Novel Cyclic Voltammetry Behavior Of 3-((Benzothiazol-2-Diazenylnaphthalene-2,7-Diol And Use It For Spectrophotometric Determination Of Iron (III )In Blood Sample

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Abstract .The azo reagent 3-((benzothiazol-2-diazenylnaphthalene-2,7-diol] was synthesized and characterized by FT-IR ,1H-NMR and 13CNMR spectral techniques. The electrochemical behavior of the azo reagent and its complex with Fe (III) has been studied at glassy carbon disk GCE electrode in different supporting electrolyte at concentration (1M) and scan rate (100mvs-1). Spectrophotometric determination of Iron (III ) is based on the formation of a 2:1 complex with above reagent. The complex has λmax at (576) nm and εmax of( 1.6451*104)L.mol-1.cm-1 . A linear correlation (0.1 – 4.0 μg. ml-1) was found between absorbance at λmax and concentration . The effect of diverse ions on the determination of Iron (III) to investigate the selectivity of the method were also studied . The stability constant of the product was (3.098*108 ) . The proposed method was successfully applied to the analysis of blood samples

Keywords: Cyclic voltammetry,3(benzothiazol-2- diazenylnaphthalen -2,7diol),Iron (III), spectroscopy.

Introduction:

Azo dyes belong to the one of the largest class of analytical reagents . Their important feature is electroactivityl ,which makes them very important reagents for the voltammetric determination of metalions (1-3). These are the largest group of organic dyes for their wide spread applications in many areas of dye- stuff industry , pharmacy and dosimetry due to the presence of azo(-N=N-) linkage (4,5) In this study , we wish to report the electrochemical behavior of this reagent and as a selective reagent in spectrophotometric determination of microamounts of Iron (III).BTHN is a tridentate via azogroup,hydroxyl group and nitrogen atom of thaizol group ; it has the following structure:
Experimental:

All chemicals used in this work were of analytical grade.

In this study the FT-IR spectra of azo compound was recorded on Schimadzu FT-IR spectrophotometer model in KBr wafer and the NMR spectra was obtained on BRUKER AV 400 AvanceIII 400MHz instrument using DMSO as solvent and reported relative to TMS as internal standard, CE440CHN/O/S Elemental Analyser was made by EAI while voltammetric experimentas were carried out using a computer – controlled electroanalysis system using ant (EZ-State by NuVant) system. A three- electrocompination system was an Ag /AgCl reference electrode, aPt wire auxiliary electrode and glassy carbone electrode as working electrode, the potential range selected was in the range(1-1.25) mV. All measurements were carried out at room temperature.

Synthesis of thiazol derivative:

2- amino Benzothiaizole(0.0066mole) 1.0000g was diazotized by dissolving it in (5ml) ethanol then (15ml) of HCl(4M) was added keeping the temperature at (0-5C°) then adding NaNO₂ solution gradually and left it about (15min) to cool well. The coupling material (2,7-dihydroxy naphthalen)(0.0066mole)(1.0650g) was dissolved in 15ml of NaOH(4M) and leave to cool well, then this solution was added to diazonium salt solution slowly drop by drop to maintain temperature (0-5C°). The mixture was allowed precipitate was filtered off and washed several times with (1:1) (alcohol:water) mixture then recrystallized from boiling ethanol and left to dry. Scheme (1).

Dark Burgundy powder, m.p 230C° Anal(calc) for C₁₇H₁₃N₃O₂S(%): C(63.48 %), H(3.42 %), N (13.07%), S(9.97%). Found(%): C(63.39 %), H (3.38 %), N (12.89 %), S (9.82 %).

Scheme (1).Synthesis of reagent (BTHN)
Reagents: Iron stock solution (1000 µg.ml⁻¹) The solution was prepared by dissolving (1.2106 g) of iron chloride in (250 ml) of deionized water.

3(benzothiazol-2-diazイン naphthalen-2,7diol(1*10⁻³M): This solution was prepared by using (0.0321 g) of reagent in (100 ml) of ethanol.

Other ions (foreign) solution: All of ions were prepared by using a suitable amount of the compound in deionized water in a calibrated flask.

Results and Discussion:

Absorption Spectra:

The reagent (BTHN) nm possess a maximum absorption at (440 nm) reacts with (FeCl₃.6H₂O) at room temperature to give a (BTHN-Fe(III) colored complex at pH 6. The absorption spectrum shows a maximum at 576 nm, whereas the reagent blank give no absorption at this wavelength (Figure 1)

![Absorption spectrum of reagent (BTHN) and Fe(BTHN) complex](image1)

Effect of pH:

The effect of pH on the absorption of the complex formed by the reaction of (BTHN) with Fe(III) was studied at different pH by using HCl or NaOH (0.05N) in the range (2-12). It was found that the chelating complex was formed at pH 6. Fig (2)

![Effect of pH on the absorption intensity of (BTHN-Fe(III) complex](image2)
Effect of (BTHN) concentration:

The effect of changing reagent concentration on the absorbance of solution keeping affixed amount of Fe(III) and pH 6 was studied. It was found that absorbance rises with increasing reagent concentration and got its maximum value on using (2) in subsequent experiment. Fig(3)

![Figure(3)](Effect of volum R3 formaitioncomlex with Fe(III) ion)

Quantification:

In order to study the range in which the colored complex adhere to Beer's law the absorbance of the complex was measured at $\lambda_{\text{max}}$ for sequence of solutions containing increasing amounts of Fe (III) at optimum conditions. The validity of Beers law, molar absorptivity and Sandals sensitivity values were estimated and are given in Table (2), showed that the method is sensitive. The proposed method showed a good linearity for the determination of Fe (III) with a good correlation coefficient (0.9959) . The relative standard deviation % (RSD) for the analysis of six replicates of Fe(III) is equal to (0.3480)showed that the method is precise and accurate, while detection limit is equal to (0.0104) .

![Figure(4)](Calibration Curve of Fe-BTHN)
Table (1) characteristics data of Fe(III)-BTHN complex

| parameter                          | Values of method         |
|------------------------------------|--------------------------|
| Beers law limits (µg.ml⁻¹)         | 0.1-4.0(µg.ml⁻¹)         |
| Molar absorptivity (L.mol⁻¹.cm⁻¹)  | 1.6451 * 10⁴             |
| LOD(µg/ml)                         | 0.0139                   |
| R.S.D %                            | 0.3480%                  |
| Correlation coefficient            | 0.9959                   |
| Sandells sensitivity µg.cm⁻²       | 0.00339                  |

Composition of complex:

In the present work, it was found that Fe(III) reacted with reagent (BTHN) in 1:2 ratio forming a complex to give intense dark green colored. The stoichiometric ratio of (BTHN) and Fe(III) was studied applying the continuous variation (Job's) and mole ratio methods (6,7) using equimolar solutions of the new ligand and Fe(III) (1*10⁻⁴). It was found that (BTHN) forms a dye coupled product with Fe(III) in the ratio 2:1 as in Figure (5) and (6).

Figure (5) continuous variation plot of the (Fe-BTHN)

Figure (6) Mole Ratio Plot of The Fe-BTHN

According to the results of the FT-IR, H-NMR, C-NMR, stoichiometric and elemental analysis the structure of complex can be suggested as the following:
Structure of (BTHN)

I.R Analysis:

The FT-IR spectra of the free ligand have a broad band about (3421-3176) cm⁻¹ which could be attributed to (-OH) stretching vibration. The shape and intensity of the band were changed that led to expect coordination was accruing in complex (Fe-BTHN), likewise the frequency corresponding to (N=N) at (1560) cm⁻¹ was shifted in complex which led to predict the chelating behavior. The bands at frequency (1651-1593) cm⁻¹ also changed as well as the band at (1645.72-1415.75) cm⁻¹ which corresponding with (C=N=N-C) and (C=N-N=C) were shifted (8.9). The FT-IR spectra of Iron complex also shows additional bands in (491.85) cm⁻¹ which is due to the formation of (M-O).

Table (2) The important IR bands of the (BTHN)

| Compound | OHν- | ν (C=N) and C=O in hydrazo tautomer | N=Nν- | C=Cν- | C-H)Ar |
|----------|------|-------------------------------------|-------|-------|--------|
| BTHN     | 3421m| 1651                               | 1560  | 1529  | 2927   |
| Fe-BTHN  | 3414 | 1604                               | 1554.63 | 157.981 | ---    |

Figure (7) The FT-IR Spectrum of the dye (BTHN)
The FT-IR Spectrum of (BTHN-Fe(III))

1H-NMR data of BTHN and its complex with Iron(III):
The 1H-NMR and 13C-NMR spectra of the prepared azo compound was made ligand in DMSO solution with tetra methylsaline as an internal standard indications the following signals as in Table(3) and Table(4).

Table (3) 1H-NMR data of BTHN and its complex with Iron (III)

| compound     | C-OHAr | CH-ar-H naphthalene | CH benzothaizol | CH3 of DMSO |
|--------------|--------|---------------------|-----------------|-------------|
| BTHN         | 10.58  | -----               | 6.93-6.184      | 7.84        | 2.5         |
| Fe-BTHN      | 10.2   | 3.4                 | 7.7-6.8         | 7.32-7.75   | 2.5         |

Table (4) 13C-NMR data of BTHN

| compound     | C-N benzothaizol | C-OH naphthalene | C-H benzothaizol | C-H naphthalene | C-N naphthalene |
|--------------|------------------|------------------|------------------|-----------------|-----------------|
| BTHN         | 160              | 156.3            | 129              | 115             | 107.7           |

The H1-NMR spectrum of azo compound (BTHN)
Interferences

The effect of different ions in the determination of Iron (III) was studied. Fe(III) can be determined in presence of 10 or more fold excess of cation and the interference via the various ions were removed by using suitable masking agent Table(5)
Table (5): Interference of ions and removed them by masking agent

| No | Foreign ions | Conc. ppm | Error% | Masking agent | Error% |
|----|--------------|-----------|--------|---------------|--------|
| 1  | Cu$^{2+}$    | 10        | 58.3   | (1ml) NaH$_2$PO$_4$ | 0.65   |
| 2  | Cd$^{2+}$    | 10        | -5.73  | (1ml) NaH$_2$PO$_4$ | 0.32   |
| 3  | Sn$^{2+}$    | 10        | -10.56 | (0.5) Thiourea   | 0.35   |
| 4  | Ni$^{2+}$    | 10        | -3.14  | (0.5) Oxalic acid | 0.22   |
| 5  | Sn$^{2+}$    | 10        | -9.43  | (0.5) Thiourea   | -0.15  |
| 6  | Cs$^{+}$     | 10        | -1.575 | ----            | ----   |
| 7  | Zn$^{2+}$    | 10        | -39.77 | (0.5) Formaldehyde | 2.10   |
| 8  | Pb$^{2+}$    | 10        | -21.79 | (0.5) Oxalic acid | 1.25   |
| 9  | Mn$^{2+}$    | 10        | -8.53  | (0.5) Formaldehyde | 0.75   |
| 10 | Hg$^{2+}$    | 10        | -14.28 | (0.5) Thiourea   | 0.65   |
| 11 | Ag$^{+}$     | 10        | 1.5    | ----            | ----   |

Estimation of Iron(III) in the blood samples taken from patients with diabetes and adults:

After collecting blood samples in tubes made of polyethylene saves at (-20 C°) temperature. First transferred to baker, a concentrated Nitric acid (10 ml) was added and heating quietly, when the reaction start to be activity, sample solution was removed and left to cool well. Then, (1ml) of concentrated H$_2$SO$_4$ was added. Next, (1.5ml) of 1% KMnO$_4$ was added also and mixed well. After this (1ml) of Sodium azid (NaN$_3$) (2.5%) and (0.5 ml) of 70%HClO$_4$ were added with heating under 70 C° for 30 min to remove any excess of NaN$_3$. Finally the solution was left to cool then neutralization with dilute Ammonium hydroxide (NH$_4$OH), then the solution was diluted to(100ml) with deionized water. All samples were ready for UV-Visible and atomic absorption spectrometric analysis.(10)

Table (6): Fe(III) levels in blood Sample

| Type of blood | Amount found by Atomic Absorption(µg.ml$^{-1}$) | Amount found by our spectrophotometric method(µg.ml$^{-1}$) |
|---------------|-----------------------------------------------|----------------------------------------------------------|
| Normal adult blood(male) | 0.36                                           | 0.3156                                                  |
| Diabetes patient blood(male) | 0.43                                           | 0.3911                                                  |

Electrochemical behavior of azo dye(BTHN)and redox mechanism in aqueous solution

The cyclic voltammograms of investigated azo dyes shown one to three irreversible cathodic peaks (11,12). The number of peaks depends on pH and nature of compounds. The peaks observed are due to the reduction of azo –N=N– center. The reduction mechanism includes the formation of hydrazo derivatives followed by the cleavage of the –N=N- bond and the final formation of amines (13,14) according to the following

\[
-N=N- +2H^+ +2e^- \rightarrow -NH=NH- \quad (1)
\]

\[
-NH=NH- +2H^+ +2e^- \rightarrow 2(-NH_2-) \quad (2)
\]

Different supporting electrolyte was be used with the reagent(BTHN) at GCE with scan rate (0.1Vs$^{-1}$) for all cyclic voltammograms. All voltammograms are shows reduction peak of azo group (-N=N-) at potential ranged (-500mv –750mv). The choice of the better supporting electrolyte depends on the higher current for oxidation peak and clarity of peak.

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For reagent (BTHN) was proposed that the best supporting electrolyte is (KCl), current was highest between other electrolytes, cyclic voltammogram shows irreversible electrochemical system in which the electron transfer rates are significantly less than the rate of mass transport and the reduction in two steps, the first reduction attributed to azo group giving a hydrazo derivative, second reduction peak to breaks N-N linkage to form two primary amine molecules. All current peak ratio shows irreversibility of electrochemical system at different electrolyte due to the Ipc/Ipa≠1, the deviation from number one due to the chemical reaction that arises subsequent transmission electron, such interactions can be complex, involving dissociation and isomerization\(^{(15)}\)

| R3 | Supporting Electrolyte | Ia₁ | Ea₁ | Ia₂ | Ea₂ | Ia₃ | Ea₃ | -Ic₁ | Ec₁ | Ec₂ | Ec₃ | Ec₃ |
|----|------------------------|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|
| 1  | KCl                    | 14.5| 461 | 5.38| 246 | --- | --- | 22.6 | 510 | 27.3 | 701 |
| 2  | KClO₃                  | 5.31| 250 | -11.8| 679 | --- | --- | 23.0 | 497 | --- | --- |
| 3  | K₂HPO₄                 | 7.95| 266 | 3.64| 113 | --- | --- | 21.4 | 701 | --- | --- |
| 4  | KNO₃                   | 7.50| 66.5| 3.41| 276 | --- | --- | 6.59 | 159 | 24.1 | 688 |
| 5  | K₂SO₄                  | 8.41| 465 | 5.45| 220 | -6.59| 677 | 5.68 | 192 | 23.9 | 599 |
| 6  | NaCl                   | 9.76| 497 | 6.19| 132 | 3.88 | 335 | 5.77 | 146 | 21.3 | 580 |
| 7  | NaH₂PO₄                | 9.62| 699 | 6.15| 89.6| --- | --- | 5.19 | 163 | 23.5 | 675 |
| 8  | Na₂HPO₄                | 9.72| 78.9| --- | --- | --- | --- | 23.1 | 596 | --- | --- |
| 9  | TBABr                  | No res. |     |     |     |     |     |     |     |     |
| 10 | B.R                    | No res. |     |     |     |     |     |     |     |     |

Enhancement in current of peak follows the following sequence:

KCl>NaCl>Na₂HPO₄>NaH₂PO₄>K₂SO₄K₂HPO₄>KNO₃>KClO₃

Figure (13) Effects of supporting electrolyte on the anodic peak current of reagent (BTHN)
Table (8) Current–Potential data for (BTHN) at different supporting electrolyte (1M) and scan rate (0.1 Vs⁻¹)

| Supporting electrolyte | Ea¹ | -Ec¹ | Ia | -Ic | ∆E | E½ | Ia/Ic |
|------------------------|-----|------|----|-----|-----|-----|------|
| 1 KCl                  | 461 | 14.5 | 510 | 22.6 | 49  | -24.5 | 0.641 |
| 2 KClO₃               | -250 | 497 | 5.31 | 23.0 | 248 | 373.5 | 0.230 |
| 3 KNO₃               | 66.5 | 159 | 7.50 | 6.59 | 225.5 | -46.25 | 1.138 |
| 4 K₂HPO₄         | 266 | 701 | 7.95 | 21.4 | 435 | -217.5 | 0.371 |
| 5 NaCl             | 497 | 146 | 9.76 | 5.77 | 643 | 175.5 | 1.691 |
| 6 Na₂HPO₄        | 78.9 | 596 | 596 | 23.1 | 674.9 | -258.55 | 0.420 |
| 7 NaH₂PO₄       | 699 | 163 | 9.62 | 5.19 | 862 | 268 | 1.85 |

Fig (14) Cyclic voltammogram of (BTHN) in supporting electrolyte 1M of KCl at scan rate 0.1Vs⁻¹

Fig (15) Cyclic voltammogram of (BTHN) in supporting electrolyte 1M of KClO₃ at scan rate 0.1Vs⁻¹

Fig (16) Cyclic voltammogram of (BTHN) in supporting electrolyte 1M of K₂HPO₄ at scan rate 0.1 V s⁻¹

Fig (17) Cyclic voltammogram of (BTHN) in supporting electrolyte 1M of KNO₃ at scan rate 0.1 V s⁻¹

Fig (18) Cyclic voltammogram of (BTHN) in supporting electrolyte of K₂SO₄ at scan rate 0.1Vs⁻¹

Fig (19) Cyclic voltammogram of (BTHN) in supporting electrolyte of Na₂HPO₄ at scan rate 0.1 V s⁻¹
Redox behavior of [Fe(III)-BTHN] complex:

Electrochemical properties of (BTHN) in the presence of Fe(III) was also studied in different electrolytes with concentration (1M) by voltammetry. Cyclic voltammograms shows clear redox peaks in three supporting electrolyte; (KNO₃, K₂HPO₄, NaH₂PO₄) that is indicated that all of them were appropriate to study electrochemical behavior of [Fe(III)-BTHN] complex. However in this work NaH₂PO₄ was selected as a suitable electrolyte due to its clarity of redox peaks also high current and simplisity of voltammogram which involve one redox peak of complex, Fig(4.74) and Table(4.18),when the CV of complex was compared with blank in the same electrolyte.,high shifting was observed in all value of current and potential, $E_{pa1}$ was suffered negative shifting from 699 mv towards 63.2 mv, while $E_{pc1}$...
was shifted from 163 to (2.94), so these values can be attributed to redox of Iron(III) to Iron(II) in one step. When the scan is reversed, oxidation was attributed to oxidation of Fe$^{2+}$ to Fe$^{3+}$.

It was observed that $\Delta E_{pI}$ values equal to (66.14mv), ratio of anodic to cathodic peak currents ($I_{pa}/I_{pc} \approx 1$) corresponds to one electron transfer process also. The difference in the value of ($E_{pc} - E_{pa}$) which is near to the value required for a reversible process (59 mv) indicating that, reduction of Iron(III) to Iron (II) complex at silver electrode is reversible character (16).

### Table 9

| Supporting Electrolyte | $I_{a_1}$ μA | $E_{a_1}$ mv | $I_{a_2}$ μA | $E_{a_2}$ mv | $I_{a_3}$ μA | $E_{a_3}$ mv | $-I_{c_1}$ μA | $E_{c_1}$ mv | $I_{c_2}$ μA | $E_{c_2}$ mv |
|------------------------|---------------|--------------|---------------|--------------|---------------|--------------|---------------|--------------|---------------|--------------|
| KCl                    | 4.06          | -100         | --            | --           | --            | --           | 3.53          | 38.2         | --            | --           |
| KClO$_3$               | 8.74          | 404          | --            | --           | --            | --           | 8.39          | 202          | --            | --           |
| KNO$_3$                | 13.9          | 773          | 8.99          | 543          | 12.1          | 62.1         | 8.32          | 14.5         | 9.58          | 241          |
| K$_2$HPO$_4$           | 7.59          | 647          | 10.2          | 162          | --            | --           | 6.68          | 53.5         | 7.38          | 155          |
| K$_2$SO$_4$            | 5.66          | 71.7         | --            | --           | --            | --           | 4.13          | 90.2         | 13.9          | 511          |
| NaH$_2$PO$_4$          | 11.7          | 63.2         | --            | --           | --            | --           | 8.81          | 2.94         | --            | --           |
| Na$_2$HPO$_4$          | 29.2          | 71.6         | 23.5          | 562          | --            | --           | 22.4          | 860          | --            | --           |
| NaCl                   | 5.07          | -155         | --            | --           | --            | --           | 5.84          | 137          | 12.7          | 441          |

Enhancement in current of peak follows the following sequence:

Na$_2$HPO$_4$ > KNO$_3$ > NaH$_2$PO$_4$ > KClO$_3$ > K$_2$HPO$_4$ > K$_2$SO$_4$ > NaCl > KCl

**Figure (22)** Enhancement of current of [Fe(III)-(BTHN)$_2$] complex in different electrolyte
Table (10) Current–Potential data for [Fe(III)-(BTHN)$_2$] at (NaH$_2$PO$_4$)(1M) as supporting electrolyte at scan rate (0.1 Vs$^{-1}$)

| compound   | $E_{a_1}$ mV | $E_{c_1}$ mV | $I_{a_1}$ $\mu$A | $-I_{c_1}$ $\mu$A | $\Delta E_{p_1}$ | $(I_{p_{a_1}}/I_{p_{c_1}})$ | $[E_{1/2}]_1$ |
|------------|--------------|--------------|-------------------|-------------------|-----------------|----------------------|----------------|
| BTHN-Fe   | 63.2         | 2.94         | 11.7              | 8.81              | 66.14           | 1.32                  | 30.13          |

Fig (23) CV for [Fe(III)-(BTHN)$_2$] complex in KCl1M

Fig (24) CV for [Fe(III)-(BTHN)$_2$] complex in KClO$_3$ 1M

Fig (25) CV for [Fe(III)-(BTHN)$_2$] complex in KNO$_3$ 1M

Fig (26) CV for [Fe(III)-(BTHN)$_2$] complex in K$_2$HPO$_4$ 1M
Conclusion:

This work employing 3-((benzothiazol-2-diazenyl)naphthalene-2,7-diol(BTHN) was successfully applied for the estimation of Iron(III) ion. Due to its sensitivity, rapidity and selectivity of the method, its application can be estimation of this ion in biological sample.

The cyclic voltammetric system of (BTHN) led to the formation of same hydrazine derivative which remains at the electrode surface according to equations:
References:

[1] G.M.G. Van den Berg, "Potentials and potentialities of cathodic stripping voltammetry of trace elements in natural waters", Analytica Chimica Acta, vol.250, no.1, pp.265-276, 1991.

[2] M.G. Paneli and A. Voulgaropoulos, "Applications of adsorptive stripping voltammetry in the determination of trace and ultratrace metals," Electroanalysis, vol.5, pp.355-373, 1993.

[3] J. Wang, J. Mahmoud, and J. Zadeii, "Simultaneous measurements of trace metals by adsorptive stripping voltammetry," Electroanalysis, vol.1, pp.229-234, 1989.

[4] A. Sakalis, D. Vanerkova, M. Holcapek and A. Voulgaropoulos, "Electrochemical treatment of a simple azodye and analysis of the degradation products using high performance liquid chromatography-diode array detection-tandem mass spectrometry", Chemosphere, 2007, 67, pp.1940-1948.

[5] A. Eriksson, "Voltammetric properties of Olsalazine Sodium and some related compounds", Acta Universitatis Upsaliensis, Comprehensive summaries of Uppsala, Dissertations from the faculty of science and technology, 638.43, ISBN 91-554-5049-0, (2001), p 1

[6] G. W. Ewing, Instrumental Methods of Chemical Analysis, Mcgraw-Hill College, USA, 5th ed. (1985).

[7] W. C. Vosburgh and G. R. Cooper, J. Am. Chem. Soc., 63, (1941) 437–442.

[8] G.D. Levitskaya, N.P. Poperechnaya, and L.O. Dubenskaya, Polarographic behavior of eriochrome red B and its complexes with rare –earth ions," Journal of Analytical Chemistry, vol. 56, no 6, (2001), pp.552-556.

[9] L. Dubenska, H. Levitska, and N. Poperechna, "Polarographic investigation of reduction process of some azo dyes and their complexes with rare –earths", Talanta, vol. 54, no 2, (2001) pp.221-231.

[10] H. M. Stahr, "Analytical methods in Toxicology ". 3rd ed. John Wiley and Sons New York 1991-75

[11] G.D. Levitskaya, N.P. Poperechnaya, and L.O. Dubenskaya, Polarographic behavior of eriochrome red B and its complexes with rare –earth ions," Journal of Analytical Chemistry, vol. 56, no 6, pp.552-556, 2001.

[12] L. Dubenska, H. Levitska, and N. Poperechna, "Polarographic investigation of reduction process of some azo dyes and their complexes with rare –earths", Talanta, vol. 54, no 2. pp.221-231, 2001

[13] G.W. Latimer, "Polarographic behavior of metal chelates of o,dihydroxyazo dyes ", Talanta, vol. 15, no.1, pp.1-14, 1968

[14] D.K. Gosser Jr., Cyclic Voltammetry : Simulation and Analysis of reaction Mechanisms , VCH Publishers, New York, NY, USA, 1993

[15] C.H. Bamford "Electrode kinetic principles and methodology" vol.23 pp.17-21, 1986.

[16] A.J. Bard and L.R. Faulkner, Electrochemical Methods, Fundamentals and Application, Wiley, New York, Ny, USA, 2nd edition, 2001.