

## Cloud Point Extraction spectrophotometric Determination of Iron by SALEN as Reagent in Some Environmental in Iraq

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### Abstract

Cloud point extraction is a separation and preconcentration, simplicity, cheapens, fast, and environmental safety to determination of iron by UV/Vis spectrophotometry in some environmental samples such as wastewater of Rustimiyah city in Iraq and DiyalaRiver, by using SALEN as reagent in the presence of Triton X-100 (as a non-ionic surfactant) at  $\lambda_{\max}$  409. The optimum conditions for the CPE respect to several experimental parameters such as pH of the solution, SALEN concentration, Triton X-100, incubation time, temperature and concentration of metals. The proposed method had a linear range for Iron 5-80  $\mu\text{gL}^{-1}$ , the recovery of analytes was in the range 97-99%, detection limits was 1.8  $\mu\text{gL}^{-1}$  and the relative standard deviation (RSD) 0.85%, pH was equal to 9.

**KEYWORD:** -Cloud point extraction, SALEN, determination Iron.

### Introduction:

Determination of trace metals such as iron in environmental samples is a subject of considerable importance because trace metal play important role in biological processes<sup>(1)</sup>, Iron is known as one of the essential nutritional elements for many living organisms due to its role in most of metabolic processes, including oxygen and electron transport, and DNA synthesis. On the other hand, exposure to excess iron can cause several diseases or disorders such as endocrine problems, arthritis, diabetes, and liver disease<sup>(2,3)</sup>. Iron has two readily inter converted oxidation states<sup>(4)</sup>. Expensive analytical methods such as inductively coupled plasma mass spectrometry (ICP-MS)<sup>(5)</sup>, and capillary electrophoresis (CE)<sup>(6)</sup>, inductively coupled plasma optical emission spectrometry (ICP-OES)<sup>(7)</sup>, chromatography<sup>8</sup>, in this paper use Ultraviolet-visible (UV-Vis) spectroscopy is a simple instrument, cheap, easy, precision, accuracy operated, rapid response time and available in many laboratories and offers acceptable analytical<sup>9</sup>, preconcentration/separation technique is generally necessary prior to the determination in order to overcome, these problem analytical chemists generally use separation-preconcentration techniques<sup>[10]</sup> including liquid-liquid extraction<sup>[11]</sup>, solid phase extraction<sup>[12]</sup>, cloud point extraction<sup>[13,14]</sup>, to determination iron by cloud point use some reagent such as O-phenanthroline (O-Phen)<sup>15</sup>, Dithizone (DZ)<sup>1</sup>, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP)<sup>16</sup>, Ferron<sup>17</sup>.

### Instrumentation and apparatus:

A thermo stated water bath model Unitemp, pH meter model BP 3001. Phase separation was achieved with centrifuge model REMI at 2500rpm in 10mL calibrated conical tube

.UV-Visible Shimadzu model UV-160 A, FTIR Shimadzu , model IR-PRESTIGE 21, made in Japan.

**Regent:**

All the chemicals used were of analytical reagent grade; deionize water use to diluting the samples and reagents. Ethylenediamine (Qualicems), salicylaldehyde (G.C.C), Triton X-100 (Merck), hydrochloric acid (BDH), Sodium hydroxide (BDH), Ethanol (G. C .C),  $\text{FeCl}_2$  (BDH),  $1000\mu\text{gL}^{-1}$  Stock solution of prepared by dissolving an appropriate amount of  $\text{FeCl}_2$  in deionize 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 0.268g 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 10g Triton X-100 in hot deionize water diluting to the mark in 100 ml volumetric flask, 0.01M hydrochloric acid , 0.01M Sodium hydroxide use to adjust pH 4-13.

**General procedure for CPE**

Aliquots 10 ml of a solution containing a known amount of Fe(II) ion, 10% (v/v) Triton x-100, and agent SALEN  $3 \times 10^{-4}$ , the pH was adjusted by 0.01M HCl , 0.01M NaOH . The mixture was shaken for 1 min and left to stand in a thermo-stated bath at  $70\text{ }^\circ\text{C}$ , for 15 min. Separation of the phases was achieved by centrifugation at 2500rpm for 20 min, the remaining of micellar phase was dissolved by DMF, a measurement of Fe (II) by UV-visible spectrophotometer at  $\lambda_{\text{max}}=409\text{nm}$ .

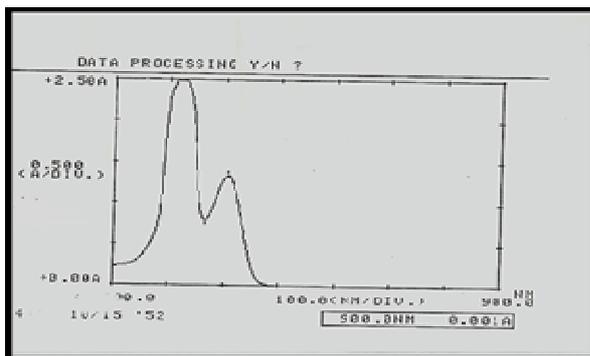
**Application of Real Samples:**

Analysis of waste water of Rustimiyah city in Iraq and Diyala River, samples for determining of analyte contents was performed as follows: About 1000 ml of sample filtering and add 3ml concentrated  $\text{HNO}_3$  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.

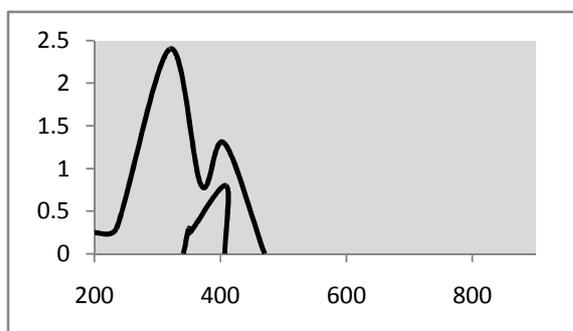
**Result and discussion:**

**Ultraviolet spectrum of ligand SALEN and Fe-SALEN :**

An absorbance and reveals at 407-406 nm Figure (1). This band caused by charge transition between C=N and conjugated benzene ring . It is also the cause of the yellow wish orange color of these components the band at 320nm may be caused by electronic transition  $n \rightarrow \pi^*$  which belongs to C=N. For the transform at 264nm may be caused by electronic transition of  $\pi \rightarrow \pi^*$  of double bond sin C=N and the aromatic ring<sup>(18, 19)</sup>. The complex with Fe-SALEN the maxima absorption at 409 was appeared at pH 9, while the reagent SALEN displays absorption maxima 320.



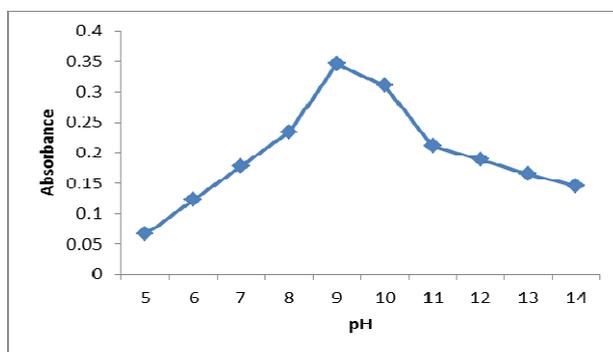
**Figure(1)Ultraviolet spectrum of ligand SALEN**



**Figure (2)Ultraviolet spectrum of complex Fe-SALEN**

**Effect of PH:**

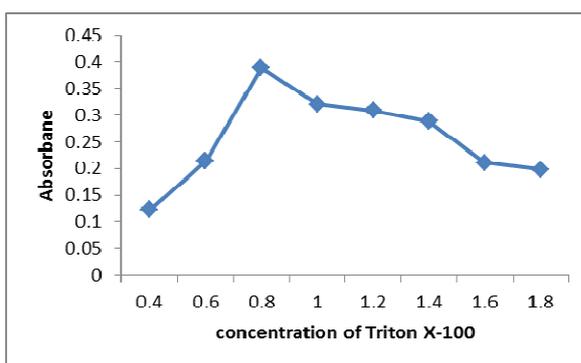
The pH plays a critical role on metallic complex formation and subsequent extraction and has been a significant parameter for CPE, Thus, extraction yield depends on the pH at which complex formation is investigated set of similar experiments<sup>20</sup> in the pH range of 3.0-14.0 were accomplished according to the described procedure in experimental section and the results are shown in Figure (3).The maximum sensitivity for CPE was obtained at pH 9.The decrease in the absorption at pH >9 is probably due to precipitation of iron as iron hydroxide, whereas, the decrease in extraction at pH <9 is due to protonation of the ligand<sup>21</sup>,therefore chosen pH 9 for these work.



**Figure (3) Show the effect of pH on the cloud point extraction of  $Fe(II)=80 \mu gL^{-1}$  SALEN=  $3 \times 10^{-4} Mol L^{-1}$ , 0.8ml 10% (V/V) (Triton X-100).**

**Effect of Triton X-100 amount:**

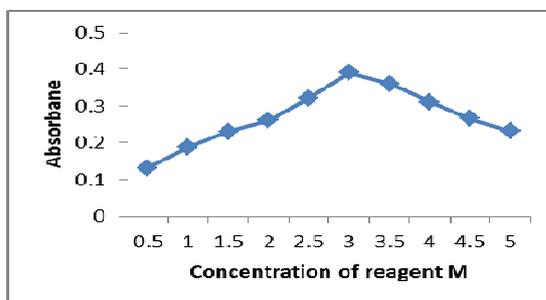
A successful cloud point extraction should maximize the extraction efficiency. The effect of surfactant concentration on the extraction of Fe (II) was examined within the Triton X-100 volume range (0.4-1.8ml) Fig(4) shows that the measured absorbance of extracted solution increases as the concentration increases and then suddenly decreased at higher amount. Therefore, 0.8ml 10% (v/v) Triton X-100 chosen.



**Figure (4) Show the effect of concentration of Triton X-100 on the cloud point extraction of  $Fe(II)=80 \mu gL^{-1}$  SALEN=  $3 \times 10^{-4} Mol L^{-1}$ , pH 9.**

**Effect of SALEN concentration:**

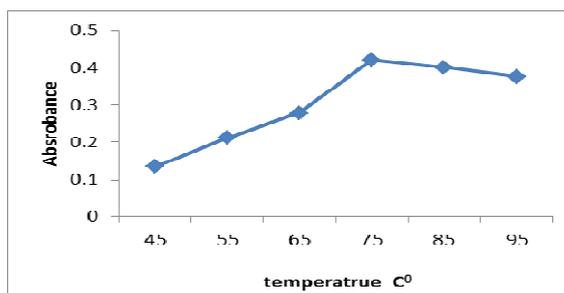
The amount of chelating agent is another important indicator as to whether the chelating action processed completely. The effect of SALEN concentrations on the CPE was investigated in the concentration range of  $(0.5 - 5) \times 10^{-4} mol L^{-1}$ , the extraction efficiency was obtained at  $3 \times 10^{-4} mol L^{-1}$  the results are shown in Figure (5), at lower than  $3 \times 10^{-4} mol L^{-1}$  of ligand, insufficient concentration caused which the complexation wasn't completely, 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.



**Figure (5) Show the effect of concentration of Triton X-100 on the cloud point extraction of  $Fe(II)=80 \mu gL^{-1}$ , pH 9, 0.8ml 10% (V/V) (Triton X-100)**

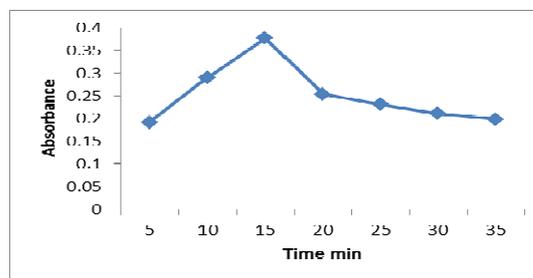
***Effect of Equilibrium Temperature and the Incubation Tim:***

The incubation (heating) temperature and time is an important parameter in CPE process for complete reaction to achieve easy phase separation and the preconcentration to be as efficient as possible. The effect of temperature and time on the extraction of iron was investigated in the range of 45C<sup>0</sup> - 95C<sup>0</sup> and 5 -35 min, respectively, while keeping all other parameters constant it can be seen that the optimum temperature at 75 C<sup>0</sup> Figure6 show the result;therefore, choose75C<sup>0</sup> higher than is probably due to the decomposition of the complex which reduces the extraction efficiency.



***Figure (6) Show the effect temperature on the cloud point extraction of Fe (II)=80 µgL<sup>-1</sup>,pH 9,0 .8ml 10% (V/V) (Triton X-100)***

Incubation time was also investigated in the range of 5-35min Figure (7)show the result excellent absorbance found at 15C<sup>0</sup>was selected to fulfill efficient separation conditions.



***Figure (7) Show the effect of time on the cloud point extraction of Fe (II)=80 µgL<sup>-1</sup>,pH 9,0 .8ml 10% (V/V) (Triton X-100)***

***Interferences study:***

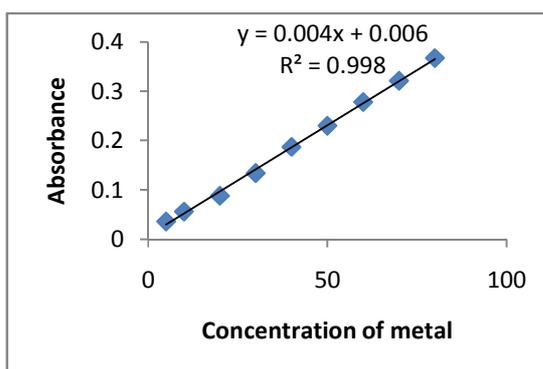
The effects of the potential interfering species were tested by contacting known amounts of some anions and cations, under the optimal conditions. The rustles are shown in Table (1)that gave a remarkable increase is due only large ionic strength of second periods the solution more than thefirstperiod.

**Table (1) effect of Interference ion**

Interfering ion	Amount added $\mu\text{g L}^{-1}$	Percentage of Cu Interference (%)
$\text{K}^+$	200	+1.5
$\text{Na}^+$	200	+2.2
$\text{Ca}^{+2}$	200	+7.8
$\text{Mg}^{+2}$	200	+8.9
$\text{SCN}^-$	200	-2.9
$\text{Br}^-$	200	-3.1
$\text{So}_4^{-2}$	200	-5.9
$\text{I}^-$	200	-6.8

**Calibration Graph:**

Under the optimized conditions established by CPE procedure liner calibration graph of Fe(II)with agent SALEN was obtained Figure (8).Which show Beer law obeyed over the concentration range of 5-80  $\mu\text{gL}^{-1}$  with correlation coefficient 0.9982all other analytical characteristics data are summarized in Table 2.



**Figure(8)calibration graph ofFe (II)**

**Table (2).Analytical characteristics data of the proposed method**

Parameter	Fe(II)
$\lambda_{max}$ nm	409
$R^2$	0.9982
RSD (%)	0.85%
Linear range	5-80 $\mu\text{g}\text{L}^{-1}$
Limit of detection LOD(3S <sub>b</sub> /m)	1.8 $\mu\text{g}\text{L}^{-1}$
Limit of quantitative LOQ(10S <sub>b</sub> /m)	6.3 $\mu\text{g}\text{L}^{-1}$
Recovery	97-99%
Molar absorptivity	2689.56132

<i>Slope</i>	<b>0.0045</b>
<i>Intercept (a)</i>	<b>0.0069</b>

**Accuracy and precision:**

The accuracy and precision of proposed methods were determined Fe(II) at two concentration level of by analyzing five replicate sample of each concentration. The relative standard deviation for results did not exceed 0.85% Table (3) show high reproducibility of results and precision of the methods.

**Table (3) Accuracy and precision of proposed methods**

<i>Amount of Fe(II) <math>\mu\text{g L}^{-1}</math></i>		<i>RSD (%)*</i>	<i>Recovery%</i>
<i>Present</i>	<i>Found</i>		
<b>80</b>	<b>79.56</b>	<b>0.78</b>	<b>99%</b>
<b>30</b>	<b>29.23</b>	<b>0.92</b>	<b>97%</b>

\* Average of seven determination

**Analytical Application:**

The suggested methods was applied to the quantitative determination of in waste water of Rustimiyah city in Iraq andDiyala River, it was gave a good accuracy and precision as shown in Table 4 the proposed method was compared successfully with other literature methods as shown in Table 5.

**Table (4) .Application of proposed method for determination**

<i>Real sample</i>	<i>Taken</i>	<i>Found</i>	<i>RSD%*</i>	<i>RSD% average</i>	<i>Recovery %</i>	<i>Recovery% average</i>
<i>Waste water (input)of Rustimiyah city</i>	<b>30</b>	<b>30.078</b>	<b>0.9</b>	<b>1.1</b>	<b>100%</b>	<b>100%</b>
	<b>10</b>	<b>10.083</b>	<b>1.3</b>		<b>100%</b>	
<i>Waste water (output) of Rustimiyah city</i>	<b>30</b>	<b>30.068</b>	<b>0.75</b>	<b>0.82</b>	<b>100%</b>	<b>100%</b>
	<b>10</b>	<b>1.075</b>	<b>0.89</b>		<b>100%</b>	
<i>Water of Diyala River</i>	<b>30</b>	<b>30.33</b>	<b>1.6</b>	<b>1.1</b>	<b>101%</b>	<b>102%</b>
	<b>10</b>	<b>10.38</b>	<b>0.6</b>		<b>103%</b>	

**Comparison of the proposed method with reported methods for the preconcentration and CPE of Fe (II).**

Chelating agent	Surfactant	Technique	Linear range	RSD%	The detection limits	Ref
<i>O-phenanthroline</i>	<i>SDS and Triton X-114</i>	<i>UV-Vis</i>	<i>25-700 ng mL<sup>-1</sup>.</i>	<i>2.46 %.</i>	<i>10µg mL<sup>-1</sup></i>	<i>15</i>
<i>Dithizone</i>	<i>Triton X-114</i>	<i>AAS</i>	<i>0.2-2.0 µg L<sup>-1</sup></i>	<i>-</i>	<i>-</i>	<i>1</i>
<i>Br-PADAP</i>	<i>Triton X-114</i>	<i>FOS</i>	<i>-</i>	<i>3.5%</i>	<i>1.5µg L<sup>-1</sup></i>	<i>16</i>
<i>EDBOCA</i>	<i>Triton X-114</i>	<i>FAAS</i>	<i>-</i>	<i>4.2%</i>	<i>1.22 µg L<sup>-1</sup></i>	<i>2</i>
<i>Ferron</i>	<i>Triton X-114</i>	<i>AAS</i>	<i>10-250µg L<sup>-1</sup></i>	<i>2.1%</i>	<i>1.7µg L<sup>-1</sup></i>	<i>17</i>
<i>SALEN</i>	<i>Triton X-100</i>	<i>UV-Vis</i>	<i>5-80µg L<sup>-1</sup></i>	<i>0.85%</i>	<i>1.6µg L<sup>-1</sup></i>	<i>My props method</i>

**Conclusion:**

Cloud point extraction is a simple, inexpensive, sensitive, an rapid method in preconcentration and separation of tracemetal TritonX-100 is used as cloud point extraction because high density, and, more importantly, it is very cheap. SALEN reagent successfully to determination Fe (II) in waste water of Rustimiyah city in Iraq and DiyalaRiver, the coupling of CPE with UV-Vis spectrophotometry is a fast and low-cost procedure for the determination of iron and does not require sophisticated and expensive instruments such as AAS and ICP-AES. The advantage of using SALEN to determination is stable, sensitive and selective complexion reagent.

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