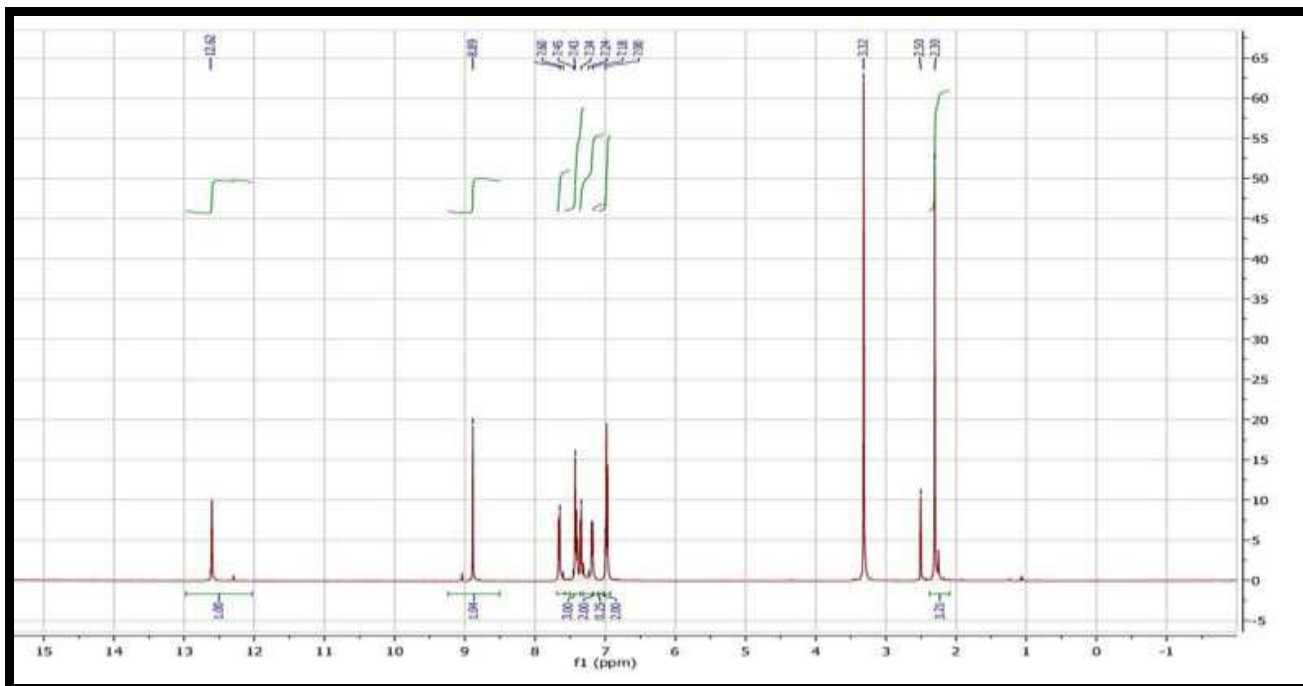| compounds	Molecular formula	Chemical shift (ppm);TMS=0 ppm
K	$C_{14}H_{12}ONHgcl$	7.0-7.8)(Ar-H ,m ,7 H)(
		8.9)(CH=N ,S, 1H)(
		12.6)(OH ,S,1 H)(
		2.3)(CH₃,S, 1H)(

Figure 3: ¹H NMR for K

Procedure for the Determination of Lead, Cademume, Cobalt

First, 1 mL each of lead(II), cademum (II), cobalt(II) solutions was transferred into a 10 mL standard flask; then 1 mL buffer solution of appropriate pH of (7) and 1 mL of reagent(k) solution were added, successively; finally, the solution was diluted to the mark with Dmso and ethanol, mixed well, and left for 2 min. The absorbance at 394, 394, 389 nm, respectively, were measured on PerkinElmer UV-Vis Spectrophotometer Lambda 35 with a cell of 1.0 cm path length against reagent blank. The total volume of the experimental solution was maintained at 10 mL, with a deviation of ±1%.

Results and Discussion

Absorption Spectra

Under the experimental conditions, the absorption spectra of (k) and [pb-k, cd-k, co-k] complexes were scanned (Fig.4, 5, 6). Absorption maximum of (k) was obtained at 231 nm, whereas the [pb-k], [cd-k], [co-k] complexes gave absorption peaks at 394, 394, 389 nm, respectively. The differences between the peak of (k) and each of the three peaks of the three complexes were (163, 163, 158, nm), successively, and could be obviously distinguished. Thus the absorption peaks at 394,394,389 nm were chosen as the determination wavelengths for the [pb-k], [cd-k], [co-k] complexes, respectively.
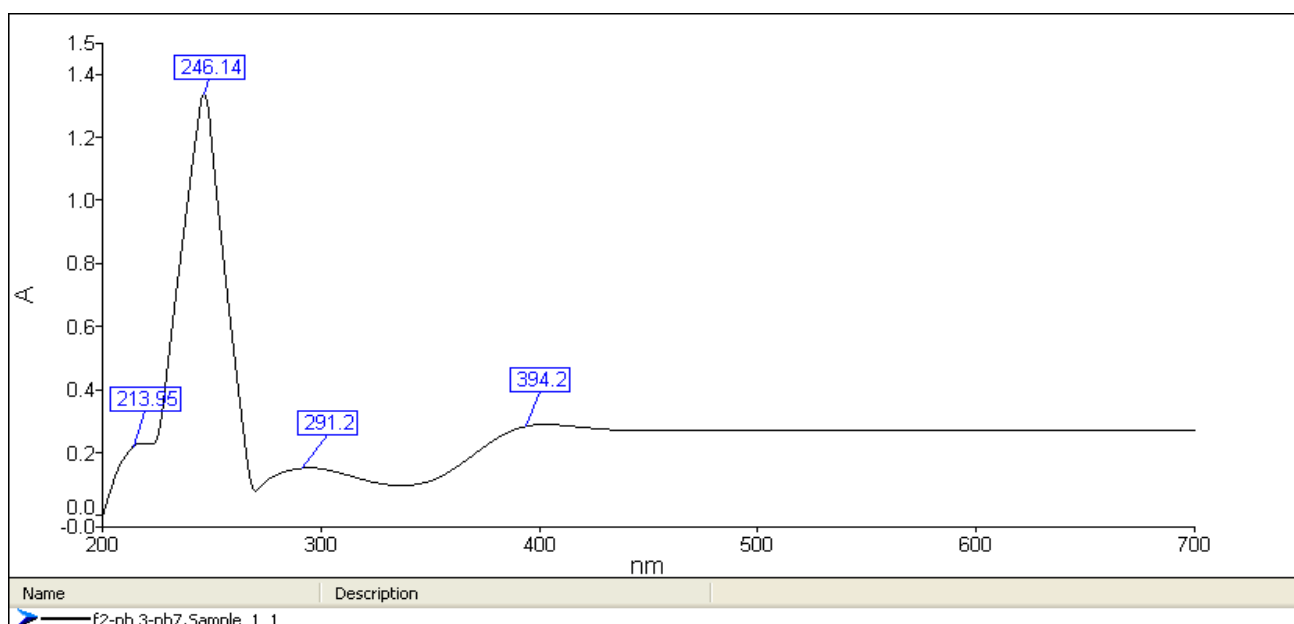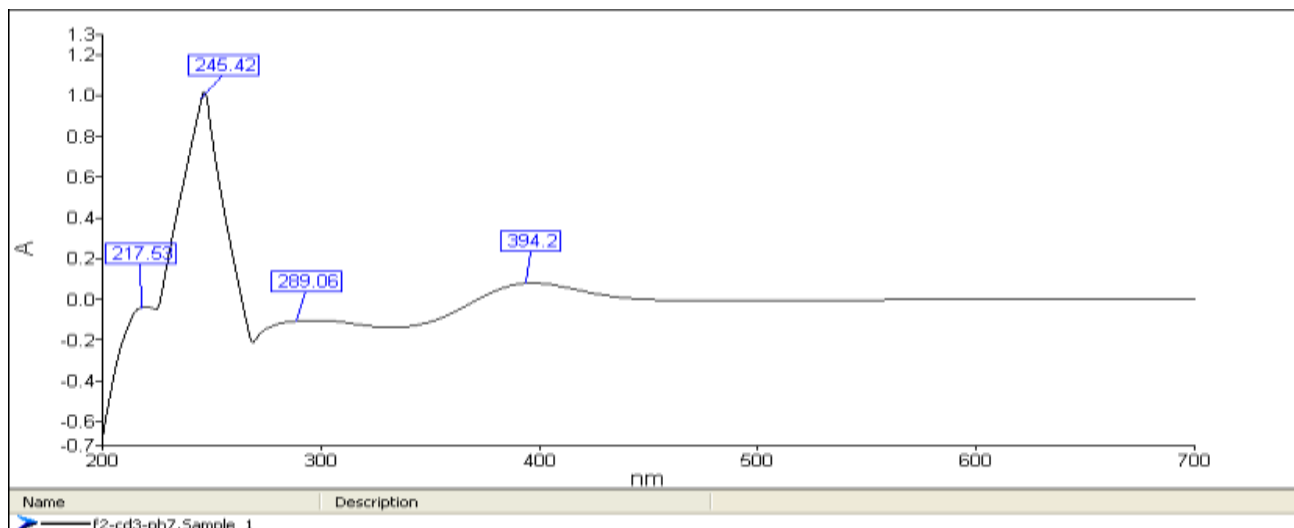

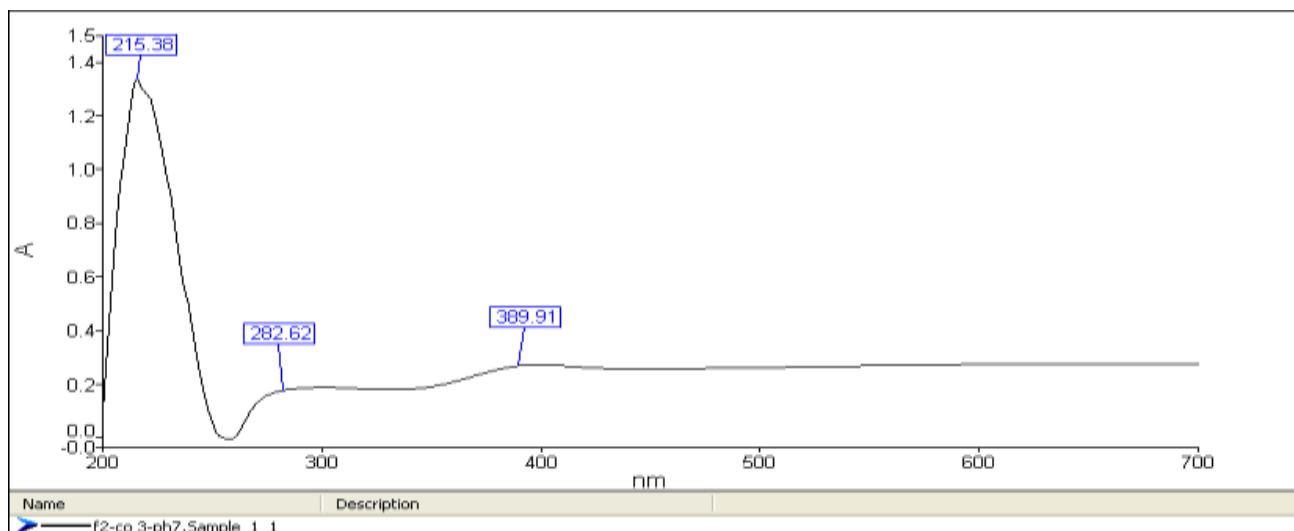**Figure 4: UV –Vis for [k +pb⁺²]**

Figure 5: UV –Vis for [k +cd^{+2}]

Figure 6: UV –Vis for [k +co^{+2}]

Effect of the Reagent Concentration and Composition of the Complex

To a series of 10 mL standard flasks with each containing 1.0 mL of lead cademume, cobalt solutions(1×10^{-4} mmol/mL) and 3.0 ml of buffer solution(pH=7) respectively, were added different volumes of the reagent solution(1×10^{-4}mmol/mL) and extracted with chloroform to obtain the maximum color formation. The absorbance of each solution was measured at 394, 394, 389 nm, respectively, against the reagent blank. From the experimental observation, it was found that beyond a ten-fold excess of the reagent, the absorbance remained almost constant. Hence, for further studies, 2.0 mL of the reagent was recommended for complete color development. The molar ratios [22] of [Pb-K]+2 [cd-K]+2 [Co-K]+2 and complexes obtained *via* Job's method [23] of continuous variation were 1:1 for[Pb-K]+2 [cd-K]+2 [Co-K] respectively.

Effect of Concomitant Species

Several anions and cations were studied in detail. Table (4, 5, 6) summarizes the tolerance limits of concomitant ions in the determination of 1×10^{-4} (pb II, cd II, co II) respectively. The tolerance limit was taken as the amount causing an error of ±2% at the peak height.

Table 4: Tolerance limits (mg/L) of non-target ions for the determination of co 1×10^{-4}M

eCo(ɪɪ):Concomitant Species	Tolerance limits	Concomitant Species
1:100	0.167+	Pb^{+2}
1:1000	0.127+	
1:1	0.011-	
1:100	0.111+	CO^{+2}

1:1000	0.11+	
1:1	0.011-	
1:100	0.341+	
1:1000	0.225+	Ni^{+2}
1:1	0.112-	
1:100	0.142+	
1:1000	0.11+	Fe^{+2}
1:1	0.1-	
1:100	0.233+	
1:1000	0.212+	Fe^{+3}
1:1	0.115-	
1:100	0.326+	
1:1000	0.321+	Zn^{+2}
1:1	0.105-	

Table 5: Tolerance limits (mg/L) of non-target ions for the determination of [K+cd] 1x10^{-4}M

Cd(**II**): Concomitant Species	Tolerance limits	Concomitant Species
1:100	0.263+	
1:1000	0.112+	Cd^{+2}
1:1	0.063_	
1:100	0.103+	Co^{+2}
1:1000	0.086+	
1:1	0.979_	
1:100	0.057+	
1:1000	0.03+	Ni^{+2}
1:1	0.18_	
1:100	0.171+	
1:1000	0.129+	Zn^{+2}
1:1	0.015_	
1:100	0.336+	
1:1000	0.224+	Fe^{+2}
1:1	0.057_	
1:100	0.171+	
1:1000	0.129+	Fe^{+3}
1:1	0.015_	

Table 6: Tolerance limits (mg/L) of non-target ions for the determination of pb 1x10^{-4}M

pb(**II**): Concomitant Species	Tolerance limits	Concomitant Species
1:100	0.148+	
1:1000	0.138+	Cd^{+2}
1:1	0.008_	
1:100	0.231+	Pb^{+2}
1:1000	0.193+	
1:1	0.011_	
1:100	0.067+	
1:1000	0.052+	Ni^{+2}
1:1	0.016_	
1:100	0.071+	
1:1000	0.043+	Zn^{+2}
1:1	0.028_	
1:100	0.319+	
1:1000	0.192+	Fe^{+2}
1:1	0.027_	
1:100	0.019+	
1:1000	0	Fe^{+3}
1:1	0.029_	

Analytical Characteristics

Calibration curves were constructed in the usual way using the aforesaid procedure. Beer's law was obeyed in the concentration range of $(1 \times 10^{-6}, 1 \times 10^{-5}, 1 \times 10^{-4}, 1 \times 10^{-3}, 1 \times 10^{-2})$ mg/L) for (pb II, cd II, co II) respectively. The simple linear-regression calibration equations for $y=0.4914x+0.333$, $y=0.7026x+0.468$, $y=0.6508x+0.45$ for (pb II, cd II,co II) respectively. The obtained apparent molar absorptivities (0.3, 0.1, 0.2),

Sandell's sensitivities, and relative standard deviations were (0.027, 0.05, 0.013 L·mol^{-1}·cm^{-1} for (pb II, cd II, co II) respectively, and49.83 %, 50%, 48.93%, for (pb II, cd II, co II) respectively. The detection limits were found to be 0.052, 0.036, 0.039 mg/L respectively. In this work, a simple selective and sensitive spectrophotometric method was developed for the determination of lead, cademume, cobalt with which was synthesized for the first time by us as shown in Tables 7.

Table 7: Analytical performance of the proposed method

S.No	Metal ion	⅄ max nm	Stability time/hr	Stability temperature C°	Complex stoiChiometry (M:R)	Beer's law range/(mg·L^{-1})	$10-4\ \varepsilon$/(L·Mol^{-1}·cm^{-1})	Detection limit/ (mg·L^{-1})	PH
1	Pb(ᵢᵢ)	394	6 hr	30	1:1	10^{-6}-10^{-2}	0.3	0.052	7
2	cd(ᵢᵢ)	394	6 hr	30	1:1	10^{-6}-10^{-2}	0.1	0.036	7
3	co(ᵢᵢ)	389	6 hr	30	1:1	10^{-6}-10^{-2}	0.2	0.039	7

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