Synthesis of New Dithiocarbamate Derivative Reagent for Micro Extraction and Determination of Iron(II) Ion in Aqueous Solution

Ivan Malik Shaker, Ahmed Fadhil Khudhair*, and Hayder Hamied Mihsen

Department of Chemistry, College of Science, University of Kerbala, Karbala 56001, Iraq

Abstract: The new reagent N-methyl-N-(((4-chlorophenyl)diazenyl)thio)carbonothioyl)aniline \( (L) \) was synthesized via the reaction of sodium N-methyl-N-phenyldithiocarbamate with 4-chlorobenzenediazonium salt. The reagent was identified with many techniques, such as CHNS elemental analysis, UV-vis spectroscopy, FTIR spectroscopy, mass spectroscopy, \(^1\)H-NMR, and \(^{13}\)C-NMR spectroscopy. The Fe(II) ion was utilized to create a metal complex by reacting 2 mol of reagent with 1 mol of iron(II) chloride. Two approaches that were utilized for M:L ratio determination are mole ratio and Job methods. All of these refer to the 1:2 ratio for the complex. The solid complex was prepared and identified with the previous techniques, and additional electrical molar conductivity, and magnetic susceptibility measurements. A tetrahedral structure for the prepared complex was suggested based on spectroscopic measurements and elemental analysis results. Cloud point extraction was created for the preconcentration and separation of Fe(II) in drug samples by forming a rich phase using Triton X-114 at 80 °C temperature and pH 5 measurements utilizing flame atomic absorption spectroscopy and UV-vis spectrophotometer at \( \lambda_{\text{max}} \) 635 nm. The calibration curve of Fe(II) was linear in the extent of 0.2–1.0 μg/mL with \( r^2 \) of 0.996. The detection limit and quantification are 0.0504 and 0.1530 μg/mL.

Keywords: dithiocarbamate derivative; pre-concentration; cloud point extraction

INTRODUCTION

Dithiocarbamate (DTC) is a soft donor reagent that can form chelates with the majority of the metal ions in the periodic table [1]. It is described as a "versatile ligand" and several researchers are concerned about DTC molecules because they have potential as helpful synthetic intermediates and protective groups in the synthesis of peptides and bonds in the organic solid phase [2]. They are organosulfur ligands that form stable complexes with metals [3]. There are numerous uses for DTC molecules and their derivatives, including antibacterial, antifungal, and anticancer properties [4-5]. Due to the possibility of functionalizing the substituents on the DTC backbone’s nitrogen atom, which aids in the creation of numerous analogues of this chemical, DTC ligands are particularly helpful in complex synthesis. This has led to a variety of structures with improved characteristics, which therefore improve their physical and chemical properties [6]. These compounds are widely used as analytical reagents with significant environmental impacts because of their propensity to form complexes. Because of their great propensity to form chelates with metal ions at extremely low concentrations (g/mL), they are useful as extractive agents in the removal, preconcentration, and detection of hazardous heavy metal ions at trace and ultra-trace levels [7].

Cloud point extraction (CPE) is a modification of liquid–liquid extraction (LLE), a micelle-mediated separation method that is one of the most widely used techniques for pre-concentrating and separating organic molecules [8]. That is based on adding a surfactant solution at a certain concentration to the analyte sample and then adjusting the temperature or adding specific additives to move the analyte into a micelle phase to achieve separation [9]. The technique is simple, highly competent, concentrates well, inexpensive, safe, and
environmentally benign. Since CPE employs much less hazardous surfactants than harmful chemical solvents, it follows the principle of "green chemistry." Moreover, surfactants are not volatile or inflammable [9-10]. CPE readily combine with fluorescence [10], flow injection [11], flame atomic absorption spectroscopy (FAAS) [12] inductively coupled plasma mass spectrometry (ICP-MS) combines with FAAS, capillary electrophoresis of graphite furnace nuclear absorption spectrometry [13], UV-vis spectrophotometer [14-17], and high-performance liquid chromatography with fluorescence detection (HPLC-FLD) [18].

In this study, the preparation of a new dithiocarbamate derivative having azo-sulfur linkage was done. Then, the new reagent was used to synthesize metal complex with Fe(II), and successfully applied to extract and determine Fe(II) ion from various local pharmaceutical samples by reacting with the new reagent N-methyl-N-(((4-chlorophenyl)diazenyl)thio)carbonothioy)aniline by easy, low cost, and simple CPE coupling with UV-vis spectrophotometric method.

**EXPERIMENTAL SECTION**

**Materials**

The chemicals used in this project were obtained from Sigma, BDH, and Fluka. In this study, extremely pure materials were utilized. N-methyl-N-(((4-chlorophenyl) diazenyl)thio)carbonothioy)aniline reagent (L) (0.01 mol/L) was prepared via dissolving 0.1609 g of reagent in 50 mL absolute ethanol. A stock solution of 1000 mg/L Fe(II) was prepared by dissolving 0.3560 g of FeCl2·4H2O in 100 mL deionized water. A 0.1 mol/L NaOH was prepared by dissolving 0.4000 g in 100 mL. Also, 0.1 mol/L of 37% v/v HCl solution was prepared in 0.83 mL of 100 mL deionized water. Surfactants (20% v/v) of Triton X-100 and Triton X-114, and surfactants (1% w/v) of sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were prepared by taking 5.00 mL and 0.2500 g from each and diluting by deionized water in 25 mL. The following salts out were also prepared by dissolving 0.1 mol/L of NaCl, KCl, NaF, Na2CO3, Na2SO4, (NH4)2SO4, and NH4Cl weighted 0.1461, 0.1863, 0.1049, 0.2649, 0.3551, 0.3303, and 0.1337 g, in 25 mL of deionized water, respectively. Stock solution of interferences (1000 mg/L) was prepared by dissolving 0.1598, 0.4577, 0.3112, 0.3104, 0.2683, 0.3602, 0.1574, and 0.1630 g from the following Pb(NO3)2, Cr(NO3)3, Ni(NO3)2, Co(NO3)2, CuCl2·2H2O, MnCl2·4H2O, AgNO3, and CdCl2, respectively, in deionized water and diluted to 100 mL.

**Instrumentation**

A potassium bromide disc (4000–400 cm−1) was utilized to record infrared spectra using an FTIR Shimadzu model 8400 equipment. 1H-NMR spectra were recorded using a BAMX 400 MHz spectrometer in DMSO-d6. Mass spectra were recorded using the mass spectrophotometer, Shimadzu LCMS 2010. A Shimadzu double beam 1800 UV was used to record UV-vis spectra, whereas CHNS was performed on an EuroEA Elemental Analyses. Estimating the melting points of compounds was done using the Gallen Kamp melting point. The molar conductivity for the iron(II) complex was measured using the Digital Conductivity Series. Magnetic susceptibility balance (Johnson Mathey) was used to calculate the magnetic susceptibility of iron(II) complex [FeL2]Cl2. Separating the aqueous phase from the rich phase was performed by the German Hettich centrifuge, model D-78532, and vortex mixer 945307 (USA). For all CPE studies, a water bath model BS-11 NO. K109.125 Korea was employed. WTW model 720 pH meter was used with a combined glass electrode and FAAS AA-6300 Shimadzu.

**Procedure**

**Synthesis of sodium N-methyl-N-phenyl dithiocarbamate**

First, 2 g of NaOH (0.05 mol) dissolved in a few deionized water in ice-cold temperature below 4 ºC, after that 3.02 g of CS2 (0.05 mol) and 5.44 mL of N-methylaniline (0.05 mol) was added. The mixture was stirred for 2 h. A yellowish-white solid product was formed, which was separated, filtered, washed with ether, and finally recrystallized from warm acetone [19]. The white solid product was dried under vacuum over CaCl2 giving 1.68 g (yield = 84%), m.p. > 300 ºC. CHNS: Found (calc.) %: C 46.80 (46.82), H 3.91 (3.92), N 6.80 (6.82), and S 31.22 (31.24).
**Synthesis of N-methyl-N-(((4-chlorophenyl)diazzenyl)thio)carbonothioyl) aniline (L)**

The p-chloroaniline weighted 0.9185 g (0.0072 mol) was dissolved in 10:10 mL of HCl/H2O and the mixture was vigorously stirred while it cooled to a temperature of 0 to 5 °C. To this solution, 0.5000 g of NaNO2 (0.0072 mol) dissolved in 3.00 mL of deionized water was added drop by drop and continued stirring in the ice bath at 0 to 5 °C. After that, a black solution was noted after 30 min of stirring. The black solution was added drop by drop to the smallest amount of the aqueous solution containing 1.5000 g of sodium N-methyl-N-phenyldithiocarbamate (0.0072 mol), and the mixture was stirred for 1 h at 0 to 5 °C. The resulting brown precipitate was filtered and washed under cold water. Yield 76%, m.p. 123 °C. CHNS: Found (calc.) %: C 52.25 (52.17), H 3.76 (3.66), N 13.06 (13.002), and S 19.92 (19.80). Scheme 1 illustrates the procedures for reagent preparation.

**Synthesis iron(II) complex**

To the 5 mL ethanolic solution of the FeCl2·4H2O (1 mol), an ethanolic solution of the reagent L (2 mol) was added, and the mixture was refluxed for 1 h. The yellowish-green formed precipitate was filtered, and washed with ethanol, and dried under vacuum. Yield 64%, m.p. 133 °C.

**Sample preparation**

The procedure for selecting thirteen tablets from three different manufacturers was applied for commercially available tablets. Each brand's tablets were weighed, then mortar-crushed and ground into a fine powder. A 1000 μg/mL solution for Fe(II) was prepared by weighing an amount equal to the active component of each pharmaceutical preparation. In deionized water, the powder was dissolved. After that, it was filtered to get rid of any undissolved residue that might have impacted the response. The filtrate was completed to 100 mL. Further dilution was necessary to allocate the concentration within the linearity of the calibration graph. Table 1 shows samples of Fe(II).

**CPE procedure**

According to the CPE procedure, aliquot of 10 mL of 10 μg/mL of iron(II) was added to 0.5 mL of 0.01 mol/L of reagent, 0.5 mL of 20% v/v Triton X-114 was then added, in a vortex mixer thoroughly mixed the solution. Place the tube in the 80 °C water bath for 10 min. Centrifugation at 4,000 rpm for 5 min was used to separate the phases. The aqueous phase was simply removed by decantation. The colored product's surfactant-rich phase was dissolved in 0.5 mL of ethanol, and the product's absorbance was measured at λ_max 635 nm in comparison to a blank reagent made under

---

**Table 1. Pharmaceutical samples of Fe(II)**

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Pharmaceutical drug company and claimed content of active ingredient</th>
<th>Average wt (g) of tablet (n = 13)</th>
<th>wt of sample (g) of active ingredient to obtain 1000 ppm in 100 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>Ferrous Sulfate, Accord, Barnstaple, 65 mg</td>
<td>0.4423</td>
<td>0.6804</td>
</tr>
<tr>
<td>B2</td>
<td>FeroFix, Pioneer, Iraq, 47 mg</td>
<td>0.3460</td>
<td>0.7361</td>
</tr>
<tr>
<td>B3</td>
<td>Iron, Mary Care, Holland, 49 mg</td>
<td>1.2867</td>
<td>2.6259</td>
</tr>
</tbody>
</table>

---

Ivan Malik Shaker et al.
optimum conditions. The proposed mechanism of Fe(II)-L complex separation by CPE is illustrated in Scheme 2. Some equations used in the extraction are shown in Eq. (1-5).

Distribution ratio (D)
\[
D = \frac{\text{concentration of analyte in rich phase}}{\text{concentration of analyte in aqueous phase}}
\]

Extraction percent (E%)
\[
E\% = \frac{D}{1+D} \times 100
\]

Recovery (%)
\[
\text{Recovery} = \frac{\text{Measured value}}{\text{Actual value}} \times 100
\]

Relative error percentage (Ere%)
\[
\text{Ere\%} = \frac{\text{Absolute error}}{\text{Actual value}} \times 100
\]

Absolute error
\[
\text{Absolute error} = \text{Actual value} - \text{Measure value}
\]

## RESULTS AND DISCUSSION

### Characterization of New Synthetic Reagent

**FTIR spectroscopy**

The prepared L reagent contains importance groups such as NCS$_2$ and -N=N-. The absorption band belonging to C–N of NCS$_2$ appeared at 1485 cm$^{-1}$ [20]. The ν(CS$_2$ asym.) and ν(CS$_2$ sym.) observed at 1006 and 1091 cm$^{-1}$, respectively [21]. Furthermore, the peaks at 1589 and 787 cm$^{-1}$ were ascribed to the ν(-N=N-) and νasym(Cl) stretching vibrations respectively [5,22]. When complexing with the Fe(II) ion, the absorption bands of these groups changed. Thioureide ν(C–N) band was detected at 1465 cm$^{-1}$ [23], whereas the ν(C–S) stretching

![Scheme 2. Proposal mechanism of Fe(II)-L complex separation by CPE method](image-url)
showed at 1168 cm$^{-1}$. The azo functional group stretched at 1590 cm$^{-1}$. The C=S characteristic stretching frequency vibrated at 1091 cm$^{-1}$ [20]. Moreover, additional band of have been noted at 497 cm$^{-1}$ related to ν(Fe–S).

**Mass, $^1$H-NMR, and $^{13}$C-NMR spectroscopy**

The mass spectra are used to measure the mass-to-charge ratio ($m/z$) of the reagent L and its complex. The experimental parent molecular ion peaks of the reagent and its complex at 321.5 and 770.2 $m/z$, respectively. As the most significant reagent are azo, thioureido, and thiocarbonyl coupled with the production of positive molecular ions and other positively charged fractions, because of their significant relative abundance, several fractionation paths were used for the reagent and complex [24]. The mass spectra of prepared compounds are noted in Fig. 1.

The $^1$H-NMR spectrum of L in Fig. 2 showed a singlet peak at $δ = 3.37$ ppm equal to the methyl group’s three protons in N–CH$_3$. A number of signals were seen in the $δ$ region of 7.02–7.33 ppm are assigned to N-phenyl rings protons as follows: at 7.02–7.06 ppm as a triplet peak corresponds to the aromatic proton, at 7.25–7.27 ppm as a triplet peak corresponding to the aromatic proton in both places and at 7.31–7.33 ppm as a doublet

![Mass spectrum of the (a) L and (b) Fe(II) complex](image_url)
peak corresponding to the aromatic proton in both places [5]. This indicates that the substitution took place on the sulfur atom during the reaction between the diazonium salt and sodium N-methyl-N-phenyldithiocarbamate to produce L. Several of the signals seen in the area of 7.35–7.54 ppm is assigned to azo-phenyl rings protons [25]. The coordination of L to the Fe(II) ion caused the most of proton signals (Fig. 2(a) and (b)) to change and shift during complexation. A singlet peak at 3.43 ppm belongs of the methyl group of N–CH₃. The numerous signals seen in the area of 7.03–7.26 ppm are assigned to the N-phenyl rings' protons [5]. Peaks at 7.38–7.61 ppm is attributed to azo-chloro benzene protons [26-27].

The ¹³C-NMR spectra of L and its complex with Fe(II) in Fig. 3(a), the thiocarbonyl carbon (C=S) signal at site 193.94 ppm in a weaker field, which is a representation of the DTC substituent in the ¹³C-NMR spectrum [19]. Signals in the range of 39.37–40.62 ppm attributed to methyl carbon attached to the nitrogen atom [28]. Singlet peaks of the ligand were shown at
120.05, 125.75, 127.44, 129.36, 135.52, 140.01, and 157.60 ppm which belong to carbons of aromatic rings. The $^{13}$C-NMR spectrum of the complex in Fig. 3(b), was recorded in DMSO-$d_6$, in comparison to the free ligand, 40 ppm up field shifts are shown for all of the complexes for NCS$_2$ carbon. This further supports the coordination by CS$_2$.

**Absorption spectra**

The electronic spectra for L and its complex are shown in Fig. 4, the spectrum of the ligand exhibited band at 411 nm for $n\rightarrow\pi^*$ transition NCS$_2$ and –N=N– group. While the complex has $\lambda_{\text{max}}$ 635 nm corresponding to charge transition [29-30].

**Enhancing the Experimental Conditions**

In order to improve the method's sensitivity and to promote the extraction effectiveness for CPE, the most significant parameters effects are optimized using the traditional optimization technique. The parameters including pH effect, order of addition, volume of surfactant effect, reagent concentration, surfactant types, temperature effect, time of heat, salt out, and interfering effect.

![Fig 3. $^{13}$C-NMR spectrum of the (a) L and (b) Fe(II) complex](image-url)
Ivan Malik Shaker et al.

**Fig 4.** Absorption spectra for L and Fe(II) complex

**Order of addition**

The most important factors studied are the addition order. A change of order was of iron complex formation by using (10 μg/mL, 10 mL) of Fe(II) and reagent (0.01 mol/L, 0.5 mL) with 0.5 mL of 20% v/v Triton X-114. then heated for 5 min temperature of 75–80 °C then separated by using a centrifuge, then add 0.5 mL of ethanol to the rich phase for solubility after that measured by UV-vis the better absorption outcome as the sequence addition L-Fe(II)-Triton X-114 were chosen.

**Reagent concentration and pH effect**

This parameter plays a critical role in the formation of metal complex and subsequent extraction, and it has been an important factor for CPE. In this work, the pH impact was studied within a pH range of 1–10 by using pH solutions of 0.1 mol/L HCl and 0.1 mol/L NaOH, and the outcomes were shown in Fig. 5. At pH above 5, the absorbance reduces due to the formation of hydroxide of iron ion.

The concentration of the ligand is one of the main elements influencing the effectiveness of extraction. Various concentrations of the reagent in the extent $0.8 \times 10^{-3}$ to $4.5 \times 10^{-3}$ mol/L were utilized. The outcomes are shown in Fig. 6. The better results are $3.5 \times 10^{-3}$ mol/L of reagent.

**Surfactant kind and Triton X-114 concentration effect**

The type of surfactant utilizes depends on the CPE efficacy. In this study, using specific concentrations of various types of surfactants, like Triton X-100, Triton X-114, CTAB, and SDS. When utilizing separate surfactant kinds, it was found that utilizing Triton X-114 produced the best results, as shown in Fig. 7(a). One of the non-ionic surfactants used frequently in CPE is Triton X-114. Because it has benefits such as high commercial purity, low toxicity, low cost, high density of the surfactant-rich phase enabling the phase separation by centrifugation,

**Fig 5.** Effect of the pH for Fe(II) complex

**Fig 6.** Effect of concentration reagent (L) on Fe(II) complex: (a) variation of reagent concentration effect and (b) distribution ratio estimation
Fig 7. Surfactant effect of Fe(II) complex: (a) type of surfactant, (b) variation volume of surfactant, (c) distribution ratio, and (d) extraction percentage

and comparatively low cloud point temperature. The impact of non-ionic surfactant amount of 20% v/v of Triton X-114 of 0.8–2.0 mL. When the amount of Triton X-114 was increased, it was found that the complexes' absorbance increased until 1.2 mL, as shown in Fig. 7(b–d).

**Incubation time and temperature effect**

The effect of the equilibrium temperature is studied because they are crucial for the successful completion of the reaction and the efficient separation of the phases. The temperature between 50 and 85 °C was examined. The optimal temperature for all later measurements was chosen at 80 °C as shown in Fig. 8(a). An investigation of the incubation time between 5 and 30 min was conducted, and the analytical signal was entirely dependent on the incubation time. Incubation time of 10 min was chosen as an appropriate amount of time for the later measurements, as shown in Fig. 8(b).

**Salt out and interference effect**

The extraction process may be impacted by the solution's addition of salt. The impact salt was studied on CPE by adding 0.5 mL of 0.1 mol/L of KCl, NaCl, NaF, NH₄Cl, (NH₄)₂SO₄, Na₂CO₃, and Na₂SO₄ to the solution after completion of the method product acquired show. All salts were seen to slightly decrease, as shown in Table 2.

Interference's impact expected was studied to know the approach selectivity under study by adding 0.5 mL from each interference of Ni(NO₃)₂, Pb(NO₃)₂, CuCl₂·2H₂O, Cr(NO₃)₃, Co(NO₃), MnCl₂·4H₂O, CdCl₂, and AgNO₃ (0.1 mol/L) with 10 mL of 10 ppm Fe(II). Noted that all interference interferes with metal and causes an increase in absorption, as shown in Table 3.
**Stoichiometry of the complex**

Two approaches were used to determine the complexes' stoichiometry. First, by using the Jobs method, solutions of $1 \times 10^{-3}$ mol/L reagent and $1 \times 10^{-3}$ mol/L of Fe(II) solution were prepared and mixed in continuous variation then measuring the solution by UV-vis spectrophotometer at 635 nm to be 1:2, Fig. 9(a) shows Job’s plot of the complex. Second by using mole ratio method, whereas in this method a solution of $1 \times 10^{-3}$ mol/L reagent and $1 \times 10^{-3}$ mol/L of Fe(II) solution were prepared, the size of Fe(II) solution was steady and the reagent size changed, or the opposite, then measured using a UV-vis spectrophotometer at 635 nm after being diluted to 10 mL of ethanol. The stoichiometry of the compound was determined to be 1:2. Fig. 9(b) shows the mole ratio plot of the complex.

---

**Table 2. Effect of salt out for Fe(II) complex**

<table>
<thead>
<tr>
<th>Salt out</th>
<th>Abs filtrate</th>
<th>D</th>
<th>E%</th>
<th>Recovery%</th>
<th>Ere%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs. without</td>
<td>0.010</td>
<td>24.900</td>
<td>96.139</td>
<td>17.351</td>
<td>82.648</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.013</td>
<td>8.846</td>
<td>89.843</td>
<td>46.184</td>
<td>53.815</td>
</tr>
<tr>
<td>KCl</td>
<td>0.011</td>
<td>18.363</td>
<td>94.835</td>
<td>175.652</td>
<td>75.652</td>
</tr>
<tr>
<td>NaF</td>
<td>0.007</td>
<td>13.285</td>
<td>93.000</td>
<td>46.039</td>
<td>53.960</td>
</tr>
<tr>
<td>Na₃CO₃</td>
<td>0.008</td>
<td>16.875</td>
<td>94.405</td>
<td>145.161</td>
<td>45.161</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.012</td>
<td>8.416</td>
<td>89.380</td>
<td>74.814</td>
<td>25.185</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>0.011</td>
<td>13.636</td>
<td>93.167</td>
<td>148.514</td>
<td>48.514</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>0.013</td>
<td>9.000</td>
<td>90.000</td>
<td>78.000</td>
<td>22.000</td>
</tr>
</tbody>
</table>

**Table 3. Effect of interference Fe(II)complex**

<table>
<thead>
<tr>
<th>Interfering ion</th>
<th>Abs filtrate</th>
<th>Abs rich phase</th>
<th>Recovery%</th>
<th>Ere%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs. without</td>
<td>0.010</td>
<td>0.249</td>
<td>18.568</td>
<td>81.431</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
<td>0.011</td>
<td>0.122</td>
<td>48.995</td>
<td>51.004</td>
</tr>
<tr>
<td>Cr(NO₃)₃</td>
<td>0.024</td>
<td>0.116</td>
<td>95.081</td>
<td>4.918</td>
</tr>
<tr>
<td>Ni(NO₃)₂</td>
<td>0.009</td>
<td>0.083</td>
<td>71.551</td>
<td>28.448</td>
</tr>
<tr>
<td>CdCl₂</td>
<td>0.010</td>
<td>0.112</td>
<td>134.939</td>
<td>34.939</td>
</tr>
<tr>
<td>Co(NO₃)₂</td>
<td>0.010</td>
<td>0.126</td>
<td>112.500</td>
<td>12.500</td>
</tr>
<tr>
<td>CuCl₂·2H₂O</td>
<td>0.044</td>
<td>0.291</td>
<td>230.952</td>
<td>130.952</td>
</tr>
<tr>
<td>MnCl₂·4H₂O</td>
<td>0.012</td>
<td>0.090</td>
<td>30.927</td>
<td>69.072</td>
</tr>
<tr>
<td>Ag NO₃</td>
<td>0.025</td>
<td>0.215</td>
<td>238.888</td>
<td>138.889</td>
</tr>
</tbody>
</table>
Fig 9. Stoichiometry of Fe(II) complex (a) Jobs method and (b) mole ratio method

**Calibration curve**

Under the predetermined optimal circumstances, by adjusting the metal ion concentration at range from 0.2–10 μg/mL, the Fe(II) calibration curve was assessed. It was shown that absorption rises with increasing concentration as it is a linear line. Absorbance and concentration were plotted in the calibration curve. Table 4 shows the results of the linear regression equation, linearity, slope, intercept, relative standard deviation (RSD%), correlation coefficient (r), coefficient of determination (r²), limit of quantification (LOQ), and limit of detection (LOD) for the estimation of Fe(II) using CPE and comparison with other published methods. It was found that the new method has high sensitivity and can be used to estimate Fe(II) in the other samples.

**Application**

After the metal study was completed of metal was studied on many medication models of drug taken from were taken and was the sampling process and the drug’s content was assessed spectrophotometric at λmax 635 nm. By utilizing the t-test and F-test to compare the results of

---

**Table 4. Comparison of the CPE-UV-vis method for estimating Fe(II) with previously published methods**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>CPE-UV-vis new method</th>
<th>CPE-UV-vis published method [31]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regression equation</td>
<td>y = 0.117x + 0.028</td>
<td>y = 0.0089x + 0.018</td>
</tr>
<tr>
<td>r</td>
<td>0.998</td>
<td>0.998</td>
</tr>
<tr>
<td>r²</td>
<td>0.996</td>
<td>0.996</td>
</tr>
<tr>
<td>Linear range (ppm)</td>
<td>0.2–1.0</td>
<td>5–112</td>
</tr>
<tr>
<td>LOD (ppm)</td>
<td>0.050</td>
<td>0.800</td>
</tr>
<tr>
<td>LOQ (ppm)</td>
<td>0.153</td>
<td>-</td>
</tr>
<tr>
<td>Slope</td>
<td>0.117</td>
<td>0.008</td>
</tr>
<tr>
<td>Intercept</td>
<td>0.028</td>
<td>0.018</td>
</tr>
<tr>
<td>RSD% (n = 5)</td>
<td>1.376</td>
<td>2.000</td>
</tr>
</tbody>
</table>

**Table 5. Statically data pair t-test for the determination of Fe(II) in pharmaceutical drugs**

<table>
<thead>
<tr>
<th>No. of sample</th>
<th>Quoted value and active ingredient</th>
<th>Practical content (conc.) mg/L</th>
<th>Xd (mg/L) New method with FAAS</th>
<th>Xd (mg/L) ± Sd</th>
<th>Paired t-test</th>
<th>Fcal</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>65 mg, (1 mg/L)</td>
<td>0.95</td>
<td>1.02</td>
<td>−0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>47 mg, (1 mg/L)</td>
<td>1.10</td>
<td>1.01</td>
<td>0.09</td>
<td>0.086 ± 0.155</td>
<td>0.967</td>
</tr>
<tr>
<td>B3</td>
<td>49 mg, (1 mg/L)</td>
<td>1.20</td>
<td>0.96</td>
<td>0.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Value of Ftab at 95% confidence level, df (3,3) = 19.00 and ttab at 95% confidence level, df = 4.303, Fcal < Ftab, non sig. difference, tcal < ttab, non sig. difference.

---

Ivan Malik Shaker et al.
the new approach with a stock FAAS method for determining Fe(II) in the sample solutions. It was found that the concentration did not match the quoted value. Therefore used the t-test and F-test, where appears that there is no significant difference between the new method and the FAAS method, as shown in Table 5.

■ CONCLUSION

Reagent L was utilized to prepare FeL complex. According to experimental data, complexes’ tetrahedral structural formula was proposed. The molar conductance values of the FeL complexes indicate a 1:2 electrolytic natures. A CPE which was ecofriendly, sensitive, and selective spectrophotometric approach was done for determining low concentration of Fe(II) using L reagent as complexing agent. The effectiveness of CPE is affected by pH at 5, 20% triton X-114, incubation time 10 min, and 80 °C of heating. The suggested method was effective, the potential advantages of the current method are time savings, reducing the quantity of reagents used as well as minimizing analyst effort. This method has been successfully applied to drugs such as Iron, FeroFix, and Ferrous Sulfate, and compared with FAAS method, there were no significant differences, and this indicates the possibility of using it as an alternative method.

■ ACKNOWLEDGMENTS

The authors would like to thank Kerbala University, Science College, Chemistry Department for financial support.

■ CONFLICT OF INTEREST

The authors do not have conflict of interest.

■ AUTHOR CONTRIBUTIONS

Ivan Malik Shaker, Ahmed Fadhil Khudhair, and Hayder Hamied Mihsen contributed to the design and implementation of the research, to the analysis of the results and to the writing of the manuscript. All authors agreed to the final version of this manuscript.

■ REFERENCES


[27] Onwudiwe, D.C., and Ajibade, P.A., 2011, Synthesis,


