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**Cloud point extraction and Flame Atomic Absorption Spectrometry in the determination of Cu (II), Cr (III), Cd(II), Fe(III) and Mn(II) using Glycerin and PO/EO-block polymer as a surfactant**

د. حمدي عبد الكريم خطاب علي / قسم الكيمياء - كلية التربية - المرج / جامعة بنغازي - ليبيا

أ. رحاب حسين عزالدين قسم الكيمياء / كلية الآداب والعلوم - المرج / جامعة بنغازي - ليبيا



## Cloud point extraction and Flame Atomic Absorption Spectrometry in the determination of Cu (II), Cr (III), Cd(II), Fe(III) and Mn(II) using Glycerin and PO/EO-block polymer as a surfactant

### Abstract:

A simple cloud point extraction (CPE) method has been proposed for the separation & preconcentration for determination of  $Cr^{3+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Fe^{3+}$  and  $Mn^{2+}$  ions by complexation with ammonium pyrrolidine dithiocarbamate (APDC) in the presence of Glycerin and PO/EO-block polymer. The phase separation occurred when micellar solution was heated at  $60^{\circ}C$ . A complete separation of the metal ions with and without addition of chelating agent could be achieved at  $PH= 3-10$  the efficiency of separation is 85-100%. Glycerin showed 75-100% separation for  $Cr^{3+}$ ,  $Cu^{2+}$  and  $Mn^{2+}$  while PO/EO-block polymer showed 60-99% for  $Cd^{2+}$  and  $Fe^{3+}$ . Other factors also tested include surfactant and metal ions concentration, temperature, time and foreign ions. One gram of surfactant is an enough amount for separation of 20 ppm of each metal ion solution. The analysis of metal ions were carried out using flame atomic absorption spectrometer with deuterium lamp background correction and calibration curve method.

**Keywords:** cloud point extraction, Glycerin , PO/EO-block polymer, APDC , flame atomic absorption spectrometry.

### الملخص :

طريقة استخلاص نقطة الغيمة البسيطة (CPE) تم اقتراحها للفصل و لتحديد أيونات  $Fe^{3+}$ ،  $Cd^{2+}$ ،  $Cu^{2+}$ ،  $Cr^{3+}$  و  $Mn^{2+}$  بتكوين معقدات باستخدام Ammonium pyrrolidine dithiocarbamate (APDC) كعامل تعقيد وفي وجود الجلسرين و البوليمر PO / EO - أكسيد لإيثيلين / أكسيد البر وبيلين كمؤثر سطحي surfactant. فصل الطور يظهر عندما تم تسخين محلول عند  $60$  درجة مئوية. يمكن تحقيق فصل كامل للأيونات المعدنية مع وبدون إضافة عامل مخلب عند درجة الحموضة = 3-10 وكفاءة الفصل هي 85-100%. أظهر الجلسرين فصل 75-100% لـ  $Cr^{3+}$ ،  $Cu^{2+}$  و  $Mn^{2+}$  بينما أظهر بوليمر PO / EO فصل 60-99% لـ  $Cd^{2+}$ ،  $Fe^{3+}$ . العوامل الأخرى التي تم اختبارها تشمل أيضاً تركيز المنشط السطحي وتركيز أيونات الفلزات ودرجة الحرارة والوقت. غرام واحد من المنشط السطحي تكفي لفصل 20 جزء في المليون من كل محلول أيون فلزي. تحليل أيونات الفلزات تم اجراءه باستخدام مطيافية الامتصاص الذري مع لمبة الديوتيريوم خلفية لتصحيح مسار المنحنى.

الكلمات المفتاحية: نقطة استخلاص الغيمة، الجلسرين، مطيافية الامتصاص الذري، درجة الحرارة.

## 1- INTRUDUCTION

Cloud point extraction is a simple and powerful technique for separation and preconcentration of metal ions and it has many advantages, such as low cost, safety, and a high capacity to concentrate a wide variety of analytes of widely varying nature with high recoveries and high concentration factors (7,19,20). Also, it offers an alternative to conventional extraction system and can be classified as a “green chemistry” process. Green chemistry can be defined as procedures reducing or eliminating the use or generation of toxic substances for the following reasons: (a) it uses inexpensive dilute surfactant solutions as extractor media, which results in an economy of reagents and the generation of small residues, and (b) surfactants are not toxic, not volatile, and not easily flammable, unlike organic solvents used in liquid–liquid extraction (13,8,14,1,21).

Temperature is a key factor and driving force for the dispersion of the modifier and surfactant into the sample solution. It is desirable to have the lowest possible equilibration temperature, which compromises the completion of the reaction and the efficient separation of phases. In the CPE process, cloud point can be altered with the increasing length of the hydrocarbon and sometimes dramatically in the presence of acids or bases, salts, and organic additives (16).

Flame atomic absorption spectrometry (FAAS) with its relative low cost and good analytical performance, is the main instrument

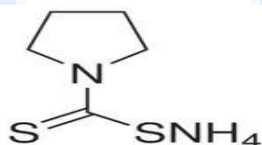
in the research laboratories for determining a variety of heavy metals. Accurate determination of traces heavy metals by flame atomic absorption spectroscopy is the one of the important problems for the analytical chemist because of their low concentrations. Also other important problem in FAAS determinations of heavy metals is influences of the matrix of the analyzed samples. In order to overcome, these problem analytical chemists generally use separation–preconcentration techniques including liquid–liquid extraction, co-precipitation, cloud point extraction, electro-deposition, solid phase extraction, etc (23,9,3,17,10).

Membrane filtration is one of the important enrichment techniques for trace heavy metal ions (4,22,11). The formation of hydrophobic species is necessary for the quantitative extraction of the desired trace element on a membrane filter. In the membrane filtration, the collection of traces metal ions is performed very quickly by filtration under suction with the aid of a vacuum aspirator. The collected analyte species on the membrane filter are dissolved together with the membrane in a small amount of mineral acids. The traces species in the final solution is determined by an instrumental method including spectrophotometry, flame or graphite furnace atomic absorption spectrometry.

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The most attractive features of membrane filtration technique are the simplicity and rapidity of the procedure, an easily attainable high concentration factor and determination with high-precision(6,15). Various application of the membrane filtration for the preconcentration of traces heavy metal ions were performed by the researchers (2,18,5,12).

### Scheme I Structure of ligand APDC



In the present work a simple, selective and sensitive CPE method for preconcentration and determination of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cr}^{3+}$  ions in various real samples using APDC as selective and sensitized complexing agent in basic media was established.

## 2- EXPERIMENTAL

### 2.1 Reagents

All solutions were prepared with deionized water. Except if otherwise stated, analytical-grade methanol, acids, and other chemicals used in this study were obtained from Merck, Darmstadt, Germany. The calibration curve was established using standard solutions. A 1.0% (w/v) Glycerin and PO/EO-block polymer from Clariant. The ligand, Ammonium pyrrolidine dithiocarbamate (APDC).

### 2.2. Instrument

A novAA 350 atomic absorption spectrometer equipped with deuterium background correction and copper, iron, chromium, cadmium and manganese hollow-cathode lamp as the radiation source was used for absorbance measurements at wavelength respectively. The instrumental parameters were adjusted according to the manufacturer's recommendations. A Hettich centrifuge was used to accelerate the phase separation process. JENWAY mode 3150pH meter furnished with a combined glass-saturated calomel electrode was used for pH measurements.

### 2.3 Test Procedure

For the cloud point extraction, aliquots of 12 ml of the simple or standard solution containing the analyte (10 ml), surfactant (1 ml), ligand(1 ml), were kept in thermostated bath at (40 – 80°C) for 15 min. Separation of the aqueous and surfactant –rich phase was accomplished by centrifugation for 2 min at 3000 rpm. After cooling in an ice (5 min), the surfactant rich phase became viscous. The supernatant aqueous phase was then separated completely a 10 ml syringe centered in the tube. The resulting solution was introduced into the flame by conventional aspiration.

### 3- RESULTS AND DISCUSSION

#### 3.1. Effect of pH

Cloud point extraction yield depends on the pH at which complex formation occurs. pH plays a unique role on metal- chelate formation and subsequent extraction. CPE of copper, cadmium, manganese and iron ions was performed in solutions of pH ranging from (3 to 10). (Fig.1) shows the effect of optimum pH on the absorbance and sensitivity of method. The pH in (from 5 to 10) showed maximum sensitivity which is an obtained.

At lower pH, the ligand is protonated and its ionic characteristics increase and lead 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. The maximum extraction efficiency was obtained with glycerin for ( $\text{Cr}^{2+}$   $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$ ) and ( $\text{Fe}^{2+}$  and  $\text{Cd}^{2+}$ ) for PO/EO-block polymer .

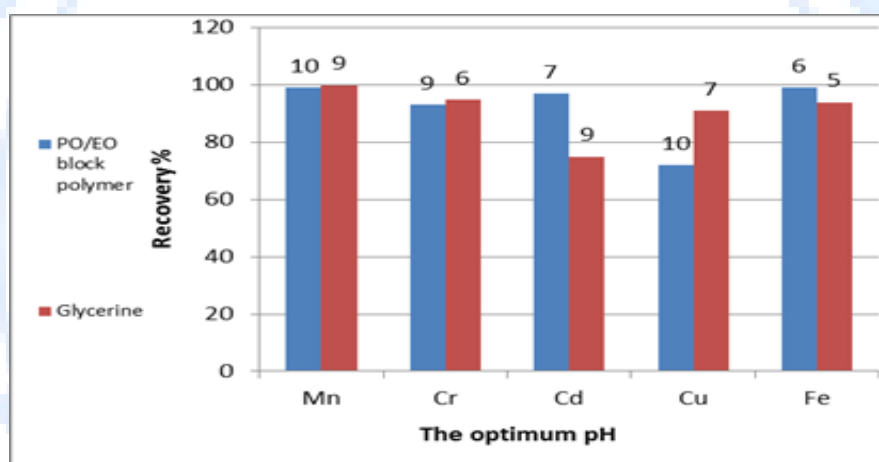


Fig.1: Effect of optimum pH on the recoveries of metal ions ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cr}^{3+}$ ).

#### 3.2. Effect of extraction procedure on recovery % on metal with &without APDC concentration

The APDC was employed as a complexing agent for chromium, copper, cadmium, manganese and iron ions CPE. The concentration of APDC was evaluated over the range (1-13 ml and without APDC). The extraction recovery as a function of the APDC concentration is shown in fig.2.

In some cases of metal ions separation it was found that there was no need to separate this metal ions without using APDC as a ligand .

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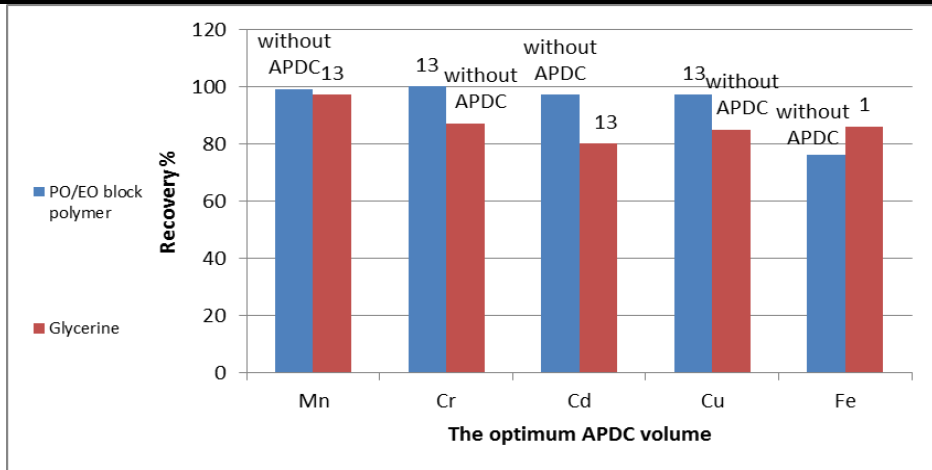


Fig.2: Influences of concentration of APDC

3.3. Effect of Glycerin and PO/EO-block polymer volume on the recovery%

The Glycerin and PO/EO-block polymer were chosen because of its commercial availability in a high purified homogeneous form, low toxicological properties and cost. Also, the high density of surfactant- rich phase facilitates phase separation by centrifugation. Additionally, the cloud point (40 – 80°C) of Glycerin and PO/EO-block polymer permits its use in the extraction and /or preconcentration of a large number of molecules and chelate in that temperature. The preconcentration efficiency was evaluated using surfactants concentration ranging from (1 to 4 and No. 5 without APDC) so we chose the optimum surfactant concentration as shown in fig.3. The maximum extraction efficiency was obtained with glycerin for ( $Cr^{2+}$ ,  $Cu^{2+}$  and  $Fe^{2+}$ ) and ( $Mn^{2+}$  and  $Cd^{2+}$ ) for PO/EO-block polymer .

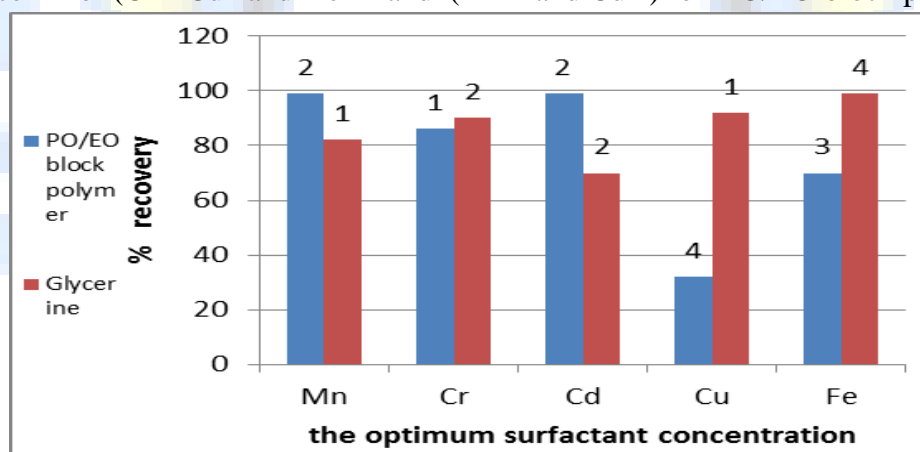


Fig.3: Effect of optimum surfactant on the recoveries of metal ions.

### 3.4. Effect of temperature on recovery%

The cloud point temperature of Glycerin and PO/EO-block polymer is (60 – 80°C) which is the preferred for cloud point temperature and analytical purposes. The maximum extraction efficiency was obtained with glycerin for ( $\text{Cr}^{2+}$   $\text{Mn}^{2+}$  and  $\text{Cd}^{2+}$ ) and ( $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$ ) for PO/EO-block polymer

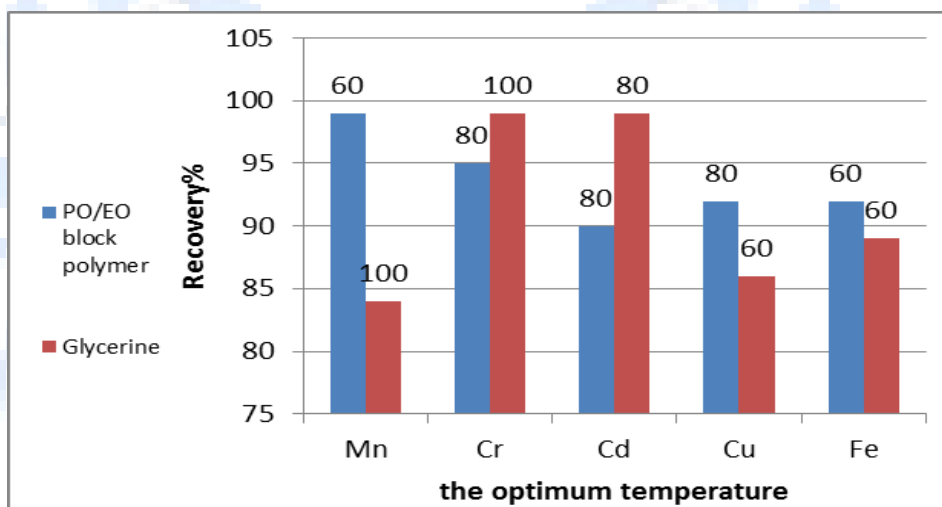


Fig4: Effect of temperature on the recovery%

### 3.5. Effect of foreign ions

The influences of some transition metal ions on metal ions recovery of the analyte ion were investigated by the presented CPE procedure fig.5. The tolerance limit is defined as the ion concentration causing a relative error smaller than ( $\pm 5\%$ ) related to the preconcentration and determination of metal ions.

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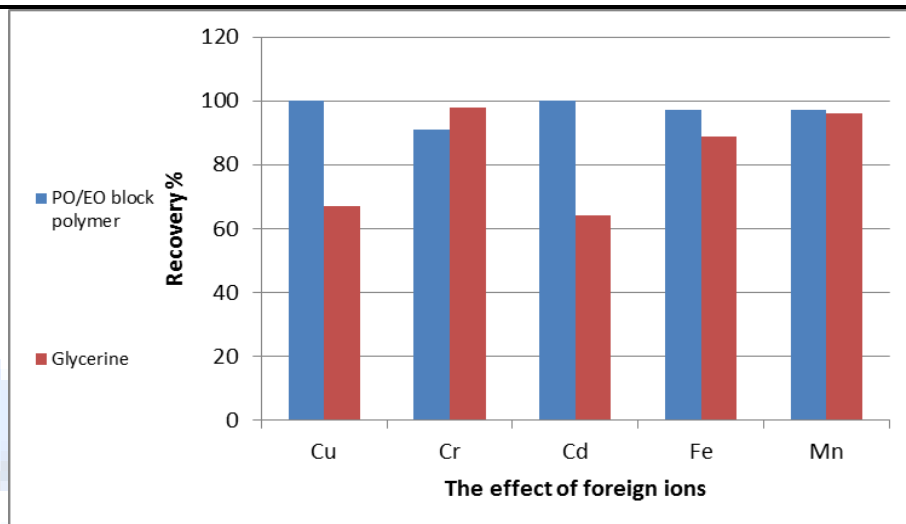


Fig.5: Effect of foreign ions on recovery%.

### 3.6. Effect of metal ions concentration on recovery%

The Most suitable concentration on recovery % was studied and formed to be 10 ppm for  $Fe^{3+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$  and  $Mn^{2+}$ , 40ppm for  $Cr^{3+}$ . As shown in figure 6. The maximum extraction efficiency was obtained with glycerin for ( $Cu^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$  and  $Cd^{2+}$ ) and ( $Cr^{2+}$ ) for PO/EO-block polymer.

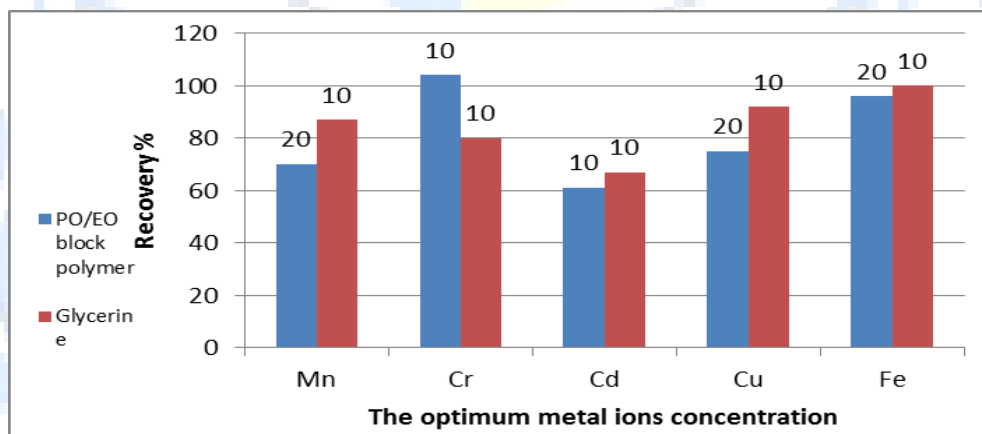


Fig.6: Effect of Metals concentration on recovery%.

### 3.7. Effect of centrifugation time and rates

It is required to preconcentrate trace amount of chromium, copper, cadmium, manganese and iron ions with high efficiency in short time. Therefore, CPE on a set of experiments of 12 ml sample at pH, 1mmol APDC, 10 ml, 10 ml ions by heating at different temperature according to the type of surfactant that we used and centrifuging in various rate and time further cooling in various time has been carried out. The results indicate the



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experiment in the optimized reagent concentration after heating for 15 min, and centrifuging by 2 min in 3000 rpm and cooling in 5 min in ice-bath to high recovery of ions in short time.

The effect of centrifugation time upon analytical signal was also studied for the rang of (2-14 min). A centrifugation time of 2 min at 3000rpm was selected for the entire procedure, since no apprecible improvement were observed for longer times.

### 4- APPLICATION (Sample analysis)

To verify the accuracy of the proposed method, the contents of metal ions in certified reference material of soil (GBW 07406) were determined by the proposed method. As we can seen in table 1, the obtained results are in good agreement with the reference values.

Table 1: Analytical results ( $\text{mg L}^{-1}$ ) for metal ions in certified reference materials

Metal ions	Conc. ppm		Certified value ppm		Recovery %	
	PO/EO	Gly	PO/EO	Gly	PO/EO	Gly
Cu	3.616	4.418	315	315	98	98
Cr	1.095	0.743	75	75	98	99
Cd	0.051	0.070	0.14	0.4	63	50
Fe	20.75	19.07	5700	5700	99	99
Mn	0.140	10.13	1450	1450	99	90

### 5- CONCLUSION

The cloud point extraction offers a simple, rapid, sensitive, inexpensive, non-polluting and environmentally benign methodology which is alternative to other separation /pre-concentration techniques. Glycerin and PO/EO-block polymer were chosen for the formation of the surfactant rich phase due to its excellent physico-chemical characteristics. The present method has been successfully applied for the determination of cadmium, copper, chromium, iron and manganese in samples. This method has the following added advantages over already reported methods. (Table-1).

1. The synthesis of metal chelating agent in the laboratory is simple and more economical.
2. The synthesis of organic reagent is distancing in terms of sensitivity, selectivity towards metal ions.
3. The risk of contamination is quite low.

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4. Foreign ions do not method gives very low LOD, good SD's and solvent free extraction of the elements from its initial matrix.

Glycerin showed an excellent extraction recovery as a surfactant with cloud point temperature (60 – 80°C) compared with PO/EO-block polymer.



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