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## The Synthesis and Identification Azo dyes Derived from Mercuried Sulfa compounds and used their as Indicator of Acid – Base.

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### ABSTRACT

Three new organomercury compounds containing azo group were prepared from sulfa compounds. The prepared compounds were synthesized and characterized by FT/IR, elemental analysis (CHN) and <sup>1</sup>H-NMR spectroscopy. According to the results of the titration of strong acid - strong base, Azo dyes have multiple uses in volumetric analysis, especially those that have different colors in acidic and basic media.

**Keywords:** Azo Dye, Acid-Base Properties, Indicator.

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## INTRODUCTION

Nowadays, synthetic azo compounds are widely used in different application fields, such as medicines, cosmetics, food, paints, plastics, shipbuilding, automobile industry, cable manufacture, etc. Azo dyes are a very important class of chemical compounds containing a heterocyclic moiety. Unlike most organic compounds, dyes possess colour because they absorb light in the visible spectrum (400–700 nm), have at least one chromophore (colour-bearing group), have a conjugated system, i.e. a structure with alternating double and single bonds, and exhibit resonance of electrons, which is a stabilizing force in organic compounds [1, 2]. Azo dyes contain one or more azo groups (-N=N-) which are linked to SP<sup>2</sup> hybridized carbon atoms, based on the number of such groups [3, 4]. The key distinction between dyes and pigments is that dyes are soluble in water and/or anorganic solvent, while pigments are insoluble in both types of liquid media. Dyes are used to colour substrates to which they have affinity. Pigments can be used to colour any polymeric substrate but by a mechanism quite different from that of dyes, in that surface only colouration is involved unless the pigment is mixed with the polymer before fiber or moulded article formation [5].

Mercury has played a rich role and has made diverse contributions to the field of bio conjugate chemistry, mercury's unique electronic properties have proved useful in designing electrochemical based thiol assay methods [6, 7]. It also forms useful amalgams with many metals, which find various applications in diverse fields. Organomercurials such as methyl mercury are more toxic than elemental mercury and other inorganic mercury compounds [8-10].

## EXPERIMENTAL

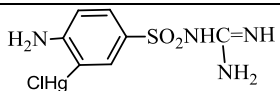
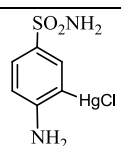
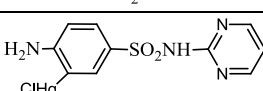
### Materials and Instruments

The following materials purchased from commercial sources: Sulfaguanidin (99%), Sulfanilamide (99%), Mercury (II) acetate (97%), absolute Ethanol (98%), Lithium Chloride (99%). <sup>1</sup>H NMR spectra were recorded on a Bruker Avance DRX 400 MHz spectrometer. DMSO-D<sub>6</sub> was used as solvent and chemical shifts recorded were internally referenced to Me<sub>4</sub>Si (0 ppm). IR spectra were obtained on a Bruker Tensor 27 FT-IR spectrophotometer. Elemental analysis was measured by Heraeus CHNS Proapparatus Elemental analyzer. Absorbance readings were obtained with a PD-303 UV-VIS-Spectrophotometer (Japan) spectrophotometer.

### Synthesis of Mercuried Amines

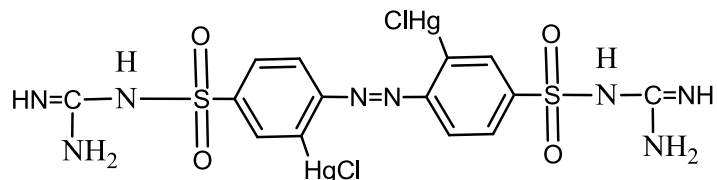
Sulfaguanidin (0.05 mole) was mixed with Mercury (II) acetate (0.05 mole) in 33 ml of absolute Ethanol. The mixture was refluxed for 6 hours with stirred, then added Lithium Chloride (0.05 mole) which solved it in 10 ml of absolute Ethanol and the mixture was refluxed for 2 hours with stirred until produce precipitate. The resulting product was filtered to give the titled compound as pale yellow solid. Other Mercuried Amines were prepared by the same procedure. As shown in Table (1).

Table 1: The Physical Properties to Prepared Mercuried Amines

Symbol	Mercuried Amines	M. Wt.	Melting Point (m.p.) °C	Color of precipitate
X1		450.29	210-215	Pale yellow
X2		408.3	205 -208	White
X3		486.37	285-290	Light Gray

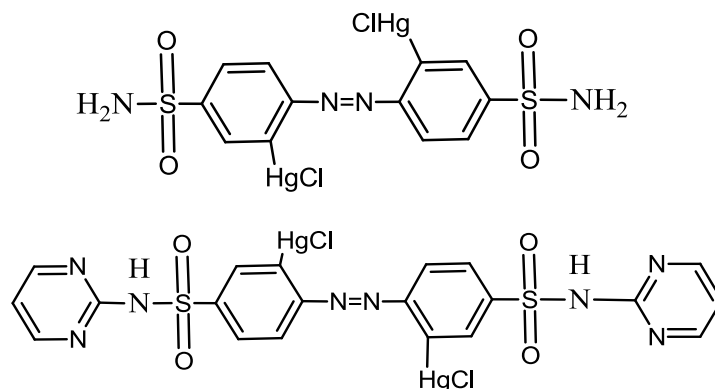
## Synthesis of symmetrically Mercuried azo compounds

1,2-Naphthoquinone- 4-methoxy (0.0005 mole) was mixed with small amount of water and added X1 (0.002 mole). The mixture was stirred for a few minutes and the resulting product was filtered, washed with water, dried and recrystallized by using H<sub>2</sub>O:DMF (2.5:10.5) to give the titled compound as reddish solid crystals in 85.2 % yield, m.p. 300-302°C, <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ = 7.62 – 7.66 (d, 2H, **CH-C-N=N-**), 8.41 – 8.45 (m, 2H, **CH-C-SO<sub>2</sub>**), 8.31 – 8.37 (m, 2H, **CH-C-HgCl**), 4.19 (s, 2H, **NH-SO<sub>2</sub>**), 8.28 (s, 4H, NH<sub>2</sub>), 7.50 (s, 2H, C=**NH**) ; FT-IR (KBr), 3172 cm<sup>-1</sup>(v NH), 3050 cm<sup>-1</sup> (v CH), 1405 cm<sup>-1</sup>(v -N=N-); Elemental Analyses calculated For C<sub>14</sub>N<sub>8</sub>H<sub>14</sub>S<sub>2</sub>O<sub>4</sub>Hg<sub>2</sub>Cl<sub>2</sub>: C 18.74; H 1.56; N 12.49; S 7.14; Found C 18.23; H 1.83; N 12.02; S 6.43. The structure of X1 is shown below:



Other symmetrically Mercuried azo compounds were synthesized by the same procedure. Where X2 was dried and recrystallized by using H<sub>2</sub>O:DMF (3.5:10) to give the titled compound as reddish solid crystals in 89.73 % yield, m.p. 300-303 °C, <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ = 8.04 – 8.09 (d, 2H, **CH-C-N=N-**), 7.71 – 7.90 (m, 2H, **CH-C-SO<sub>2</sub>**), 8.38 – 8.33 (d, 2H, **CH-C-HgCl**), 3.35 (s, 4H, NH<sub>2</sub>); FT-IR (KBr), 3362 cm<sup>-1</sup>(v NH), 3050 cm<sup>-1</sup> (v CH), 1405 cm<sup>-1</sup>(v -N=N-); Elemental Analyses calculated For C<sub>12</sub>N<sub>4</sub>H<sub>10</sub>S<sub>2</sub>O<sub>4</sub>Hg<sub>2</sub>Cl<sub>2</sub>: C 17.72; H 1.23; N 6.89; S 7.87; Found C 17.04; H 1.88; N 6.15; S 8.30. The structure of X2 is shown below:

While X3 was dried and recrystallized by using H<sub>2</sub>O:DMF (12.4:7) to give the titled compound as reddish solid crystals in 86.51 % yield, m.p. 310-312 °C, <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ = 8.03 – 8.04 (d, 2H, **CH-C-N=N-**), 8.14 – 8.18 (m, 2H, **CH-C-SO<sub>2</sub>**), 8.48 – 8.49 (d, 2H, **CH-C-HgCl**), 4.43 (s, 2H, **NH-SO<sub>2</sub>**), 8.38 – 8.42 (m, 4H, N-**CH**), 7.61 – 7.65 (d, 2H, CH=**CH**) ; FT-IR (KBr), 3250 cm<sup>-1</sup>(v NH), 3075cm<sup>-1</sup> (v CH), 1407 cm<sup>-1</sup>(v -N=N-); Elemental Analyses calculated For C<sub>20</sub>N<sub>6</sub>H<sub>14</sub>S<sub>2</sub>O<sub>4</sub>Hg<sub>2</sub>Cl<sub>2</sub>: C 24.78; H 1.44; N 11.56; S 6.60; Found C 24.10; H 1.92; N 11.02; S 6.23. The structure of X3 is shown below:



## Preparation of solutions

- Stock solutions of (1\*10<sup>-3</sup>) M azo dye was prepared by dissolving accurate weight of each dye X1, X2, X3 (0.0448, 0.0406, 0.0484) g respectively, in small amount of DMSO, and completes the volume to 50 ml absolute ethanol.
- Universal buffer solutions of pH (0.7-12).

## RESULTS AND DISCUSSION

Azo dyes have multiple uses in volumetric analysis, especially those that have different colors in acidic and basic media. This behavior is possible because each acid-base indicator exists in conjugate acid and base forms. This property is utilized to set the end point of the interaction in the quantitative estimation. The dyes (B1, B2, B3) were used as acid – base indicator in strongly acidic and basic solutions because it has a clear change in color when change the media from acidic to basic.

## Titration of strong acid - strong base

### Volumetric titration (invisible)

In this type was calibrated hydrochloric acid 0.099M as a standard solution was already calibrated with anhydrous sodium carbonate solution 0.1M with non standard solution of sodium hydroxide solution, It was found that the concentration of the base 0.101 M when presence of phenolphthalein indicator. Then compared this concentration with concentration of sodium hydroxide at the end point of the interaction in presence of several concentration of dyes (B1, B2, B3) as indicator rather than phenolphthalein, as shown in table (2) which illustrates the optimal concentration of these dyes as indicator and the relative error, where it found that the optimum concentration of the dyes (B1, B2, B3) which gave the lowest relative error were ( $2 \times 10^{-5}$  -  $6 \times 10^{-5}$  M), ( $2 \times 10^{-5}$  -  $4 \times 10^{-5}$  M), ( $3 \times 10^{-5}$  -  $8 \times 10^{-5}$  M), respectively.

**Table 2: The Suggested Concentrations Values of Dyes as Indicator**

B3		B2		B1		[D] × 10 <sup>-5</sup> M as Indicator
Relative Error	[NaOH]M at V <sub>end</sub>	Relative Error	[NaOH]M at V <sub>end</sub>	Relative Error	[NaOH] M at V <sub>end</sub>	
-3.036	0.099	0.097	0.1022	0.979	0.1031	2
-0.783	0.1013	0.195	0.1023	-0.195	0.1019	3
1.077	0.1032	-0.097	0.102	-0.783	0.1013	4
0.097	0.1022	-4.995	0.097	-0.097	0.102	5
-0.979	0.1011	-3.036	0.099	-0.979	0.1011	6
-0.195	0.1019	-5.974	0.096	-4.015	0.098	7
-0.881	0.1012	-4.015	0.098	-3.036	0.099	8

[NaOH] = 0.1021 M

### Spectrophotometric Titrations

The Breakeven point was obtained by using spectrophotometric titrations method in range of concentration ( $2 \times 10^{-5}$  -  $8 \times 10^{-5}$  M) at maximum wavelengths for each dye, as shown in tables (3), (4), (5). It can be observed, as shown in figures (1), (2), (3) that the suitable concentrations which were used and gave less relative error were ( $3 \times 10^{-5}$  -  $6 \times 10^{-5}$  M) for B1, ( $3 \times 10^{-5}$  -  $7 \times 10^{-5}$  M) for B2 and ( $3 \times 10^{-5}$  -  $5 \times 10^{-5}$  M) for B3, as shown in tables (6), (7), (8).

The values of  $A_{1/2}$  and  $V_{end}$  can calculate from following equations:

$$(A_{1/2}) = (A_{max} + A_{min}) / 2$$

$A_{1/2}$ : Absorption at end point;

$A_{max}$ : The maximum Absorption;

$A_{min}$ : The minimum Absorption;

$$V_{end} = V_{NaOH} = V \text{ at } A_{1/2}$$

$V_{end}$ : The volume of sodium hydroxide at end point of reaction;

The convergence of the concentrations of sodium hydroxide, which was obtained from the two methods invisible and spectrophotometric that means the possibility of using these dyes as indicator in titration (strong acid - strong basic).

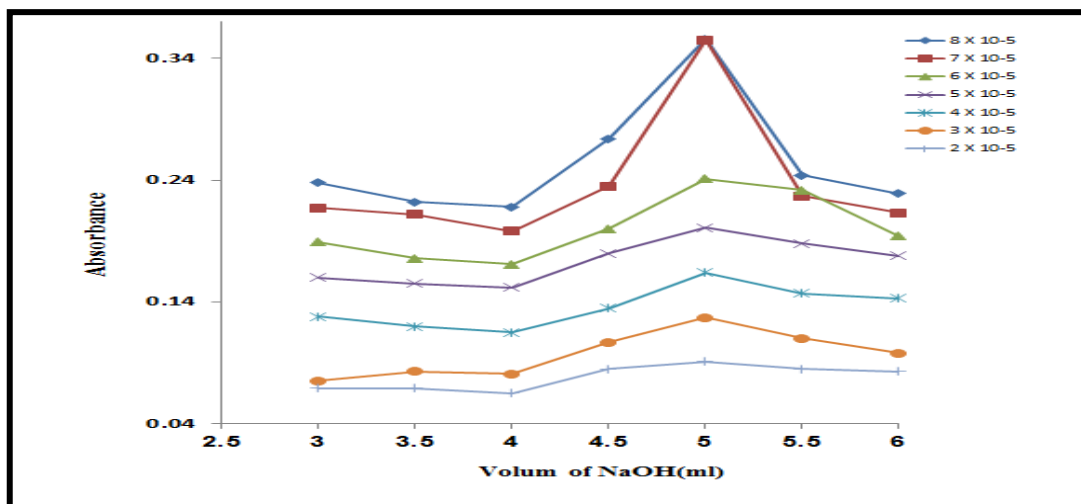


Figure 1: Curved Resulting From The Absorption Values Of The Solution That Produce From Titration 5 ML Of Standard Solution Hcl (0.097m) Versus Sodium Hydroxide Solution In The Presence B1 As Indicator

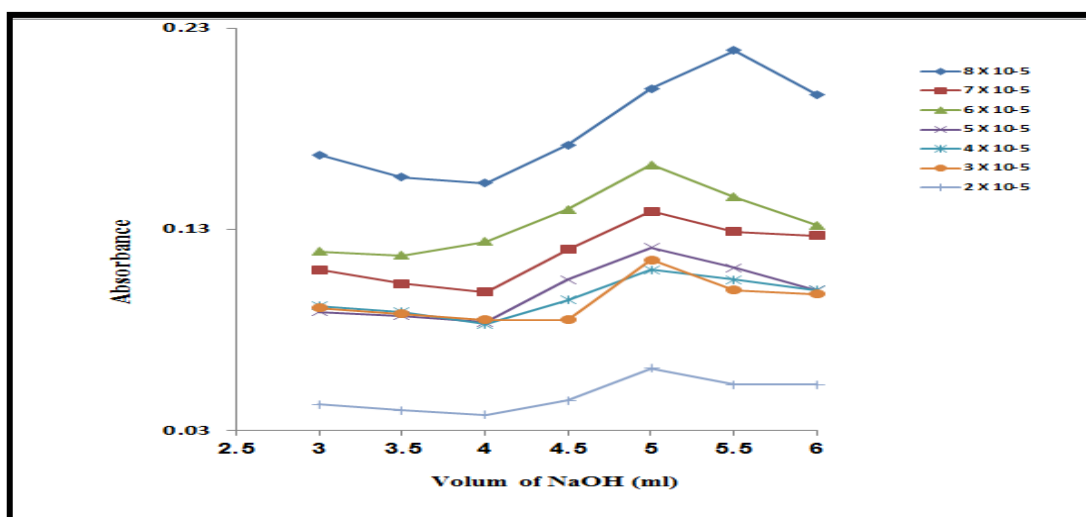


Figure 2: Curved Resulting From The Absorption Values Of The Solution That Produce From Titration 5 ML Of Standard Solution Hcl (0.097m) Versus Sodium Hydroxide Solution In The Presence B2 As Indicator

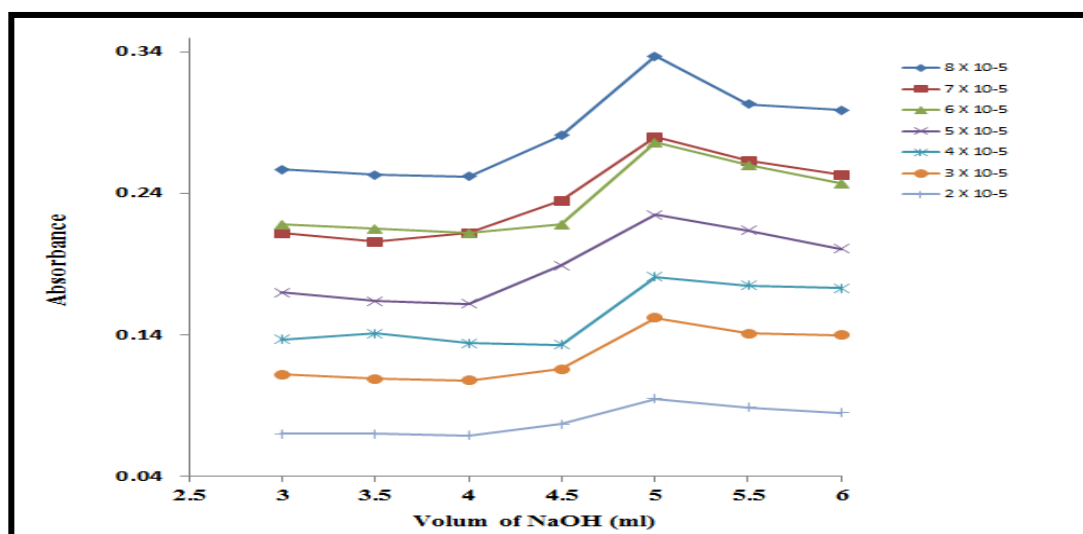


Figure 3: Curved Resulting From The Absorption Values Of The Solution That Produce From Titration 5 ML Of Standard Solution Hcl (0.097m) Versus Sodium Hydroxide Solution In The Presence B3 As Indicator

**Table 3: Absorption Values From Titration 5 ml Of Standard Solution HCl (0.097M) Versus Sodium Hydroxide Solution In The Presence B1 As Indicator**

Absorption at ( $\lambda_{max}=450$ )							Vml NaOH
$8 \times 10^{-5}$	$7 \times 10^{-5}$	$6 \times 10^{-5}$	$5 \times 10^{-5}$	$4 \times 10^{-5}$	$3 \times 10^{-5}$	$2 \times 10^{-5}$	
0.334	0.306	0.255	0.219	0.174	0.126	0.097	0.5
0.311	0.272	0.237	0.199	0.164	0.112	0.091	1
0.288	0.260	0.223	0.187	0.155	0.097	0.083	1.5
0.268	0.249	0.213	0.172	0.147	0.080	0.079	2
0.251	0.237	0.199	0.169	0.130	0.089	0.072	2.5
0.238	0.217	0.189	0.160	0.128	0.075	0.069	3
0.222	0.212	0.176	0.155	0.120	0.083	0.069	3.5
0.218	0.198	0.171	0.152	0.115	0.081	0.065	4
0.274	0.235	0.220	0.180	0.135	0.107	0.085	4.5
0.356	0.355	0.241	0.201	0.164	0.127	0.091	5
0.244	0.227	0.232	0.188	0.147	0.110	0.085	5.5
0.229	0.213	0.194	0.178	0.143	0.098	0.083	6
0.219	0.210	0.185	0.169	0.135	0.092	0.077	6.5
0.201	0.200	0.176	0.160	0.130	0.083	0.074	7
0.193	0.190	0.168	0.155	0.120	0.073	0.064	7.5
0.180	0.181	0.160	0.154	0.115	0.067	0.051	8
0.180	0.173	0.152	0.147	0.099	0.060	0.049	8.5
0.173	0.165	0.1145	0.132	0.081	0.051	0.041	9
0.164	0.152	0.145	0.122	0.079	0.042	0.033	9.5
0.160	0.141	0.141	0.109	0.070	0.036	0.025	10

**Table 4: Absorption values from titration 5 ml of standard solution HCl (0.097M) Versus Sodium hydroxide solution in the presence B2 as indicator**

Absorption at ( $\lambda_{max}=450$ )							V (ml) NaOH
$8 \times 10^{-5}$	$7 \times 10^{-5}$	$6 \times 10^{-5}$	$5 \times 10^{-5}$	$4 \times 10^{-5}$	$3 \times 10^{-5}$	$2 \times 10^{-5}$	
0.221	0.141	0.164	0.119	0.113	0.117	0.064	0.5
0.210	0.138	0.147	0.113	0.110	0.114	0.057	1
0.199	0.130	0.141	0.101	0.108	0.108	0.050	1.5
0.181	0.125	0.135	0.095	0.103	0.098	0.045	2
0.173	0.119	0.127	0.090	0.097	0.094	0.044	2.5
0.167	0.110	0.119	0.089	0.092	0.091	0.043	3
0.156	0.103	0.117	0.087	0.089	0.088	0.040	3.5
0.153	0.099	0.147	0.084	0.083	0.085	0.038	4
0.202	0.120	0.150	0.112	0.107	0.085	0.057	4.5
0.200	0.139	0.162	0.121	0.110	0.115	0.061	5
0.219	0.129	0.146	0.111	0.105	0.100	0.053	5.5
0.197	0.127	0.132	0.100	0.100	0.098	0.053	6
0.189	0.122	0.127	0.095	0.095	0.094	0.049	6.5
0.184	0.119	0.120	0.095	0.094	0.085	0.042	7
0.178	0.110	0.117	0.091	0.086	0.071	0.038	7.5
0.171	0.101	0.110	0.091	0.082	0.069	0.033	8
0.162	0.096	0.095	0.083	0.077	0.063	0.026	8.5
0.153	0.095	0.090	0.080	0.071	0.057	0.016	9
0.146	0.091	0.086	0.074	0.069	0.056	0.010	9.5
0.14	0.084	0.079	0.069	0.062	0.048	0.008	10

**Table 5: Absorption values from titration 5 ml of standard solution HCl (0.097M) Versus Sodium hydroxide solution in the presence B3 as indicator**

Absorption at ( $\lambda_{max}=450$ )							V ml NaOH
$8 \times 10^{-5}$	$7 \times 10^{-5}$	$6 \times 10^{-5}$	$5 \times 10^{-5}$	$4 \times 10^{-5}$	$3 \times 10^{-5}$	$2 \times 10^{-5}$	
0.369	0.302	0.305	0.223	0.189	0.156	0.102	0.5
0.328	0.274	0.274	0.207	0.173	0.145	0.086	1
0.303	0.257	0.249	0.195	0.172	0.138	0.082	1.5
0.286	0.235	0.231	0.189	0.162	0.132	0.078	2
0.267	0.222	0.231	0.173	0.146	0.126	0.075	2.5
0.257	0.212	0.218	0.170	0.137	0.112	0.070	3
0.253	0.206	0.215	0.164	0.141	0.109	0.070	3.5
0.252	0.212	0.212	0.162	0.134	0.108	0.069	4
0.281	0.269	0.218	0.205	0.133	0.116	0.077	4.5
0.337	0.280	0.276	0.209	0.181	0.152	0.095	5
0.303	0.263	0.260	0.214	0.175	0.141	0.089	5.5
0.299	0.253	0.257	0.201	0.173	0.140	0.085	6
0.296	0.242	0.256	0.206	0.169	0.135	0.082	6.5
0.280	0.221	0.243	0.182	0.161	0.129	0.073	7
0.273	0.210	0.231	0.185	0.152	0.121	0.061	7.5
0.259	0.192	0.221	0.179	0.145	0.117	0.055	8
0.243	0.189	0.218	0.170	0.140	0.110	0.043	8.5
0.225	0.181	0.210	0.165	0.135	0.096	0.033	9
0.210	0.178	0.199	0.157	0.121	0.089	0.022	9.5
0.195	0.162	0.182	0.140	0.103	0.080	0.011	10

**Table 6: The Suggested concentration values for B1 that Used as indicator when titration 5 ml of standard solution HCl (0.097M) Versus Sodium hydroxide solution for determination end point of reaction**

% Relative Error	[NaOH] M at $A_{1/2}$	$V_{end}(ml)$ at $A_{1/2}$	$A_{1/2}$ At (460)nm	The difference between the highest and lowest Value of the absorption close End point	[D] $\times 10^{-5}$ M
4.799	0.107	4.5	0.088	0.006	2
0.881	0.103	4.7	0.117	0.02	3
-0.907	0.1011	4.79	0.149	0.029	4
-0.097	0.102	4.75	0.190	0.021	5
-1.077	0.101	4.8	0.230	0.021	6
-3.036	0.099	4.9	0.295	0.12	7
-2.056	0.1	4.85	0.315	0.081	8

[NaOH]= (0.1021M)

**Table 7: The Suggested concentration values for B2 that Used as indicator when titration 5 ml of standard solution HCl (0.097M) Versus Sodium hydroxide solution for determination end point of reaction**

% Relative Error	[NaOH] M at $A_{1/2}$	$V_{end}(ml)$ at $A_{1/2}$	$A_{1/2}$ at(455)nm	The difference between the highest and lowest Value of the absorption close End point	[D] $\times 10^{-5}$ M
1.860	0.104	4.65	0.059	0.004	2
-0.097	0.102	4.75	0.1	0.03	3
-1.077	0.101	4.8	0.108	0.003	4
-0.097	0.102	4.75	0.116	0.009	5
-1.077	0.101	4.8	0.156	0.012	6
-0.097	0.102	4.75	0.129	0.019	7
-3.036	0.099	4.90	0.210	0.017	8

[NaOH]= (0.1021M)

**Table 8: The Suggested concentration values for B3 that Used as indicator when titration 5 ml of standard solution HCl (0.097M) Versus Sodium hydroxide solution for determination end point of reaction**

% Relative Error	[NaOH] M at $A_{1/2}$	$V_{\text{end}}$ (ml) at $A_{1/2}$	$A_{1/2}$ at(440)nm	The difference between the highest and lowest Value of the absorption close End point	[D] $\times 10^{-5}$ M
1.860	0.104	4.65	0.086	0.018	<b>2</b>
- 0.097	0.102	4.8	0.134	0.036	<b>3</b>
- 0.097	0.102	4.8	0.157	0.048	<b>4</b>
- 0.097	0.102	4.8	0.207	0.004	<b>5</b>
- 2.056	0.1	4.85	0.247	0.058	<b>6</b>
- 4.015	0.098	4.95	0.274	0.011	<b>7</b>
- 2.056	0.1	4.85	0.309	0.056	<b>8</b>

[NaOH]= (0.1021M)

#### REFERENCES

- [1] S Wang, S Han, X Cui and X Qiu. IJRRAS 2013;15:292 – 296.
- [2] TA Fahad, AA Ali and HK Ebraheem. J Basrah Sci 2014;32:1 – 31.
- [3] H Zollinger. 'Color chemistry: 1991, synthesis, properties and Application of organic Dyes and Pigments, VCH.
- [4] Hawraa Mehdi Farhan. World J Med Medical Sci Res 2014;2:26 – 34.
- [5] M Prasad Naidu and P Aruna. IJABT 2013;4:117 – 123.
- [6] Kirkan B, and Gup R. Turk J Chem 2008;32:9-17.
- [7] Vikram Singh NK, Kaushik, and Ram Singh. Asian J Res Chem 2011;4:339 – 347.
- [8] Tarek A Fahad and Shaker A N AL-Jadaan. J Adv Chem 2014;7:1338 – 1346.
- [9] Tarek A Fahad, Assad A Ali, and Hawraa K Ebraheem. J Adv Chem 2013;2:1402-1410.
- [10] L Abd-Alredha, R Al-Rubaie, and R Jameel Mhessn. E-J Chem 2012;9:465-470.