Cloud Point Extraction Spectrophotometric Determination of Copper, Chromium and Cobalt by Salen as Reagent in Wastewater of Iraq

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Cloud point extraction is a separation and preconcentration, simplicity, low cost, fast and environmental safety to determination of copper and cobalt by UV/visible spectrophotometry in some environmental samples such as wastewater of Rustimiyah city in Iraq and industrial sewage of Tannery Factories in Zafaraniyah, by using Salen as reagent in the presence of Triton X-100 (as a non-ionic surfactant) at λ_{max} for copper 361 and for cobalt 378, 382 chromium. The optimum conditions for the cloud point extraction respect to several experimental parameters such as pH of the solution, Triton X-100 and Salen concentration incubation time, temperature and concentration of metals. The proposed method had a linear range for copper 10-70 $\mu g\ L^{-1}$ and for cobalt 10-70 $\mu g\ L^{-1}$, chromium 10-70 $\mu g\ L^{-1}$ the recovery of analytes was in the range, detection limits was 2.62, 2.19 and 0.5003 $\mu g\ L^{-1}$ for for Cu = 0.9991, for Co = 0.9984, Cr = 0.9972 relative standard deviation (RSD) for Cu = 0.9108, Co = 0.9109 pH was equal to 10 for chromium, cobalt and 8 for copper.

Keywords: Cloud point extraction, Salen, Determination Cu(II), Co(II) and Cr(III).

INTRODUCTION

Heavy metals are of the great importance for the life. Some of these metal ions such as Cu, Cr, Co and Fe are essential to humans[1]. However, these metals may be harmful to life taken in excessive amounts Cobalt can be beneficial for humans because it is part of vitamin B_{12}. However it can also be harmful, because exposure to high levels of cobalt can result in lung and heart effects and dermatitis[2]. Copper is an essential element required for normal growth and development and for a variety of metabolic functions but long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches and stomach aches. The high uptakes of copper may cause liver and kidney damage and even death[3,4]. Chromium(III) is an essential nutrient for humans and shortages may cause heart conditions, disruptions of metabolisms and diabetes. But the uptake of too much chromium(III) can cause health effects as well, for instance skin rashes[5]. Lowing occupational and environmental exposure due to the low concentration of these metals in the environmental and biological samples and interfering effects, a preconcentration/separation technique is generally necessary prior to the determination in order to overcome, these problem analytical chemists generally use separation-preconcentration techniques[6], including liquid-liquid extraction[7], coprecipitation[8], cloud point extraction[9,10], electrodeposition, solid phase extraction[11]. Ultraviolet-visible spectroscopy is a simple instrument, low cost, easy operated, rapid response time, available in many laboratories[12]. Most reports in chemical literatures for pre-concentration and detection of Cu, Co and Cr in various matrices by cloud point extraction have relied on commercial organic reagents to form chelate (hydrophobic) with one or two metals at specific pH, apt to interact with surfactant in solution. These including 1-(2-thiazolazo)-2-naphthol (TAN)[13], 1-(2-pyridylazo)-2-naphthol (PAN)[14], 2-(5-bromo-2pyridylazo)-5-diethylaminophenol (5-Br-PADAP)[15], pyrrolidinedithiocarbamate (APDC)[16], [4-(-pyridylazo)resorsinol monosodium] (PAR)[17], O,O-diethyldithio-phosphate (DDTP)[18], N-salicylideneaniline (SA)[19], *bis*(2-methoxy benzaldehyde)ethylenediimine[20], 1,5-diphenylcarbazide 2-[(2-mercaptophenylimino)-methyl]phenol (MPMP)[21], N-benzoyl-N-phenyhydroxylamine (BPHA)[22].

EXPERIMENTAL

A thermostated water bath model Unitemp, pH meter model BP 3001. Phase separation was achieved with centrifuge model REMI at 2500 rpm in 10mL calibrated conical tube. UV-visible Shimadzu model UV-160 A, FTIR Shimadzu, model IR-PRESTIGE 21, made in Japan, CHN Euro Vectro-3000A Element Analyzer at Al-Bayat University, Jordan.

All the chemicals used were of analytical reagent grade; deionize water use to diluting the samples and reagents. Ethylenediamine (Qualilcems), salicylaldehyde (G.C.C.),

Triton X-100 (Merck), hydrochloric acid (BDH), sodium hydroxide (BDH), ethanol (G.C.C.), copper(II) nitrate [$Cu(NO_3)_2 \cdot 3H_2O$] (Fluka), chromium(III) chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) (BDH), cobalt(II) nitrate hexahydrate [$Co(NO_3)_2 \cdot 6H_2O$] (BDH) 1000 µg L^{-1} stock solution of Cu, Cr and Co was prepared by dissolving an appropriate amount of $Cu(NO_3)_2 \cdot 3H_2O$, $CrCl_3 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ in deionized water and diluting to the mark in 100 mL volumetric flask. Working stock solution was prepared daily from the stock by appropriate dilution with water. Salen stock solution was prepared by dissolving 0.268 g in 10 % (v/v) Triton X-100 and diluting to the mark in 100 mL. Non-ionic surfactant, Triton X-100 10 % (v/v) was prepared by dissolving 10 g Triton X-100 in hot deionize water diluting to the mark in 100 mL volumetric flask, 0.01 M hydrochloric acid, 0.01 M sodium hydroxide use to adjust pH 2-14.

General procedure for cloud point extraction: Aliquots 10 mL of a solution containing a known amount of Cu(II), Co(II) and Cr(III) ions, 10 % (v/v) Triton X-100 and agent Salen 3 × 10^{-4}, the pH was adjusted by 0.01 M HCl, 0.01 M NaOH. The mixture was shaken for 1 min and left to stand in a thermo-stated bath at 70 °C, for 15 min. Separation of the phases was achieved by centrifugation at 2500 rpm for 20 min, the remaining of micellar phase was dissolved by DMF, a measurement of Cu(II), Co(II) and Cr(III) was followed by UV-visible spectrophotometer at λ_{max} = 361, 378 and 382 nm.

Application of real samples: Analysis of waste water of Rustimiyah city in Iraq and industrial sewage of Tannery Factories in Zafaraniyah for determining of analyte contents was performed as follows: About 1000 mL of sample filtering and add 3 mL concentrated HNO$_3$ was added to eliminate and decompose organic matter. The wastewater samples were stored in polyethylene bottles. The aliquots of waste water was extracted and analyzed for the metals according of the proposed procedure of cloud point extraction.

RESULTS AND DISCUSSION

Characterization of ligand Salen: An absorbance reveals at 407-406 nm (Fig. 1). This band caused by charge transition between C=N and conjugated benzene ring. It is due to the yellowish orange colour of these components the band at 320 nm may be caused by electronic transition n → π* which belongs to C=N. For the transform at 264 nm may be caused by electronic transition of n → π* of double bond due to C=N and the aromatic ring[23,24]. The complex with Cu-Salen the maxima absorption at 361 was appeared at pH 8, 70 µg L^{-1} and 0.8 mL Triton X-100. Co-Salen complex displays an absorption maxima at 378 was appeared at pH 10, 70 µg L^{-1}, 0.4 mL Triton X-100 and Cr-Salen complex the absorption maxima at 382 was appeared at pH 10, 70 µg L^{-1}, 0.6 mL Triton X-100 while the reagent Salen displays an absorption maxima 320 are shown in Figs. 2-4.

Effect of pH: Cloud point extraction yield depends on the pH at which complexes formation occurs. pH plays a unique role on metal-chelate formation and subsequent extraction cloud point extraction of copper, cobalt and chromium a set of similar experiments in the pH range of 2-14 were accomplished according to the described procedure and the results
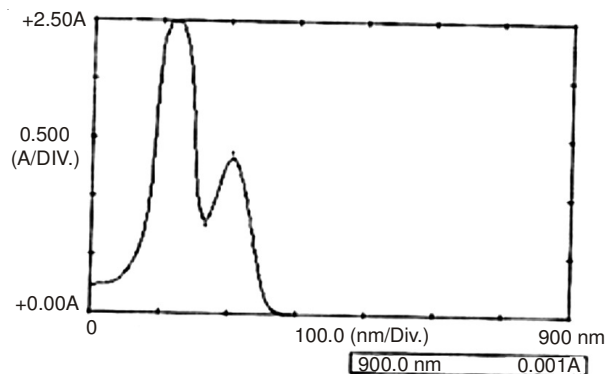

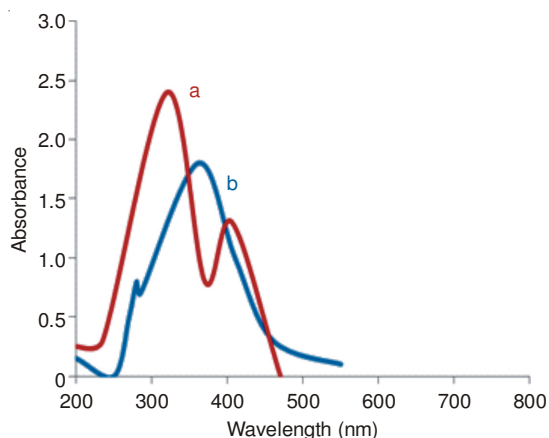Fig. 1. Ultraviolent spectrum of ligand Salen

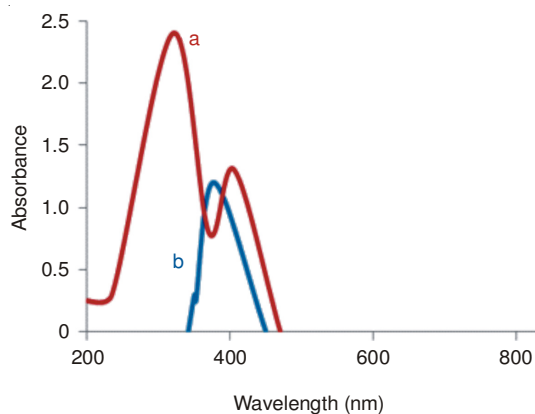Fig. 2. Ultraviolent spectrum of complex Cu-Salen *versus* ligand Salen

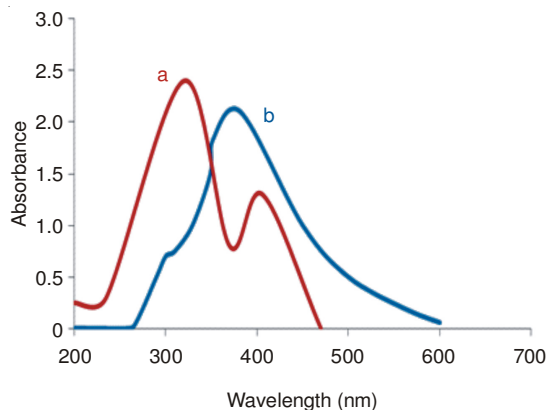Fig. 3. Ultraviolent spectrum of complex Co-Salen *versus* ligand Salen

Fig. 4. Ultraviolent spectrum of complex Cr-Salen *versus* ligand Salen

are shown in Fig. 5. The maximum sensitivity for cloud point extraction was obtained at pH 10 for Co, Cr and pH 8 for Cu, at lower pH, the ligand is protonated and its ionic characteristics increase and led to decrease in its solubilization in the hydrophobic micelles. At higher pH, the ligand is deprotonated and it behaves like a hydrophilic molecule and easily gets solubilized in the micelles on the other hand, at pH > 10 for Co, Cr and 8 for pH > 8 the signal decreases yielding lower absorbance due to precipitation of $M(OH)_2$ or $M(OH)^+$ ions in the form of hydroxides. Owing to this behaviour pH = 10, 8 was selected for the subsequent.
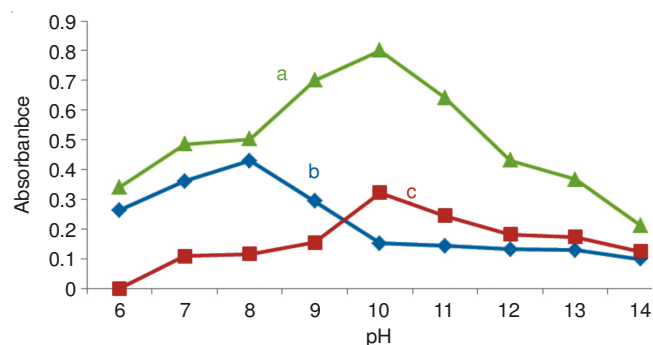

Fig. 5.   Effect of pH on the cloud point extraction of (a) cobalt, (b) copper and (c) chromium conditions: Cu(II) = 70 μg L^{-1}, Co = 70 μg L^{-1}, Cr = 70 μg L^{-1} Salen = 3 × 10^{-4} mol L^{-1} and 0.8, 0.4, 0.6 mL 10 % (v/v) (Triton X-100)

Effect of Triton X-100 amount: The concentration of surfactant used in the cloud point extraction is an important factor. Triton X-100 was chosen because of its commercial availability in a high-purified homogenous form, low toxicological properties and cost. The effect of surfactant concentration on the extraction of Cu(II), Co(II) and Cr(III) was examined within the Triton X-100 volume range from 0.2-1.8 mL 10 % (v/v) Fig. 6 shows that the measured absorbance of extracted solution increases as the surfactant concentration increases and then suddenly decreased at higher amount. Therefore, 0.8, 0.4, 0.6 mL 10 % (v/v) Triton X-100 was used as the optimum concentration for copper, cobalt and chromium.
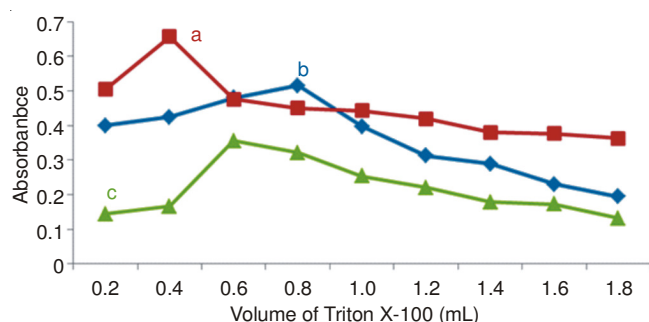

Fig. 6.   Effect of volume of Triton X-100 on the cloud point extraction of (a) cobalt, (b) copper and (c) chromium conditions: Cu(II) = 70 μg L^{-1}, Co = 70 μg L^{-1}, Cr = 70 μg L^{-1} Salen = 3 × 10^{-4} mol L^{-1} at pH 10 for cobalt, chromium and 8 for Cu

Effect of Salen concentration: The effect of concentration of Salen on the cloud point extraction of Co (II), Cu(II) and Cr(III) was investigated in the concentration range of (0.5

-5.0) × 10^{-4} mol L^{-1}. The maximum absorbance was obtained at 3 × 10^{-4} M (Fig. 7). At lower than (3 × 10^{-4}) of ligand, insufficient concentration caused which the complexation wasn't complete. A possible explanation for the decrease with higher concentrations may be attributed to the formation of charged complexes with excess ligand in the medium or remaining of excess of ligand in aqueous solution and competitive with surfactant-rich phase for formation of complex with metal ions in aqueous phase.
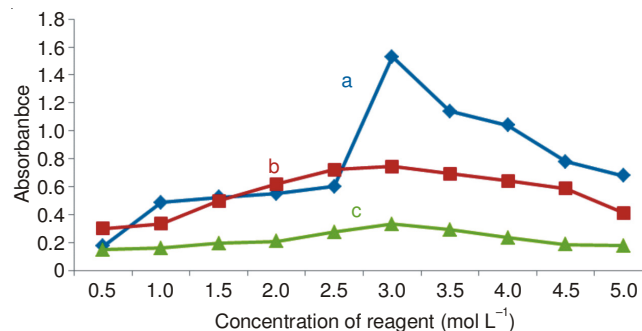

Fig. 7.   Effect of concentration of the Salen ligand on the cloud point extraction of (a) cobalt, (b) copper and (c) chromium conditions: Cu(II) = 70 μg L^{-1}, Co = 70 μg L^{-1}, Cr = 70 μg L^{-1} at pH 10 for cobalt, chromium and 8 for copper and 0.8, 0.4, 0.6 mL 10 % (v/v) (Triton X-100)

Effect of equilibrium temperature and the incubation time: In order to optimize the method, it was necessary to examine the effect of the temperature on cloud-point extraction. Consequently a study was carried out to choose the range of temperature that enhances higher absorbance signals. Absorbance was investigated in the range of 35-95 °C and 5-35 min, respectively, while keeping all other parameters constant. Excellent absorbance was found at 50 °C for cobalt, 70 °C for Cu and 80 °C for Cr (Fig. 8). Therefore choose 50, 70, 80 °C higher than is probably due to the decomposition of the complex which reduces the extraction efficiency.
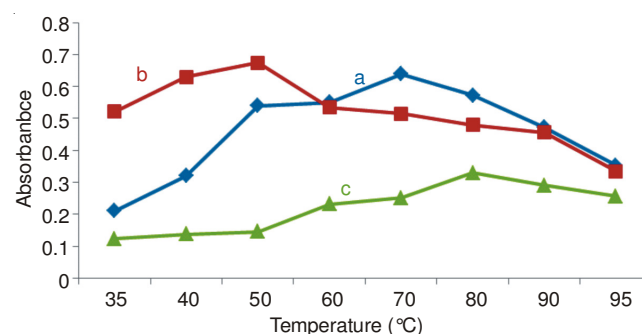

Fig. 8.   Effect of temperature (°C) on the cloud point extraction of (a) copper, (b) cobalt and (c) chromium conditions: Cu(II) = 70 μg L^{-1}, Co = 70 μg L^{-1}, Cr = 70 μg L^{-1} Salen = 3 × 10^{-4} mol L^{-1} at pH 10 for cobalt, chromium and 8 for copper

Incubation time was also investigated in the range of 5-35 min (Fig. 9). Excellent absorbance found at 10, 15, 30 min, the time for 10, 15, 30 min were selected to fulfill efficient separation conditions.

Interferences study: In order to evaluate the usage of the presented cloud point extraction procedure in analytical applications, the effects of the potential interfering species
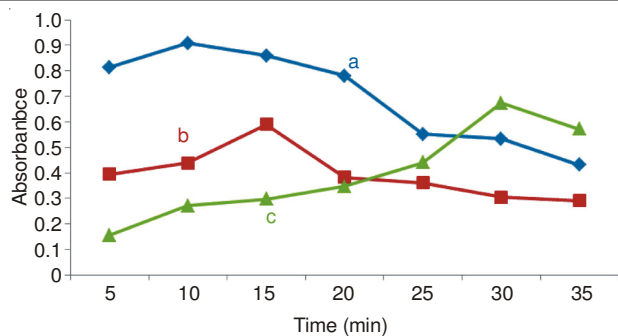
Fig. 9. Effect of time min on the cloud point extraction of (a) cobalt, (b) copper and (c) chromium conditions: Cu(II) = 70 μg L^{-1}, Co = 70 μg L^{-1}, Cr = 70 μg L^{-1} Salen = 3 × 10^{-4} mol L^{-1} at pH 10 for cobalt, chromium and 8 for copper

Fig. 10. Continuous variation of Cu(II)-Salen

Fig. 11. Continuous variation of Co-Salen

were tested by contacting known amounts of some anions and cations, under the optimal conditions. The results are shown that gave a remarkable increase is due only large ionic strength of second periods the solution more than the first periods. The impact of cation and anion in the aqueous phase of its importance in the processes of extraction equilibrium the presence of cations in the aqueous phase may be compete with the cation under study in correlation with organic reagent the anion may led to restrict metal ion under study in the aqueous phase this would reduce the efficient. The result is given in Table-1.

TABLE-1
EFFECT OF INTERFERENCE ION

Interfering ion	Amount added (μg L^{-1})	Interfering ion (%)		
		Cu	Co	Cr
K$^+$	200	+3.4	+3.7	+0.52
Na$^+$	200	+7.2	+0.8	+4.7
Ca^{2+}	200	+10.3	+6.4	+8.7
Mg^{2+}	200	+15	+8.31	+11.08
SCN$^-$	200	-3.4	-2.28	-4.4
Br$^-$	200	-6.1	-3.91	-7.3
SO$_4^{2-}$	200	-9.9	-12.47	-2.9
I$^-$	200	-10.9	-17.2	-5.2

Continuous variation method: A series of 1, 2, 3, 4, 5, 6, 7, 8, 9 mL of 3 × 10^{-4} mol L^{-1} Co(II), Cu(II) and Cr(III) was pipetted into each of 10 mL volumetric flask, then 9, 8, 7, 6, 5, 4, 3, 2, 1 mL of 3 × 10^{-4} mol L^{-1} Salen, ligand added into each volumetric flasks at optimum pH, the absorbance of the solutions were measured by UV-visible spectrophotometer at λ$_{max}$ for each complex. Figs. 10-12 show the continuous variation the stoichiometric ratio between Cu(II)-Salen Co(II)-Salen and Cr(II)-Salen and ligand is 1:1. The probable chemical structure show in Figs. 13-15.

Calibration graph: Employing the optimum conditions described in the procedure of cloud point extraction, linear calibration graph of copper, cobalt and chromium with ligand Salen was obtained Fig. 16 (chromium), Fig. 17 (copper) and Fig. 18 (cobalt) which show Beers law obeyed over the concentration range of 10-70 μg L^{-1} with correlation coefficient Cu(II) and Co(II) and Cr(III) equal to 0.9991, 0.9984 and 0.9972. All other analyticalcharacteristics data are summarized in Table-2.

Accuracy and precision: The accuracy and precision of proposed methods were determined at two concentration level of Co(II), Cu(II) and Cr(III) by analyzing five replicate sample
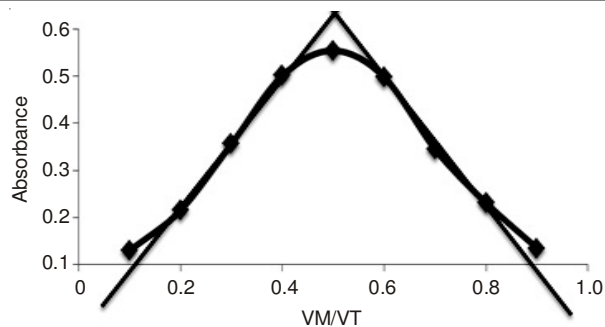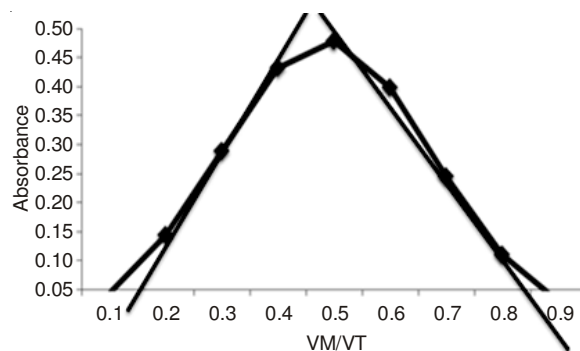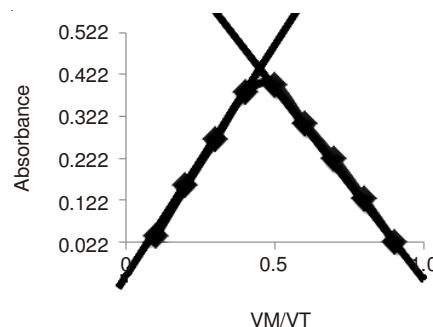

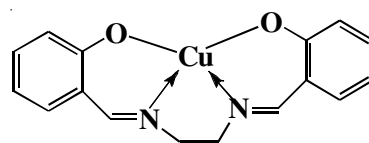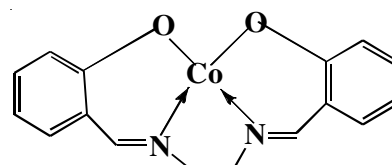
Fig. 12. Continuous variation of Cr-Salen

Fig. 13. Probable structure of Cu(II) complex of Salen

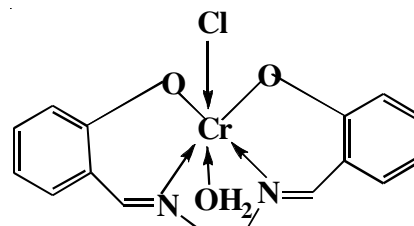Fig. 14. Probable structure of Co(II) complex of Salen

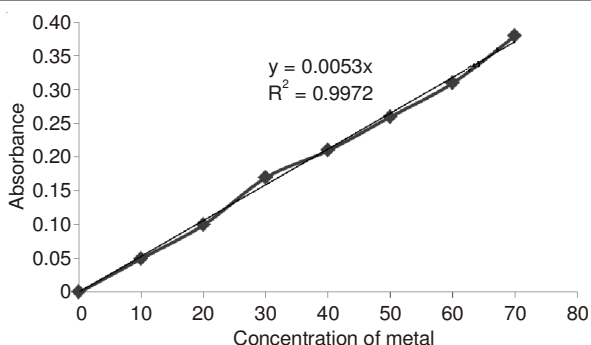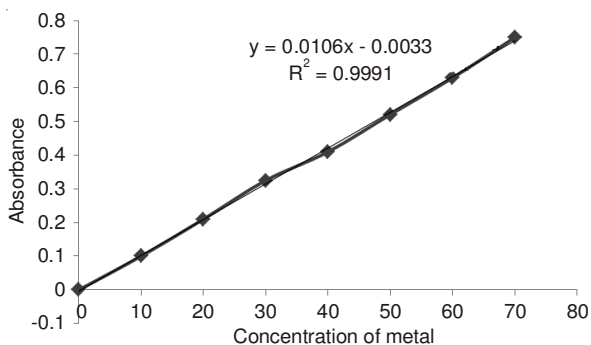Fig. 15. Probable structure of Cr(III) complex of Salen

$y = 0.0053x$
$R^2 = 0.9972$

Fig. 16. Calibration graph of chromium

$y = 0.0106x - 0.0033$
$R^2 = 0.9991$

Fig. 17. Calibration graph of copper

$y = 0.01x + 0.0031$
$R^2 = 0.9984$
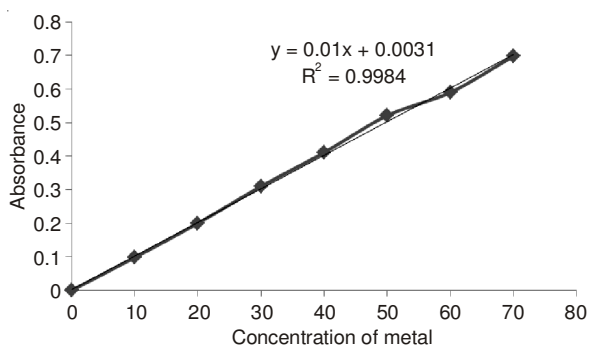
Fig. 18. Calibration graph of cobalt

TABLE-2 ANALYTICAL CHARACTERISTICS DATA OF THE PROPOSED METHOD			
Parameter	Cu(II)	Co(II)	Cr(III)
λ_{max} (nm)	361	378	382
R^2	0.9991	0.9984	0.9972
RSD (%)	0.9108	0.9109	0.15
Linear range (μg L^{-1})	10-70	10-70	10-70
Limit of detection ($3S_b$/m) (μg L^{-1})	2.62	2.1	0.500
Limit of quantitative ($10S_b$/m) (μg L^{-1})	8.75	7.3	1.667
Recovery (%)	97-99	94-99	95-98
Molar absorptivity	2588.571429	2901.98485	1446.6057
Slope	0.0106	0.01	0.0053
Intercept (a)	0.0033	0.0031	0.0017

of each concentration. The relative standard deviation for results did not exceed 0.9108, 0.9109 and 0.15 %. Table-3 show high reproducibility of results and precision of the methods.

TABLE-3 ACCURACY AND PRECISION OF PROPOSED METHODS			
Amount of Cu(II) (μg L^{-1})		RSD (%)*	Recovery (%)*
Present	Found		
70	69.78	0.91	99
30	29.56	0.92	98
Amount of Co(II) (μg L^{-1})		RSD (%)*	Recovery (%)*
Present	Found		
70	69.88	0.91	99%
Amount of Cr(III) (μg L^{-1})		RSD (%)*	Recovery (%)*
Present	Found		
70	69.22	0.15	98%
30	29.05	0.21	96%
*Average of seven determination.			

Analytical application: The suggested methods was applied to the quantitative determination of Cu(II), Co(II) and Cr(III) in wastewater of Rustimiyah city in Iraq and industrial sewage of Tannery Factories in Zafaraniyah. The results obtained are good accuracy and precision as shown in Table-4. The

TABLE-4 APPLICATION OF PROPOSED METHOD FOR DETERMINATION OF Cu(II), Co(II) AND Cr(III)							
	Real sample	Taken	Found	RSD (%)*	RSD (%) average	Recovery (%)	Recovery (%) average
Copper	Wastewater (input) of Rustimiyah city	10	9.33	1.18	0.74	93.0	95.90
		30	29.65	0.30		98.8	
	Wastewater (output) of Rustimiyah city	10	9.55	1.50	0.94	95.5	96.90
		30	29.54	0.44		98.4	
	Wastewater of Tannery Factories	10	9.95	1.10	0.75	99.9	99.70
		30	29.8	0.38		99.3	
Cobalt	Wastewater (input) of Rustimiyah city	10	9.63	0.89	0.73	96.0	97.50
		30	29.77	0.58		99.0	
	Wastewater (output) of Rustimiyah city	10	9.79	0.78	0.62	97.9	98.45
		30	29.77	0.47		99.0	
	Wastewater of Tannery Factories	10	9.96	0.90	0.70	99.9	98.95
		30	29.45	0.55		98.0	
Chromium	Wastewater (input) of Rustimiyah city	10	9.89	1.10	0.74	98.9	98.85
		30	29.64	0.38		98.8	
	Wastewater (output) of Rustimiyah city	10	9.45	1.30	0.81	94.5	97.00
		30	29.85	0.33		99.5	
	Wastewater of Tannery Factories	10	10.99	0.70	0.46	109.0	106.00
		30	31.00	0.23		103.0	

TABLE-5
COMPARISON OF THE PROPOSED METHOD WITH REPORTED METHODS FOR THE
PRECONCENTRATION AND CLOUD POINT EXTRACTION OF COPPER, COBALT, CHROMIUM

Ions	Chelating agent	Surfactant	Technique	λ_{max} (nm)	Linear range	RSD (%)	Detection limits	Ref.
Co	HCPTS	Triton X-114	GFAAS	242.5	0.02-200	2.19	0.0165	25
Cu				324.8	0.03-200	3.35	0.019	
Cu	MPMP	Triton X-114	FAAS	–	1-150 µg L^{-1}	1.8	0.15	26
Cu	MPKO	Triton X-114	FAAS	–	10-250 µg L^{-1}		1.6	2
Cu	NTPHPI	Triton X-114	FAAS	–	0.007-0.33	2.44	0.001	27
Co					0.007-0.33	1.06	0.006	
Co	4-(2-Pyridylazo)-resorcinol	Triton X-114	ICP-OES		10-500	5.57	1.2	28
Cr(III)	APDC and 8-hidroxyquinoline	Triton X-114	FAAS	–	–	–	1.4	29
Co	APDC	Triton X-114	FAAS	–	–		5 µg L^{-1}	30
Cr	DDTC	Triton X-114	HPLC		50-1000 µg L^{-1}	0.6	3.4 µg L^{-1}	31
Cu	BIYPYBI	Triton X-114	FAAS		15-200 ng mL^{-1}	4.1	1.4	32
Co	(APDC)	Triton X-114	TS-FF-AAS		2.1-100 µg L^{-1}	5.8	2.1 µg L^{-1}	33
Cr(III)	8-Hydroxyquinoline	Triton X-100	ICP-OES		-	2.1	1.29 ngL^{-1}	34
Co						3.4	1.31 ngL^{-1}	
Co	Salen	Triton X-100	UV/VIS	378	10-70 µg L^{-1}	0.910	2.1 µg L^{-1}	Proposed methods
Cu				361	10-70 µg L^{-1}	0.912	2.62 µg L^{-1}	
Cr				382	10-70 µg L^{-1}	0.150	0.5003 µg L^{-1}	

MPKO = Methyl-2-pyridylketone; HCPTS = 2-(Pyridine-2-yl)-N-*p*-chlorohydrazine carbothioamide; MPMP = 2-[(2-Mercaptophenylimino)-methyl]phenol; NTPHPI = N(2-Thiophenyl)-1-(2-hydoxyphenyl)imine; APDC = Ammonium pyrrolidine dithiocarbamate; BIYPYBI = 2-(6-(1*H*-benzo[d]imidazol-2-yl)pyridin-2-yl)-1*H*-benzo[d]imidazole

proposed method was compared successfully with other literature methods (Table-5).

Conclusion

Cloud point extraction preconcentration is an easy, safe and inexpensive methodology for separation and preconcentration of trace metals in aqueous solutions. Schiff base ligand was successfully to formed complex with the some metals ion by cloud point extraction. Salen successfully used as an analytical reagent in the determination of Cu(II), Co(II) and Cr(III) in wastewater of Rustimiyah city in Iraq and indus-trial sewage of Tannery Factories in Zafaraniyah with Triton X-100.

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