CHAPTER VI

VISIBLE SPECTROMETRIC STUDIES OF 2,7-BIS[(2-HYDROXY-5-NITROPHENYL)AZO]-1,8-DIHYDROXY -3,6-NAPHTHALENEDISULFONIC ACID (5N-DYE)

6.1 Acid-Base Property of 5N-Dye

Twelve 10.0 mL aliquots of 10^{-4}F 5N-dye solution were pipetted into a series of 100 mL beakers. The pH of the solution was adjusted to 1.00-12.00 by using nitric acid or ammonia solution. Suitable amount of water was added. The pH of solution was recorded by a pH meter. The solutions were then quantitatively transferred to a series of 25 mL volumetric flasks and made up to the mark with deionized water. The color changes were observed and corresponding colors are reported in Table 6.1.

The color of the free dye was found to change with pH. The change in color may be ascribed to the change in the structure caused by ionization. The change in color when pH was lowered is due to the attachment of a proton to the auxochromic groups on one of nitrogen atoms of the azo group and by increasing the pH, the process is reversed.

$$\text{R-N=N-R} \rightleftharpoons \text{R-N=N}^{+}\text{H-R}$$

The color changes as reported in Table 6.1 shown that 5N-dye has acid-base property. At pH 1, the color changed from purple to dark blue after 5-10 minutes. After leaving overnight, the colour changed to light yellow with some precipitates. This indicated the decomposition of the dye in strong acid condition due to the autoxidation of nitro groups in the dye molecules attacking azo (-N=N-) groups.

Table 6.1 Colors observed at particular pH values for the 5N-dye

pH	Color observed	λ_{max} (observed)
1	purple, about 5 minutes color change to dark blue	550
2	purple	550
3	purple	550
4	purple	550
5	mauve-blue	554
6	blue	598
7	greenish-blue	658
8	bluish-green	672
9	bluish-green	672
10	bluish-green	678
11	bluish-green	678
12	greenish-blue	636

6.2 Visible Spectra of 5N-Dye at Various pH Values

Procedure :

The 5N-dye solutions prepared in section 6.1 were used for spectra study. The absorption spectra of the dye solutions at various pH values were recorded from wavelength of 400 nm to 800 nm using water as reference.

The absorption spectra obtained are shown in Figure 6.1 the maximum absorbance occurs at about 550-554 nm over the pH range of 1.00 to 5.00, it shows a bathochromic shift above pH 6.

Figure 6.2 is the spectra of 5N-dye at pH 1.00 showing the change of its spectra after 5 minutes due to gradual decomposition.

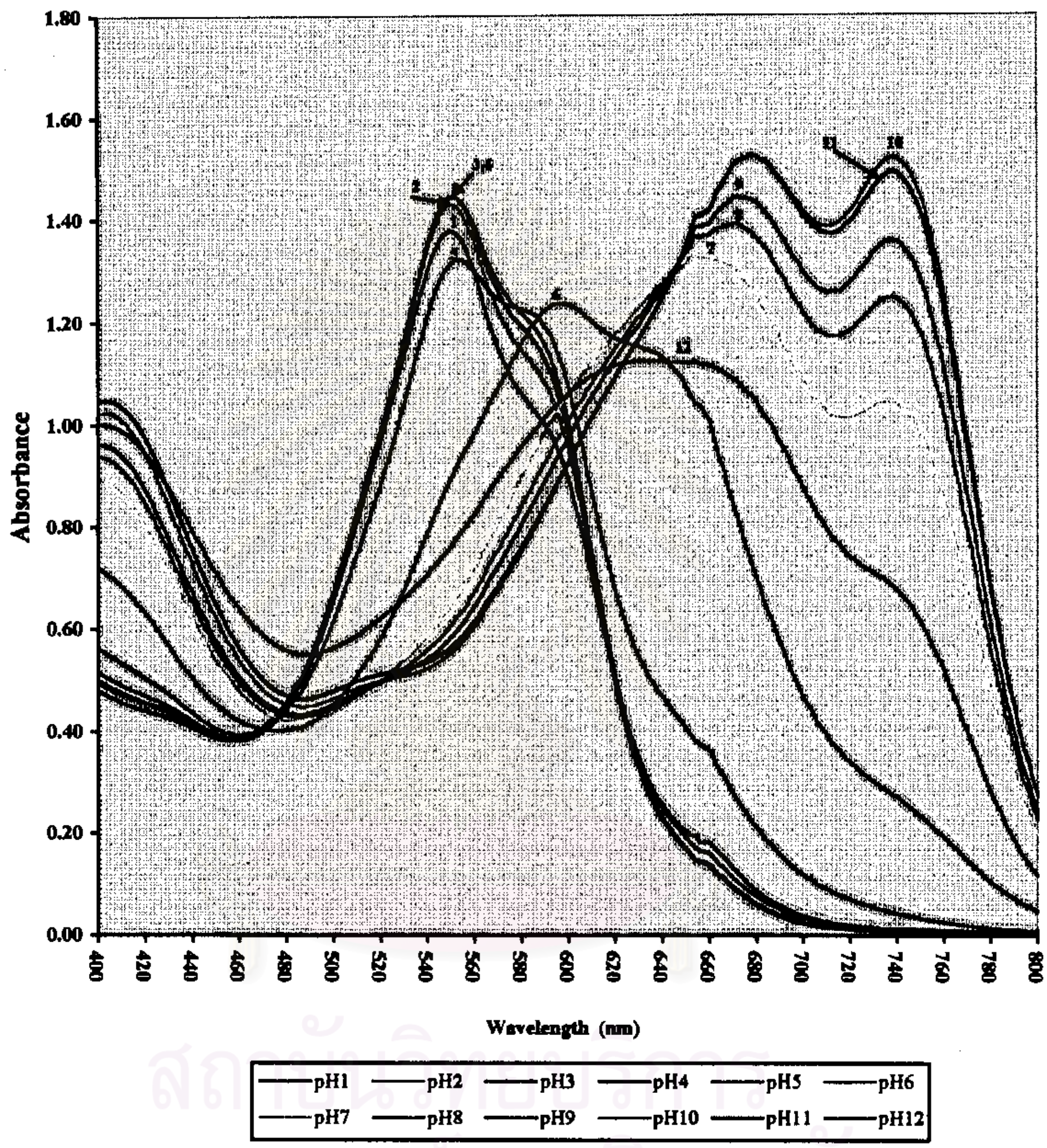

Figure 6.1 Absorption spectra of the 5N-dye at various pHs (1.00-12.00)

Dye	: 10^{-4} F, 10.0 mL
Final volume	: 25 mL
Reference	: water

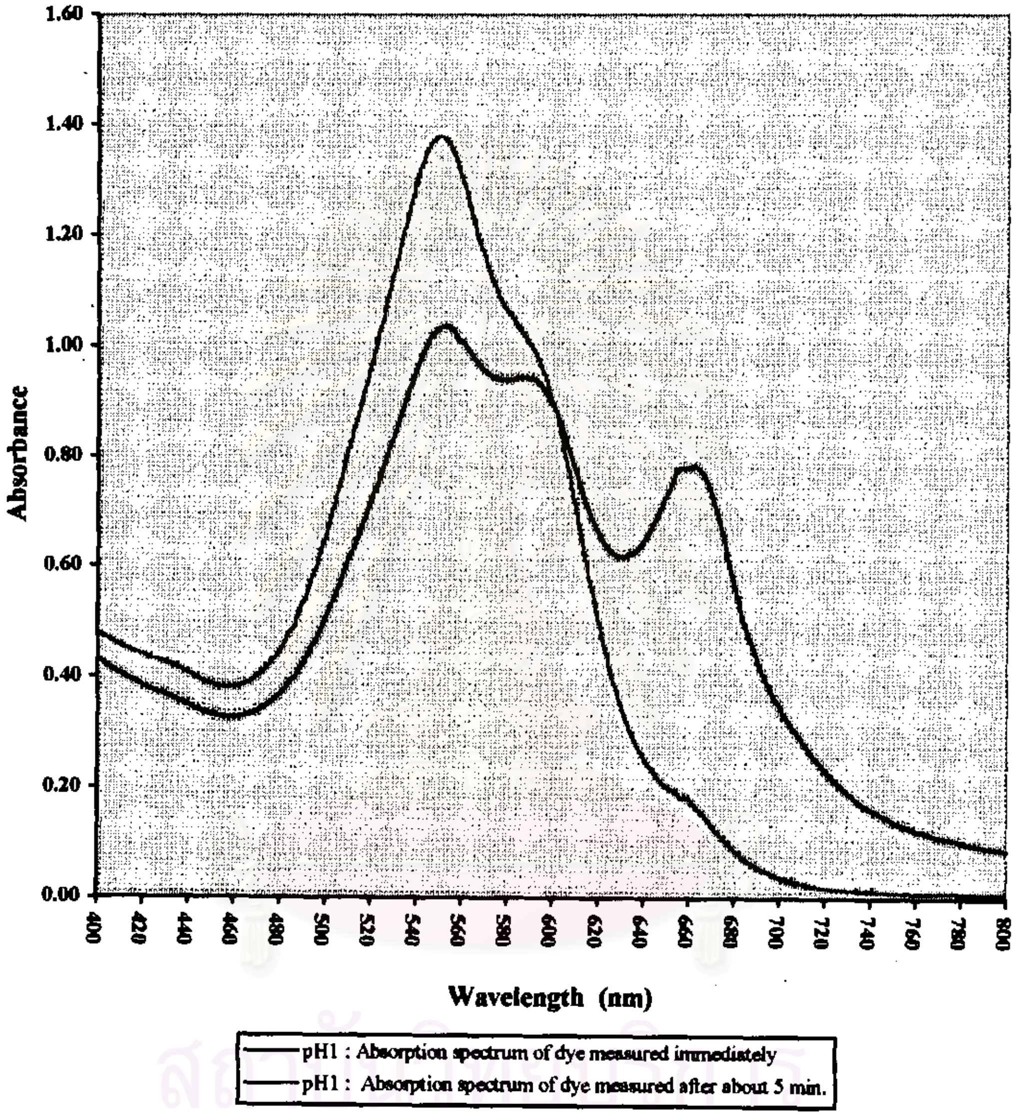

Figure 6.2 Absorption spectra of the 5N-dye at pH 1.00

Dye	: 10^{-4} F, 10.0 mL
Final volume	: 25 mL
Reference	: water

6.3 Visible Spectra of Bismuth(III)-5N Dye at Various pHs in Final Volume 100 mL

The previous results obtained from the preliminary studies of the 5N-dye indicated that the suitable pH range for bismuth(III)-5N dye complex formation is in the acid range. Therefor, the spectra of the complex were performed in the pH range 1.50 to 5.50.

Procedure

Twelve 10.0 mL aliquots of 10^{-4}F bismuth(III) were pipetted into a series of 100 mL beakers containing accurately 10.0 mL each of 10^{-4}F 5N-dye solution. The pHs of the solutions were adjusted to 1.50-5.50 by using nitric acid and ammonia solutions. The solutions were then quantitatively transferred into a series of 100 mL volumetric flask. Small amount of water was added to the mark. The solutions were set aside for complete color development. The absorption spectra of bismuth(III)-5N dye complex at pH 1.50-5.50 measured (water as reference) were recorded from 400-800 nm. The absorbances of solutions were also measured against a reagent blank treated in a similar manner as a reference at 560-780 nm (in expanded scale) for easily observation.

Figures 6.3 and 6.4 show the absorption spectra of the bismuth(III)-5N dye complex at various pHs measured against water and reagent blank as references, respectively.

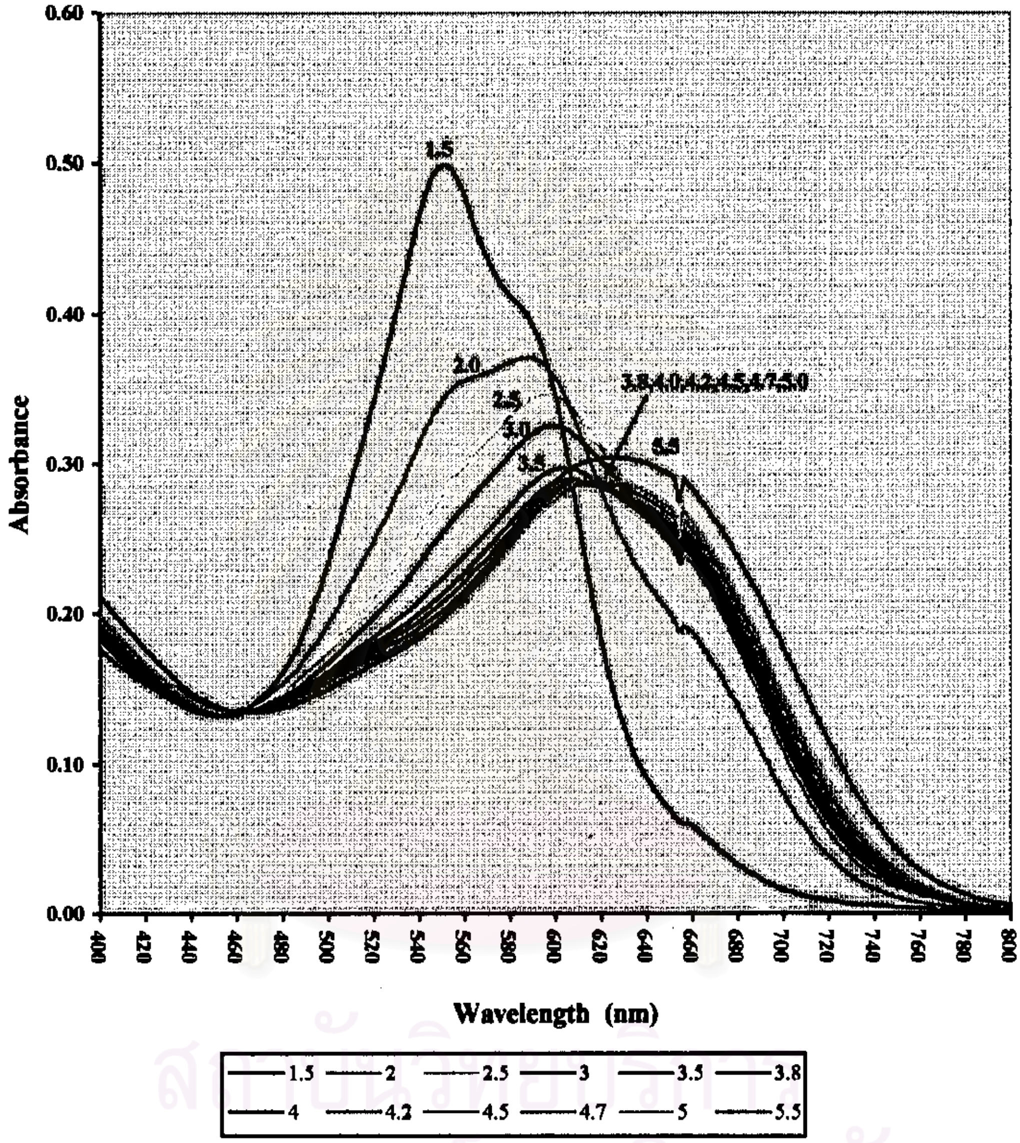

Figure 6.3 Absorption spectra of bismuth(III)-5N dye complex at various pHs (1.50-5.50) measured against water

Bismuth(III)	:	10^{-4} F, 10.0 mL
Dye	:	10^{-4} F, 10.0 mL
Final volume	:	100 mL
Reference	:	Water

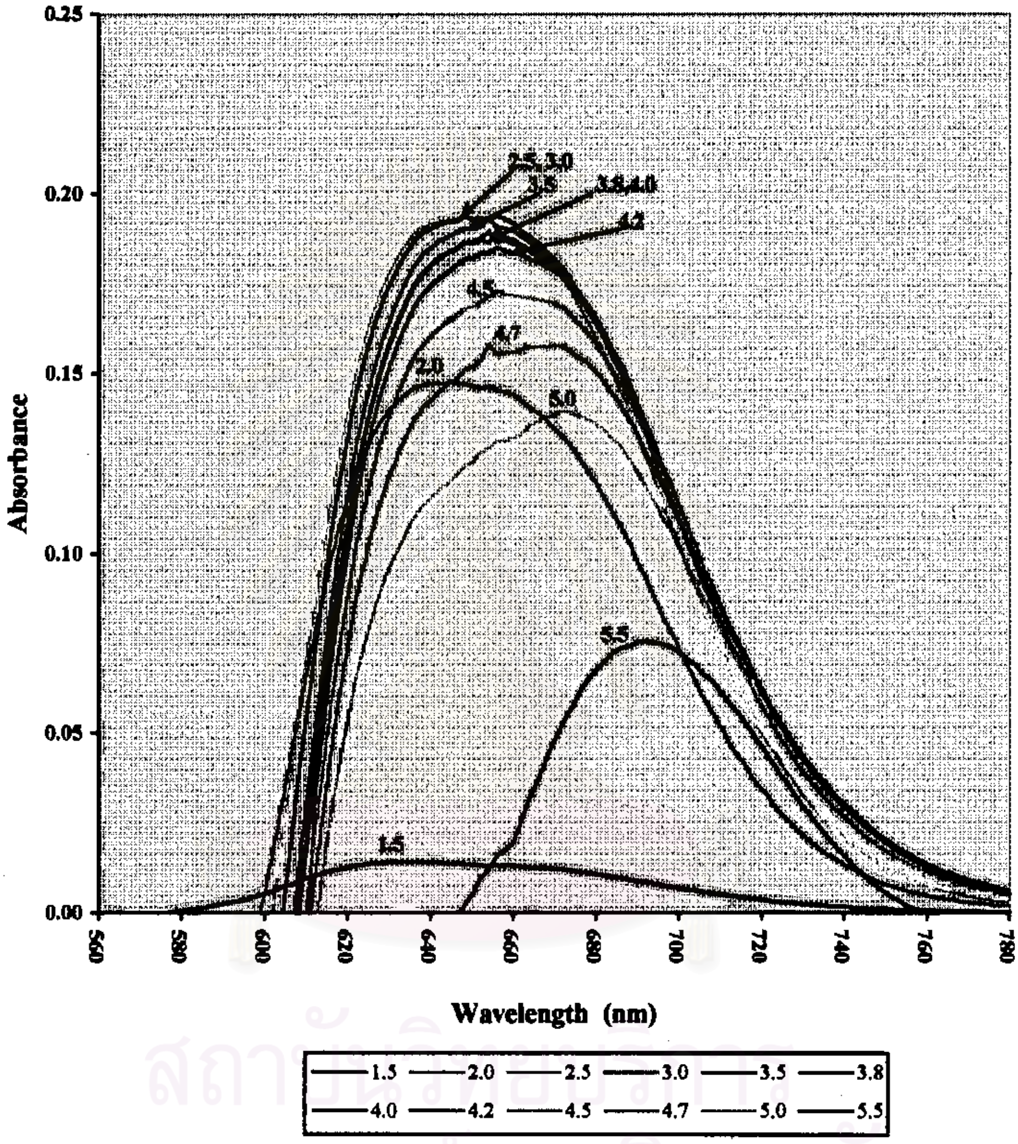

Figure 6.4 Absorption spectra of bismuth(III)-5N dye complex at various pHs (1.50-5.50) measured against dye as reagent blank

Bismuth(III)	:	10^{-4} F, 10.0 mL
Dye	:	10^{-4} F, 10.0 mL
Final volume	:	100 mL
Reference	:	Reagent blank (dye solution)

6.4 Development of Spectrometric Method for the Determination of Bismuth(III) Using the 5N-Dye as Metallochromic Reagent in Final Volume 100 mL

Procedure :

In order to determine bismuth spectrophotometrically using 5N-dye as a reagent, the following conditions should be carefully studied and established:

1) Optimal wavelength for bismuth - 5N dye complex
2) Optimal pH
3) Sequence of addition
4) Optimal amount of 5N-dye
5) Optimal time for color development
6) Adherence to Beer-Bouguer-Lambert law
7) Repeatability of the method
8) Effect of diverse ions
9) Nature of bismuth(III)-5N dye complex

Optimal Wavelength

Two sets of solutions with different conditions, that is in one solution the excess of dye is used whereas the other the excess of metal is employed, were prepared for investigation of the optimal analytical wavelength. The absorption spectra of the dye alone and the bismuth(III)-5N dye complex at pH 2.50 were recorded from 400-800 nm. The free dye was measured against water as a reference. The bismuth(III)-5N dye complex was measured against both water and reagent blank. The absorption spectra and experimental condition are shown in figure 6.5.

Inspection of the curves shows that a wavelength of approximately 648 nm gives the greatest difference in absorbance between the reagent blank and the complex.

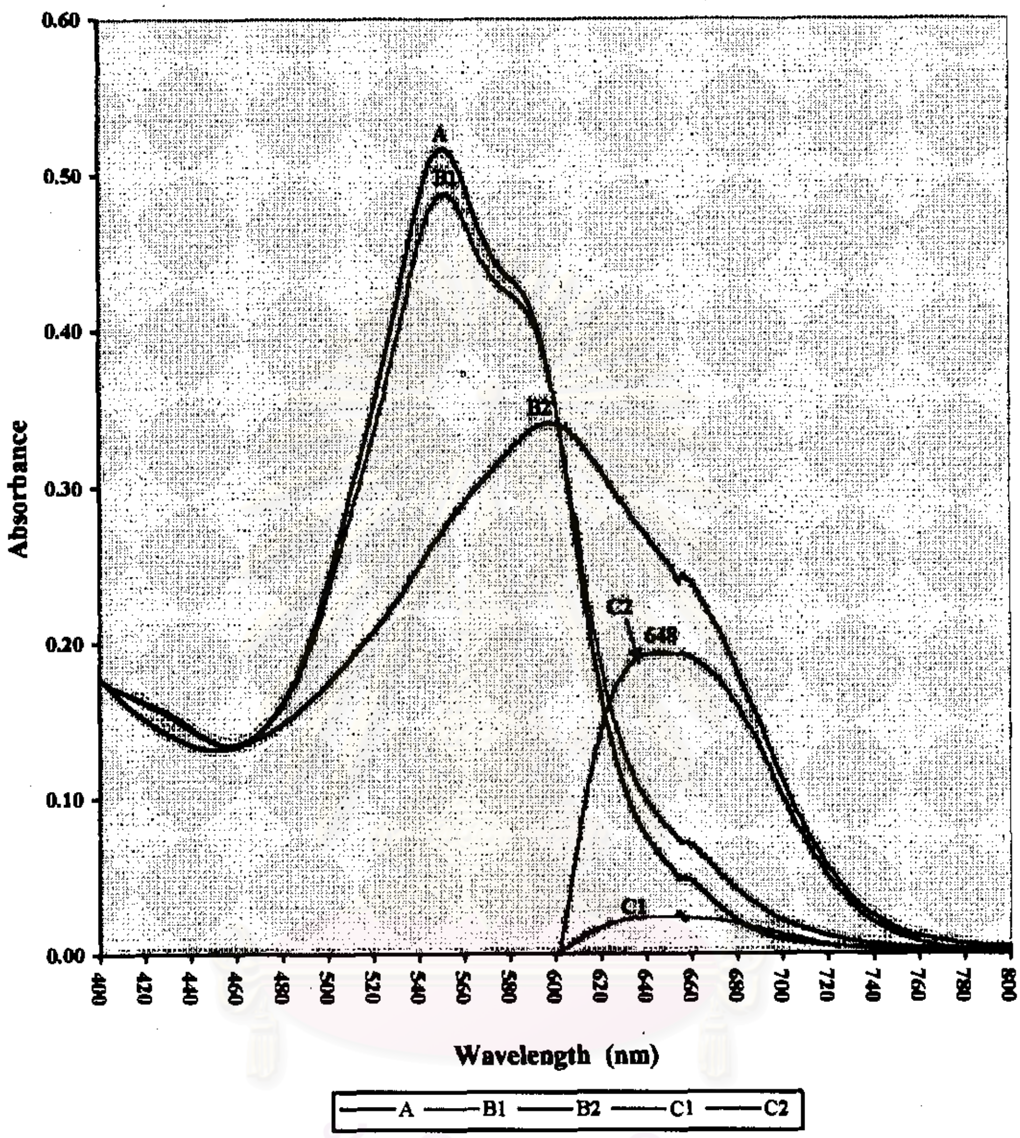

Figure 6.5 Optimal wavelength of the dye and its bismuth(III)-5N dye complex at pH 2.50

A	:	Dye 10^{-4}F, 10.0 mL
B_1 and B_2	:	Dye 10^{-4}F, 10.0 mL, Bismuth(III) 10^{-4}F 1.00 mL and 10.0 mL
A, B_1 and B_2 Reference	:	water
C_1 and C_2	:	Spectra of B_1 and B_2 against A
Final volume	:	100 mL

Optimal pH

The effect of pH on the absorbance of the bismuth(III)–5N dye complex was investigated. A series of solutions containing 3.00 mL of 10^{-4}F bismuth(III), 10.0 mL of 5N-dye solution and appropriate amount of water was prepared. Nitric acid and ammonia solutions were used for pH adjustment (between 2.00 and 5.00). The final volume was 100 mL. After the color was developed, the absorbances of solutions were measured at 648 nm against the reagent blank, which was treated in similar manner. The results obtained are shown in Table 6.2 and the corresponding plot appears in Figure 6.6.

It can be seen that the optimum pH range for analytical purpose lies in a narrow range between 2.50 and 4.20. Therefore, a pH of 2.50 was selected for all further work of the dye because working in a pH range in acid can avoid some interferences.

Sequence of Addition

The effect of the sequence of addition of all solutions concerned in the bismuth(III)–5N dye complex. Color development is shown in Tables 6.3 and 6.4.

From the result above, it is rather clear that the order of the addition of solutions shows no effect on the color development of bismuth(III)-5N dye complex. In practice, the sequence No.1 was chosen for the subsequent experiments.

Table 6.2 Optimal pH of bismuth(III)-5N dye complex

pH	Absorbance at 648 nm
1.50	0.003
2.00	0.049
2.50	0.071
3.00	0.072
3.50	0.071
4.00	0.072
4.20	0.070
4.50	0.064
4.70	0.059
5.00	0.051

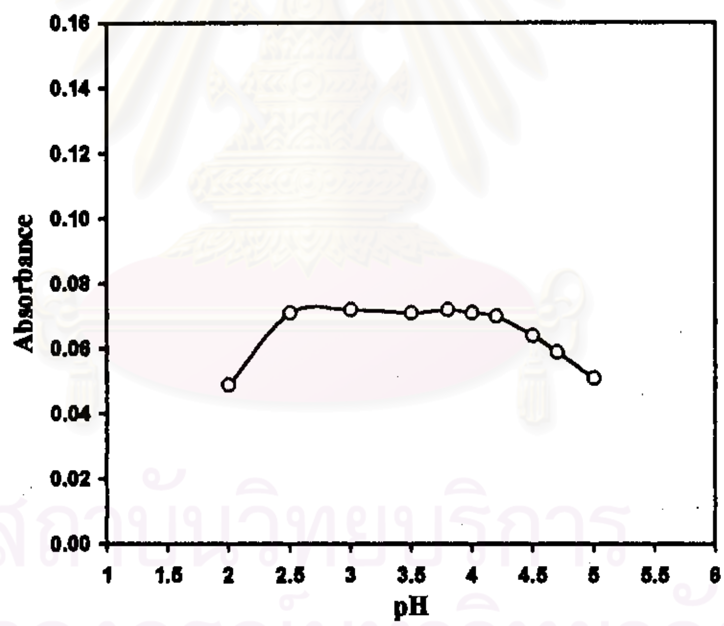

Figure 6.6 Effect of pH on absorbance of bismuth(III)-5N dye complex measured against reagent blank at 648 nm

Dye	: 10^{-4}F, 10.0 mL
Bismuth(III)	: 10^{-4}F, 3.00 mL
Reference	: Reagent blank
Final volume	: 100 mL

Table 6.3 Sequence of addition

Sequence No.	Sequence of reagent addition
1	dye , metal , pH adjustment
2	dye , pH adjustment , metal
3	metal , dye , pH adjustment
4	metal , pH adjustment , dye
5	pH adjustment , dye , metal
6	pH adjustment , metal , dye

Table 6.4 Absorbance of solution from the above table

Sequence No.	Absorbance at 648 nm (against blank)
1	0.071
2	0.071
3	0.070
4	0.070
5	0.071
6	0.070

Note

Dye : 10^{-4} F, 10.0 mL
Bismuth(III) : 10^{-4} F, 3.00 mL
Final volume : 100 mL
pH : 2.50

Optimal Amount of Dye

The effect of the amount of dye on the absorbance of the bismuth(III)-5N dye complex system was studied by varying the molar ratio of the reagent to bismuth. The amount of metal was kept constant. A series of solutions containing 3.00 mL of 10^{-4}F bismuth and various amount of 10^{-4}F dye solution from 2.00 to 22.00 mL were pipetted into appropriate amount of water in 100 mL volumetric flask. The pH of each solution was adjusted to 2.50 by the addition of 1 F nitric acid solution about 0.38 mL for reagent blank and 0.32 mL for the bismuth–5N dye solution. Then adjusted to 100 mL with deionized water. The absorbance of each solution was measured at 648 nm against the reagent blank using 1 cm cell.

The absorbance of solution containing various ratios of dye to bismuth at pH value of 2.50 are shown in Table 6.5 and the corresponding plot appears in Figure 6.7.

The results in Figure 6.7 show that the absorbance increases with increasing amount of dye reagent up to 6.00 mL and then remains reasonably constant up to 20.00 mL. Therefore in this system 10.0 mL of 10^{-4}F dye was adopted to be used in the subsequent experiments.

Table 6.5 Optimal amount of dye for bismuth(III)-5N dye complex

Bi(III) 10^{-4}F (mL)	Dye 10^{-4}F (mL)	Absorbance at 648 nm
3.00	2.00	0.039
3.00	4.00	0.058
3.00	6.00	0.068
3.00	8.00	0.070
3.00	10.00	0.071
3.00	12.00	0.072
3.00	14.00	0.072
3.00	16.00	0.072
3.00	18.00	0.071
3.00	20.00	0.069
3.00	25.00	0.065

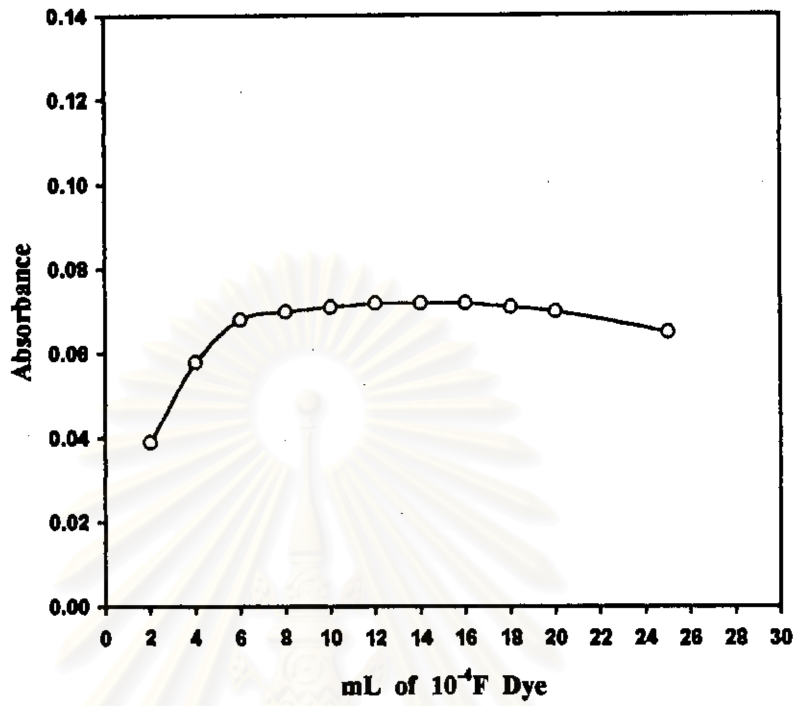

Figure 6.7 Effect of reagent concentration

Bismuth(III)	:	10^{-4} F, 3.00 mL
Reference	:	Reagent blank
Final volume	:	100 mL

Optimal Time for Color Development

3.00 mL of 10^{-4}F bismuth(III) solution was pipetted into a 100 mL volumetric flask containing exactly 10.0 mL of 10^{-4}F 5N-dye solution. 0.32 mL of 1F nitric acid solution was added into the bismuth-5N dye solution whereas 0.38 mL of 1F nitric acid was added into the reagent blank for adjust pH to 2.50. Both solutions were then made up to 100 mL mark with deionized water. The absorbance of bismuth(III)–5N dye solution was measured immediately after dilution against a reagent blank at 648 nm, using 1 cm cell. The absorbance of the bismuth(III)-5N dye complex solution was then measured periodically at the specified time intervals. Results are shown in Table 6.6 and corresponding Figure 6.8.

The result obtained shows that the color of the complex is developed instantaneously and remains constant for at least 24 hours.

Table 6.6 Effect of time on color development of complex

Time (min)	Absorbance at 648 nm	Time (hr)	Absorbance at 648 nm
0	0.074	2	0.071
5	0.071	4	0.071
10	0.072	6	0.070
15	0.072	8	0.070
20	0.072	10	0.070
25	0.073	12	0.071
30	0.072	18	0.071
45	0.071	24	0.070
60	0.072		

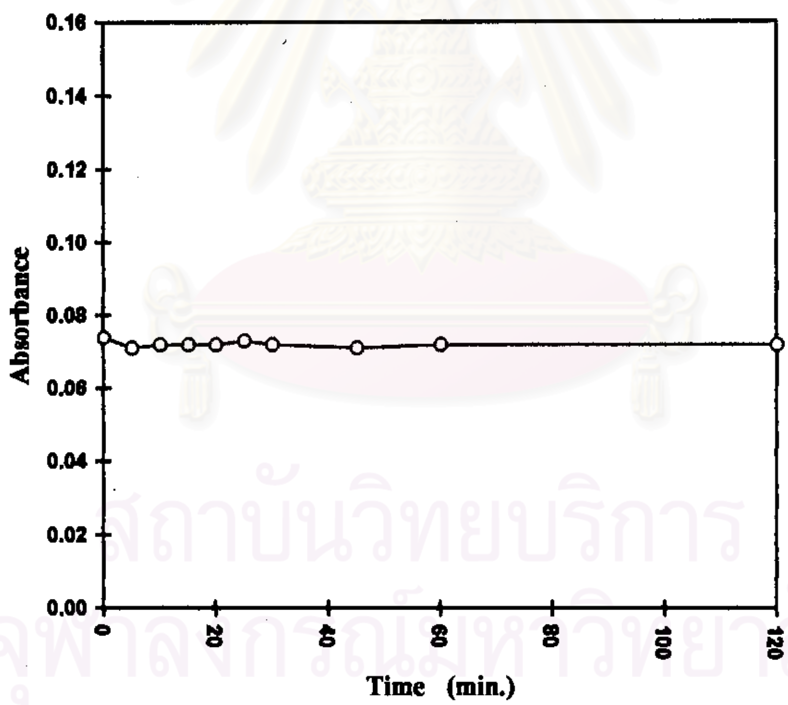

Figure 6.8 The influence of time on the absorbance of the bismuth(III)-5N dye complex

Dye	: 10^{-4} F, 10.0 mL
Bismuth(III)	: 10^{-4} F, 3.00 mL
Reference	: Reagent blank
Final volume	: 100 mL

Adherence to Beer-Bouguer-Lambert law

Calibration Curve

The linear relationships between the absorbance of the bismuth(III)-5N dye complex and the bismuth concentration was investigated. In this study, 0.50 to 15.00 mL of 10^{-4}F bismuth solutions were pipetted into a series of 100 mL volumetric flask containing 10.0 mL of 10^{-4}F 5N-dye solution and appropriate amount of water. The pHs of solutions were then adjusted to pH 2.50 by add 1F nitric acid solution about 0.20-0.38 mL and adjusted volume to the mark with deionized water. The absorbances of these solutions were measured at 648 nm against the reagent blank using 1 cm cell. The data obtained is shown in Table 6.7 and corresponding plot in Figure 6.9.

The calibration curve is found to obey Beer-Bouguer-Lambert law very well over the range of 20.90 to 146.29 μg of bismuth in 100 mL of solution at 648 nm. The molar absorptivity (ε) is 2.3×10^4 L mol^{-1} cm^{-1}, equivalent to the specific absorptivity (a) of 0.11 mL g^{-1} cm^{-1} and the Sandell sensitivity (S) of 0.0091 μg cm^{-2}.

Table 6.7 Calibration curve of bismuth(III)-5N dye complex: fixed concentration of 5N-dye 10^{-4}F 10.0 mL and pH 2.50

bismuth(III) 10^{-4}F.		Absorbance at 648 nm
mL	μg/100.0 mL	
0.50	10.45	0.009
1.00	20.90	0.025
2.00	41.80	0.048
3.00	62.69	0.072
4.00	83.59	0.094
5.00	104.49	0.115
6.00	125.39	0.137
7.00	146.29	0.155
8.00	167.18	0.171
9.00	188.08	0.184
10.00	208.98	0.193
11.00	229.88	0.200
12.00	250.78	0.202
13.00	271.68	0.207
14.00	292.57	0.210
15.00	313.47	0.212

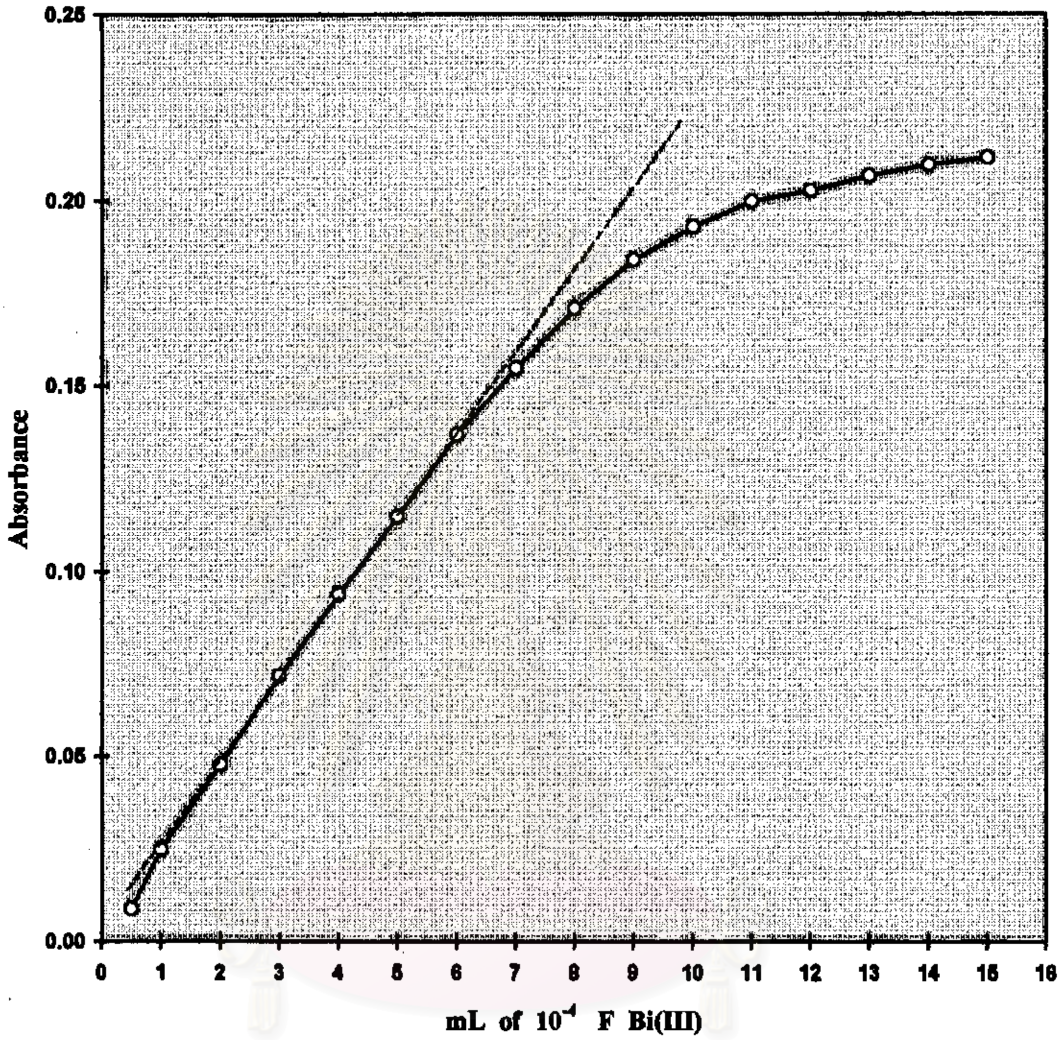

Figure 6.9 Calibration curve of bismuth(III)-5N dye complex

Repeatability of the Method

The repeatability of the developed method was checked by means of the standard deviation of the determination obtained from measuring the absorbance of 10 sets of solution, each containing 10.0 mL of 10^{-4}F 5N-dye solution and 4.00 mL of 10^{-4}F bismuth(III). 0.31 mL of 1F nitric acid solution was added into the bismuth(III)-5N dye solution for adjusting pH to 2.50 then solutions were made up to 100 mL with deionized water. The data obtained is reported in Table 6.8.

The standard deviation, s, was calculated using the formula;

$$s = \pm\sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$$

Where

x = individual value
$\bar{x}$ = mean value
n = number of value measurements
$\bar{x}$ = 0.095
n = 10
s = 0.0011

∴ Percent standard deviation = 0.11

Percent Relative Standard Deviation

$$\%RSD = \left(\frac{s}{\bar{x}}\right)x100$$

$$= 1.2$$

Table 6.8 Standard deviation study of the method, fixed concentration of 5N-dye 10^{-4}F 10.0 mL, bismuth(III) 10^{-4}F 4.00 mL, and pH 2.5

No.	Absorbance at 648 nm
1	0.095
2	0.094
3	0.096
4	0.094
5	0.093
6	0.095
7	0.096
8	0.094
9	0.094
10	0.096

Effect of Diverse Ions

The effect of 20 cations and 9 anions on the determination of bismuth was examined in various concentrations.

A series of solutions containing 4.00 mL of 10^{-4}F bismuth(III), 10.0 mL of 10^{-4}F 5N-dye solution with various mole ratios of the diverse ions to bismuth (1000 : 1 , 200 : 1, 100 : 1, 50 : 1, 20:1 , 10:1 and 1:1) were prepared using 8.00 mL of 0.1 F, 8.00 mL, 4.00 mL, 2.00 mL of 10^{-2} F, 8.00 mL, 4.00 mL of 10^{-3}F and 4.00 mL of 10^{-4}F diverse ions solutions.

These diverse ions were added individually to a bismuth(III)-5N dye solution. The pHs of the solutions were adjusted to 2.50 by nitric acid and ammonia solutions (0.01, 0.1 and 1F). The final volume was 100 mL.

The absorbances of the solutions were measured at 648 nm against a reagent blank using 1 cm cell. The results obtained are shown in Tables 6.9 and 6.10.

Table 6.9 Effect of some cations

Diverse ion	From	Absorbance at 648 nm of Bi(III) : ion						Remark
		1:1	1:10	1:20	1:50	1:100	1:200	
Bi(III)alone	$Bi(NO_3)_3.5H_2O$	0.094	0.094	0.094	0.094	0.094	0.094	
+ Na(I)	$NaNO_3$	0.093	0.093	0.094	0.093	0.093	0.092	1:1000 = 0.091
+ Ni(II)	$Ni(NO_3)_2.6H_2O$	0.092	0.094	0.094	0.094	0.097	0.099	
+ Pb(II)	$Pb(NO_3)_2$	0.094	0.094	0.096	0.096	0.095	0.313	1:110 = 0.102
+ Cd(II)	$Cd(NO_3).4H_2O$	0.093	0.093	0.093	0.094	0.094	0.093	
+ Mn(II)	$Mn(NO_3)_2.4H_2O$	0.093	0.092	0.092	0.093	0.093	0.256	
+ Ag(I)	$Ag(NO_3)$	0.094	0.094	0.094	0.094	0.095	0.096	
+ Fe(II)	$(NH_4)SO_4FeSO_4.6H_2O$	0.095	0.098	0.101	0.112	0.120	0.133	
+ Fe(III)	$Fe(NO_3)_3.9H_2O$	0.112	0.151	0.135	0.120	0.117	0.116	
+ Co(II)	$CoSO_4.7H_2O$	0.094	0.094	0.093	0.095	0.093	0.094	
+ Sn(II)	$SnCl_2.2H_2O$	0.046	0.026	0.033	ppt	ppt	ppt	
+ Zr(II)	$Zr(SO_4)_2.H_2O$	0.096	0.147	0.196	0.254	0.326	0.368	
+ Cu(II)	$CuCl_2.2H_2O$	0.149	0.365	0.389	0.402	0.404	0.401	

Table 6.9 (cont.)

Diverse ion	From	Absorbance at 648 nm of Bi(III) : ion						Remark
		1:1	1:10	1:20	1:50	1:100	1:200	
+ Cr(III)	$Cr(NO_3)_3.9H_2O$	0.099	0.100	0.105	0.197	0.273	ppt	
+ Mg(II)	$Mg(NO_3)_2.6H_2O$	0.093	0.092	0.094	0.095	0.094	0.099	
+ Ti(IV)	$TiCl_4$	0.161	0.192	-	-	-	-	
+ Pd(II)	$Pd(NO_3)_2$	0.157	0.302	-	-	-	-	
+ Ba(II)	$Ba(NO_3)_2$	0.095	0.092	0.095	0.119	0.314	-	
+ Al(III)	$Al(NO_3)_3.9H_2O$	0.091	0.093	0.109	0.175	0.250	-	
+ Zn(II)	$Zn(NO_3)_2.4H_2O$	0.094	0.093	0.093	0.095	0.097	0.121	
+ Y(III)	$Y(NO_3)_3.5H_2O$	0.098	0.100	0.104	0.181	0.201	ppt	

Table 6.10 Effect of some anions

Diverse ion	From	Absorbance at 648 nm of Bi(III) : ion						Remark
		1:1	1:10	1:20	1:50	1:100	1:200	
Bi(III)alone	$Bi(NO_3)_3.5H_2O$	0.094	0.094	0.094	0.094	0.094	0.094	
+ EDTA	$C_{10}H_{14}N_2Na_2O_8.2H_2O$	0.000	0.001	0.001	0.000	0.001	0.001	
+ F^-	NaF	0.094	0.094	0.094	0.091	0.080	0.078	1:1000 = 0.017
+ Cl^-	NaCl	0.093	0.093	0.093	0.092	0.092	0.093	1:1000 = 0.091
+ SO_4^{2-}	Na_2SO_4	0.094	0.096	0.094	0.094	0.093	0.092	1:1000 = 0.092
+ CO_3^{2-}	Na_2CO_3	0.094	0.093	0.093	0.094	0.094	0.093	1:1000 = 0.092
+ Acetate	$CH_3COONa.3H_2O$	0.093	0.094	0.094	0.095	0.095	0.094	
+ Citrate	$Na_3C_6H_5O_7.2H_2O$	0.073	0.027	0.016	0.006	0.004	-	
+ Oxalate	$Na_2C_2O_4$	0.053	0.005	0.002	0.000	0.001	0.000	
+ Phosphate	$Na_3PO_4.12H_2O$	0.093	0.092	0.092	0.089	0.085	0.084	

It can be concluded from Tables 6.9 and 6.10 based on the deviation ± 5.0 from the absorbance of bismuth(III) alone as Table 6.11.

Table 6.11 Tolerable amount of some coexisting ions

Cations	Anions	Tolerable amount (folds of Bi(III))
Na(I)	Cl^- , SO_4^{2-}, CO_3^{2-}	1000
Ni(II), Cd(II), Ag(I), Co(II) , Mg(II)	Acetate	200
Pb(II), Mn(II) Zn(II)	-	100
-	F^-, PO_4^{3-}	50
Ba(II)	-	20
Fe(II), Al(III)	-	10
Zr(II), Cr(III), Y(III)	-	1
Fe(III), Sn(II), Cu(II), Ti(VI), Pd(II)	EDTA, Citrate Oxalate	Seriously interfere

Nature of Bismuth(III)-5N Dye Complex

The empirical formula of bismuth(III)-5N dye complex at the analytical condition was determined by three conventional spectrometric methods.

Method of Continuous Variation (Job's Method)

Procedure

A series of solution of bismuth(III)-5N dye mixtures containing various mole fraction of bismuth from 0-1 was prepared. The sum of the concentrations of bismuth and the dye was kept at 1 × 10^{-5} mole per liter.

After adjustment the pH to 2.50, mixtures were diluted to 100 mL The absorbance of each solution was measured at 648 nm against water as the reference using 1 cm cell. The data is shown in Table 6.12 and the corresponding Job's plot is shown in Figure 6.10.

From Figure 6.10, it shows that a 1:1 mole ratio complex is formed between bismuth(III) and the 5N-dye.

The apparent stability constant of the bismuth(III)-5N dye complex under the conditions of this experiment was evaluated. On the basis of the previous experiments, a 1:1 metal-ligand complex is assumed,

$$M + L \longrightarrow ML$$

It is possible to write the stability constant as ;

$$K = \left(\frac{1-\alpha}{\alpha^2 C}\right)$$

Where ∝, the degree of dissociation, was established from the relationship:

$$\alpha = \frac{A_m - A_s}{A_m}$$

C is the concentration of the complex in mole per liter.

A_m is the maximal absorbance obtained from the extrapolation of the curve.

and A_s is the absorbance at the stoichiometric molar ratio of metal to reagent.

The continuous variation curve (Figure 6.10) may be used to obtain the values of A_m and A_s. From Figure 6.10, it was found that A_m equals to 0.108 and A_s equals to 0.094 for a solution that was 5×10^{-6} M in bismuth. The degree of dissociation constant was then calculated to be 0.130. The value of the apparent stability constant, K, under these particular conditions was found to be 1.0×10^7 with pK values of 7.0. This value indicates that at pH 2.50 the complex-formation between bismuth(III) and 5N-dye is rather strong and stable.

Table 6.12 The detailed data of the continuous variation method (Job's method)

Dye 10^{-4} F (mL)	Bi(III) 10^{-4}F (mL)	Mole fraction of bismuth Bi/Bi+dye	Absorbance at 648 nm	
			not corrected	corrected
10.00	0.00	0.0	0.061	0.061-0.061 = 0.000
9.00	1.00	0.1	0.080	0.080-0.055 = 0.025
8.00	2.00	0.2	0.097	0.097-0.049 = 0.048
7.00	3.00	0.3	0.112	0.112-0.043 = 0.069
6.00	4.00	0.4	0.125	0.125-0.037 = 0.088
5.00	5.00	0.5	0.125	0.125-0.031 = 0.094
4.00	6.00	0.6	0.112	0.112-0.024 = 0.088
3.00	7.00	0.7	0.089	0.089-0.018 = 0.071
2.00	8.00	0.8	0.063	0.063-0.012 = 0.051
1.00	9.00	0.9	0.035	0.035-0.007 = 0.028
0.00	10.00	1.0	0.000	0.000-0.000 = 0.000

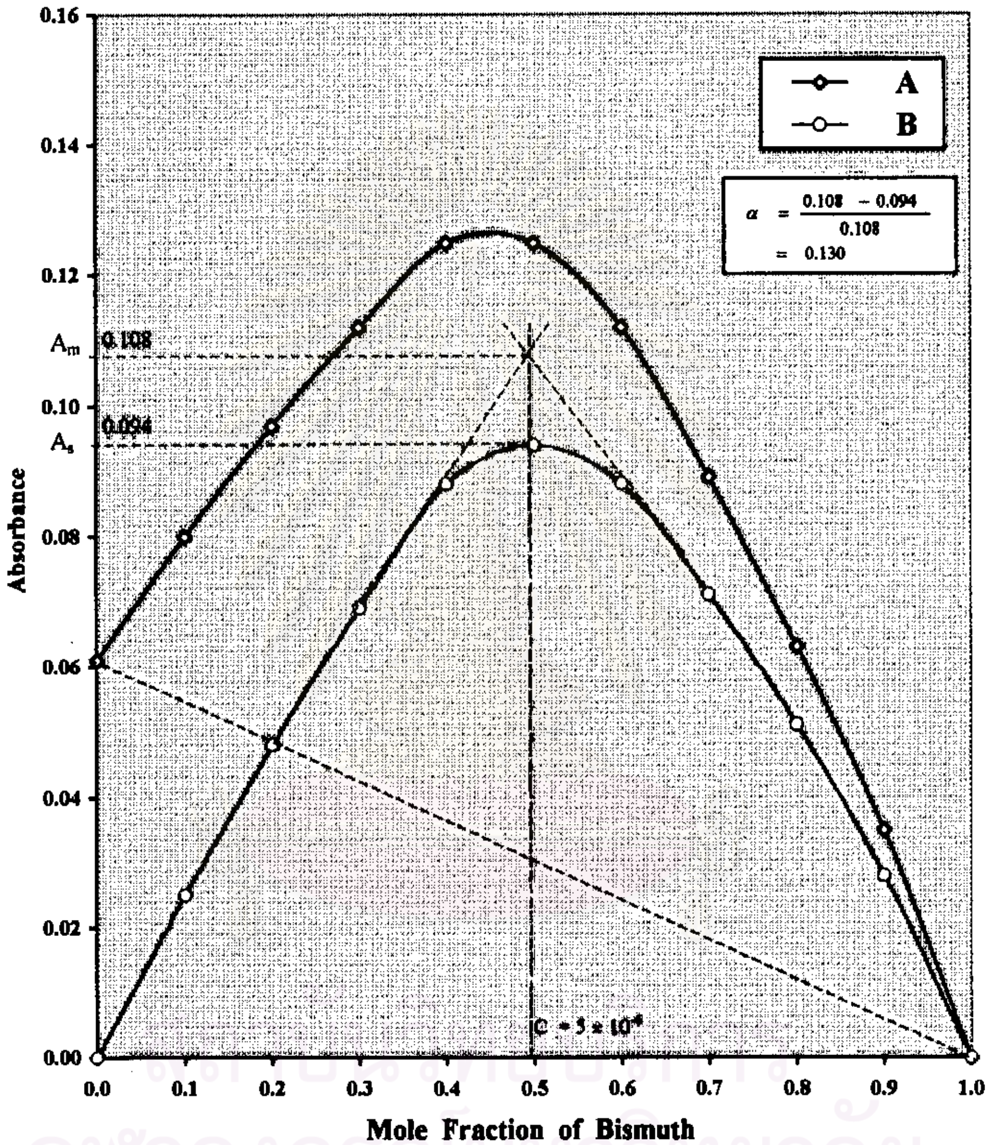

Figure 6.10 Continuous variation method

A : experimental absorbance value (not corrected)
B : absorbance after graphical subtraction of the Absorbance of the reagent (corrected)

The Mole Ratio Method

Procedure

A series of solutions containing equal formal concentration of the dye but different formal concentrations of bismuth were prepared. The concentration of dye was fixed at 5×10^{-6} mole per liter (5.0 mL of 10^{-4}F 5N-dye solution per 100 mL) with variation of 10^{-4}F bismuth 0.00-10.00 mL. The pHs of the solutions were adjusted to 2.50 and final volumes were 100 mL. The absorbance of the solution was measured against a reagent at 648 nm using 1 cm cell. The detailed data is shown in Table 6.13 and the mole ratio plot is shown in Figure 6.11.

From Figure 6.11; the curve exhibits a deflection at 4.9 : 5.0 mole ratio of bismuth : dye indicating 0.98 : 1 or 1:1 bismuth : dye complex.

Table 6.13 The detailed data of the molar ratio method

Bi(III) 10^{-4}F (mL)	Absorbance at 648 nm
0.00	0.000
1.00	0.023
2.00	0.044
3.00	0.064
4.00	0.077
5.00	0.089
6.00	0.097
7.00	0.102
8.00	0.104
9.00	0.105
10.00	0.105

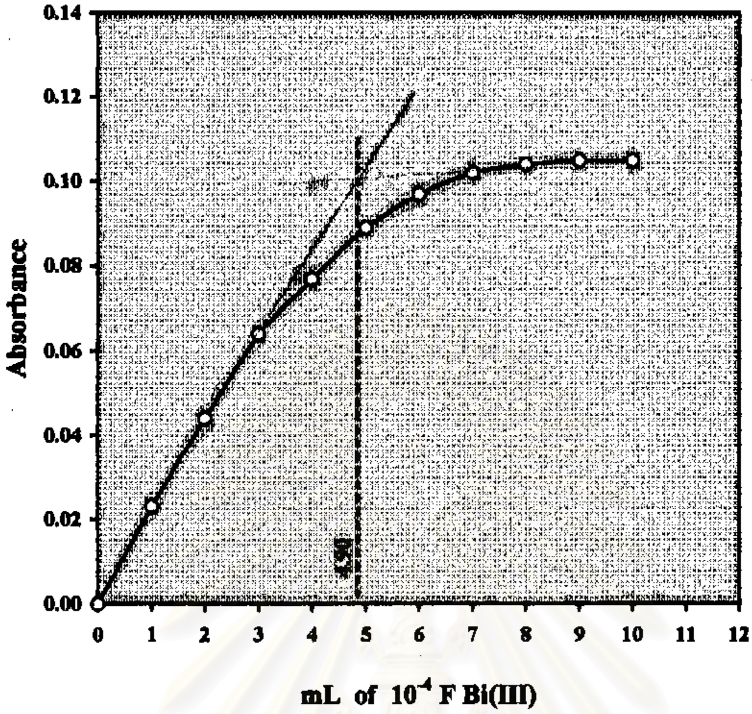

Figure 6.11 Mole ratio method

Fixed dye : 5.0 mL of 10^{-4}F
Final volume : 100 mL

Slope Ratio Method

Procedure :

For the study by this method, two series of solution (series A and B) were prepared.

A. <u>Condition of Excess Metal Concentration</u>

A series of solution was prepared by adding fixed amount of bismuth solution (10.00 mL of 10^{-4}F solution) to the varied amount of dye solution (1.00-5.00 mL of 10^{-4}F solution). The pH of each solution was adjusted to 2.50 by the addition of appropriate amount of 0.01 F nitric acid and then diluted to 100 mL with deionized water. The absorbances of solutions were measured at 648 nm against water as a reference using 1 cm cell. Data are shown in Table 6.14 with the corresponding plot in Figure 6.12.

B. Condition of Excess Dye Concentration

The procedure for the preparation of solutions was the same as that described in A, expect the fixed amount of 10.00 mL 10^{-4}F dye solution and varied amount of bismuth solution were employed. The absorbance of each solution was measured at 648 nm against reagent blank using 1 cm cell. Results are shown in Table 6.14 and Figure 6.12

From the two curves, it is shown that the ratio of the slope of curve A to the slope of curve B is equal to 1.2:1 corresponding to 1:1 mole ratio of Bi : 5N-dye complex.

Table 6.14 The detailed data of the slope ratio method

A. Bi(III) >> dye (Bi(III) 10^{-4}F 10.00 mL)		B. Dye >> Bi(III) (Dye 10^{-4}F 10.00 mL)	
Dye 10^{-4}F (mL)	Absorbance at 648 nm	Bi(III) 10^{-4}F (mL)	Absorbance at 648 nm
0.00	0.000	0.00	0.000
1.00	0.031	1.00	0.024
2.00	0.061	2.00	0.050
3.00	0.090	3.00	0.071
4.00	0.117	4.00	0.096
5.00	0.143	5.00	0.116

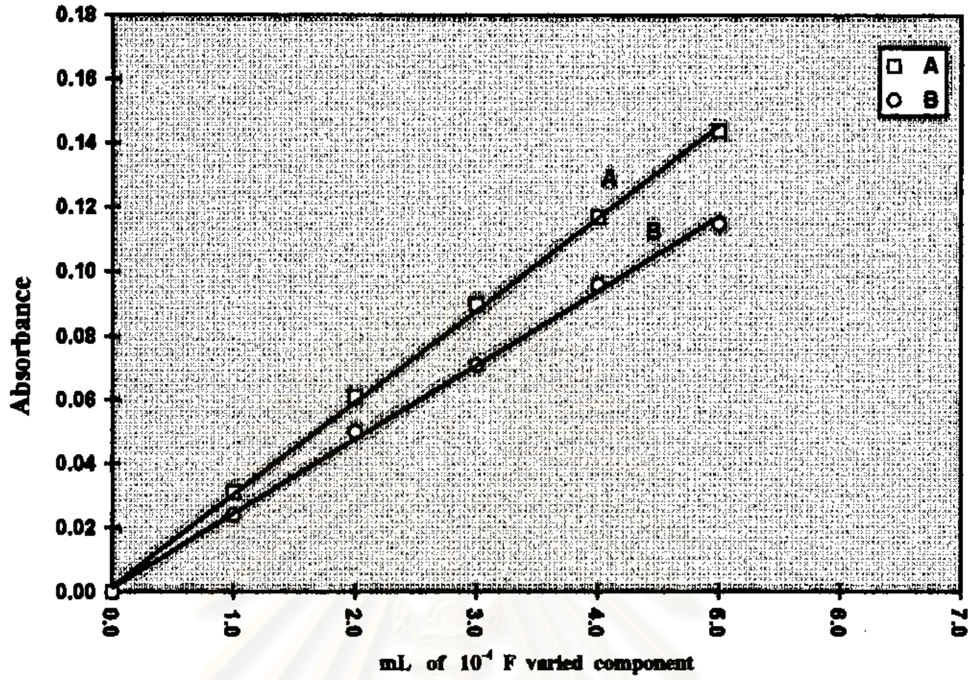

Figure 6.12 Slope ratio method

A : Fixed Bi(III) : 10.00 mL of 10^{-4}F
B : Fixed 5N-Dye : 10.00 mL of 10^{-4}F
Final volume 100 mL

Result obtained from the study of the nature of bismuth(III)-5N dye complex by method of continuous variation, mole ratio method and slope ratio method reveals that the 1:1 mole ratio of bismuth(III)–5N dye complex is formed. This is also confirmed by the absorption spectra of the complex in the next section.

Confirmation of the Nature of the Bismuth(III)–5N Dye Complex by Absorption Spectra

A series of solutions containing various molar ratios of dye to bismuth was prepared. 10.0 mL of 10^{-4}F dye solution was used in each case with 5.0 mL, 10.0 mL, and 20.0 mL of 10^{-4} F bismuth to make a mole ratio of dye to bismuth of 2:1, 1:1, and 1:2 receptively. The pHs of the solutions were adjusted to 2.50 by using 1F nitric acid. The final volume is 100 mL. The spectra of the three solution systems were recorded from 560-800 nm using 1 cm cell and the reagent blank as a reference. The results obtained are shown in Figure 6.13.

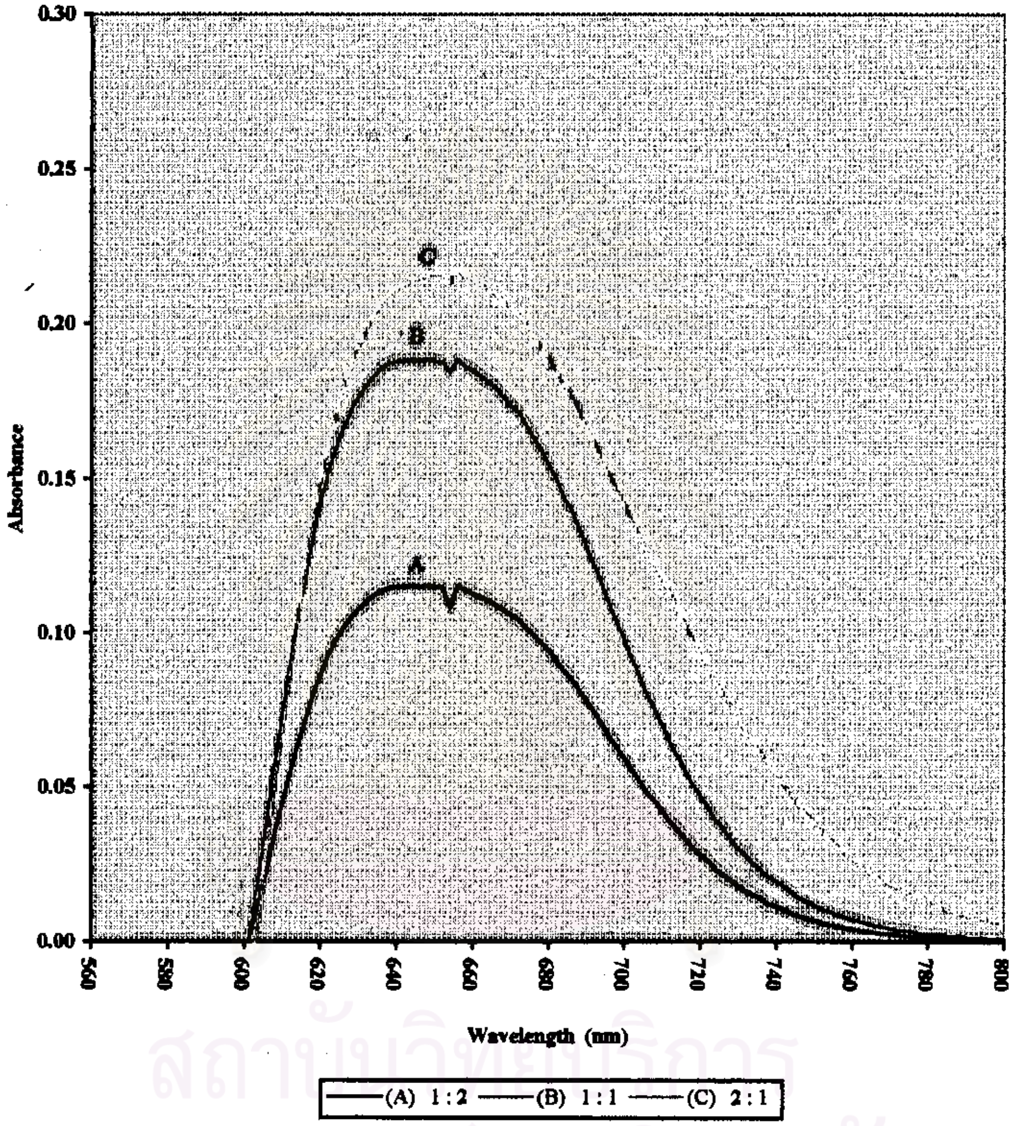

Figure 6.13 Absorption spectra of various bismuth(III)–5N dye ratios at pH 2.50

Bismuth(III)	:	10^{-4}F , 5.0 , 10.0 and 20.0 mL
Dye	:	10^{-4}F, 10.0 mL
Final volume	:	100 mL
Reference	:	Reagent blank

6.5 Visible Spectrometric Studies of Bismuth(III)-5N Dye in Final Volume 25 mL

Visible Spectra of the Complex at Various pHs

Procedure

Eight 10.0 mL aliquots of 10^{-4}F bismuth(III) were pipetted into a series of 50 mL beakers containing accurately 10.0 mL each of 10^{-4} 5N-dye solution. The pHs of the solutions were adjusted to 2.00-6.00 by using nitric acid and ammonia solutions. The solutions were then quantitatively transferred into a series of 25 mL volumetric flask. Small amount of water was added to adjust the volume. The solutions were set aside for complete color development. The absorption spectra of bismuth(III)-5N dye complex at pH 2.00-6.00 measured water as a reference were recorded from 400-800 nm. The absorbances of solutions were also measured against a reagent blank treated in a similar manner as a reference at 560-800 nm (in expanded scale) for easily observation.

Figures 6.14 and 6.15 show the absorption spectra of the bismuth(III)-5N dye complex at various pHs measured against water and reagent blank as references, respectively.

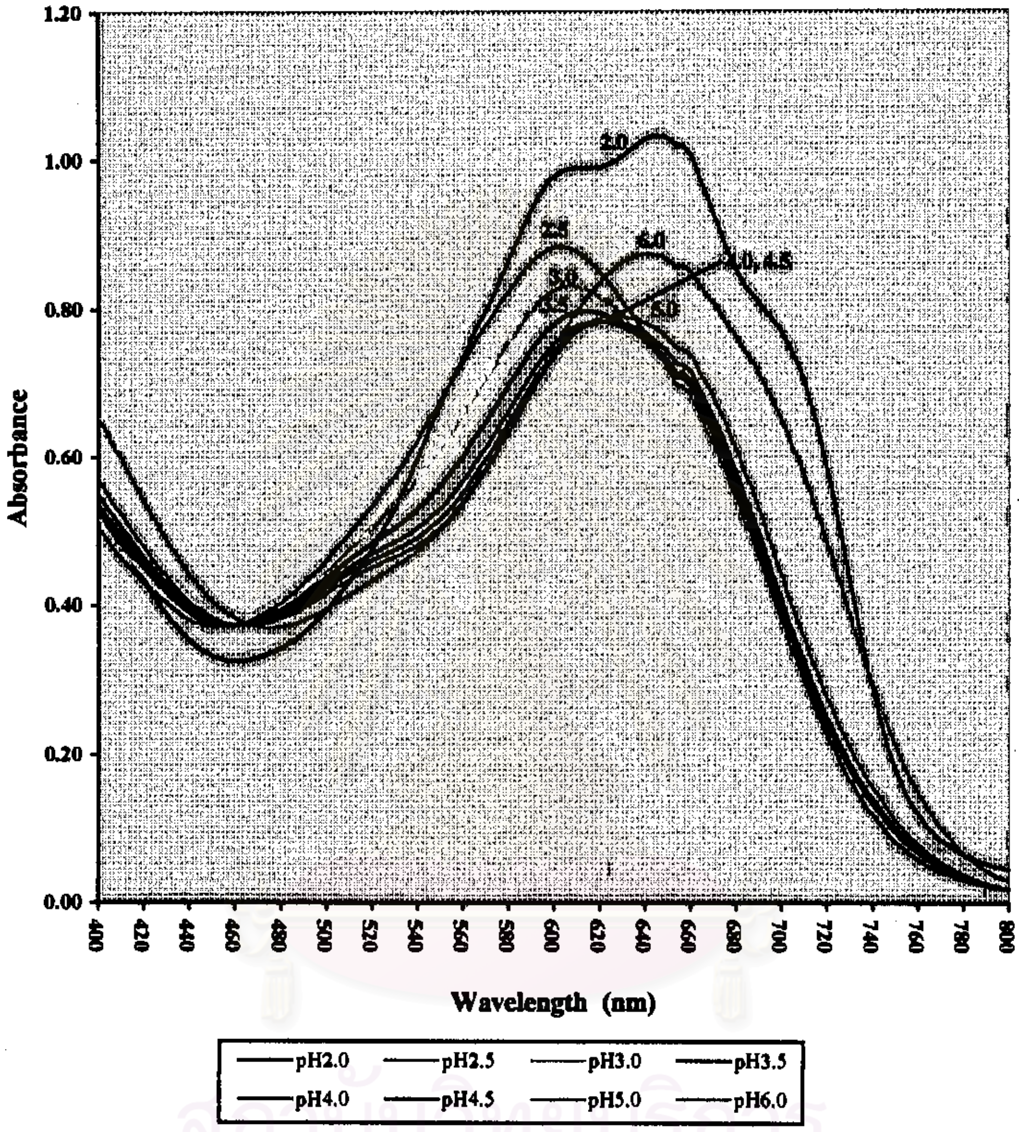

Figure 6.14 Absorption spectra of bismuth(III)-5N dye complex at various pHs (2.00-6.00) measured against water

Bismuth(III)	:	10^{-4} F, 10.0 mL
Dye	:	10^{-4} F, 10.0 mL
Final volume	:	25 mL
Reference	:	Water

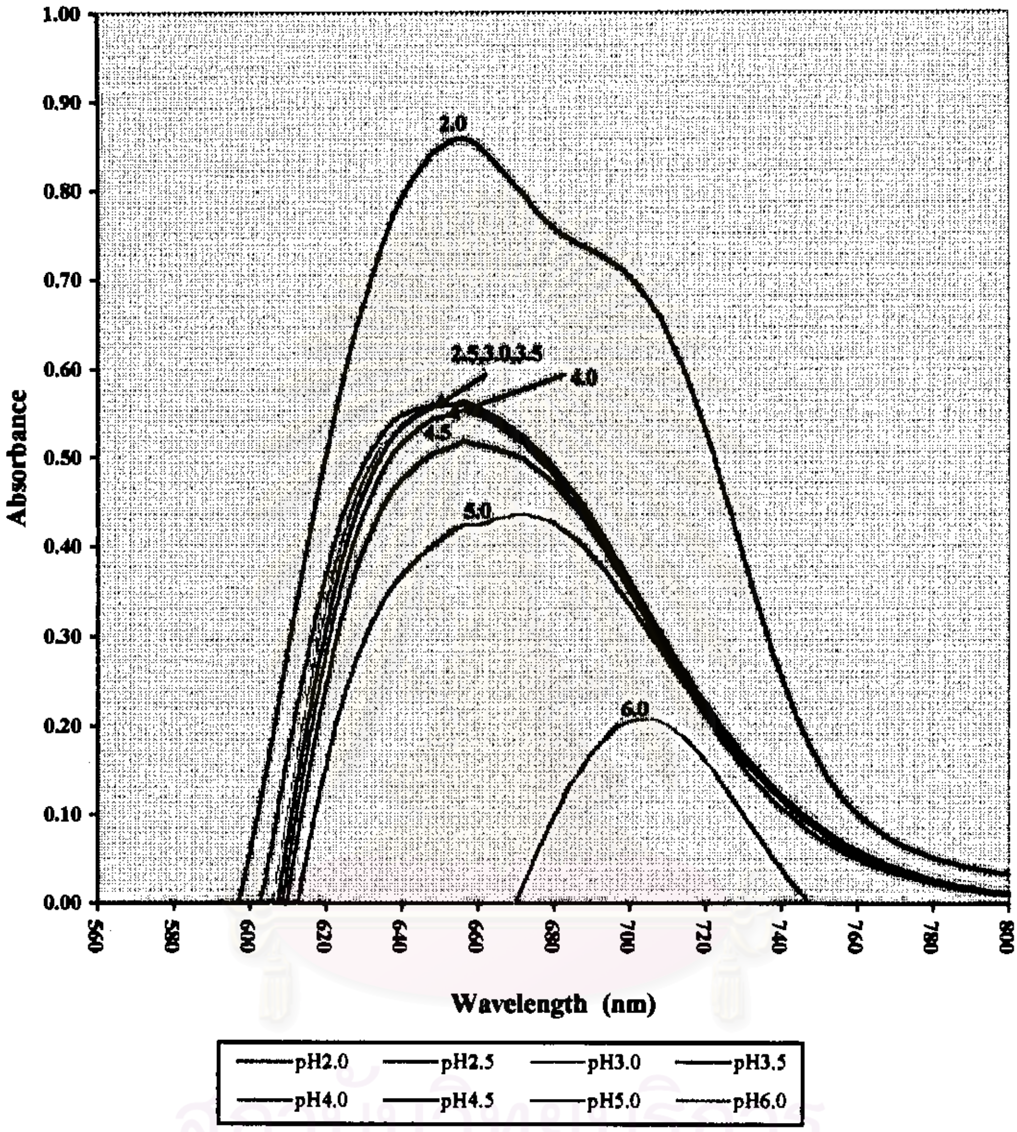

Figure 6.15 Absorption spectra of bismuth(III)-5N dye ccomplex at various pHs (2.00-6.00) measured against dye as reagent blank

Bismuth(III)	:	10^{-4} F, 10.0 mL
Dye	:	10^{-4} F, 10.0 mL
Final volume	:	25 mL
Reference	:	Reagent blank (dye solution)

6.6 Development of Spectrometric Method for the Determination of Bismuth(III) Using 5N-Dye as Metallochromic Reagent in Final Volume 25 mL

Optimal Wavelength

10.0 mL of 10^{-4}F dye solution was pipetted into two 50 mL beakers. One was followed by 1.00 mL of 10^{-4}F bismuth(III) solution. The pHs of bath solutions were adjusted to value of 3.50. Each content was transferred qualitatively to a 25 mL volumetric flask. The spectra of solutions were recorded using water as a reference, scanning from 400-800 nm. The spectra obtained are shown in Figure 6.16.

Inspection of the curves shows that a wavelength of approximately 648 nm gives the greatest difference in absorbance between the reagent blank and the complex.

Optimal pH

The effect of pH on the absorbance of the bismuth(III)–5N dye complex was investigated. A series of solutions containing 4.00 mL of 10^{-4}F bismuth, 10.0 mL of 5N-dye solution and appropriate amount of water was prepared. Nitric acid and ammonia solutions were used for pH adjustment (between 2.0 and 5.0). The final volume was 25 mL. After the color was developed, the absorbances of solutions were measured at 648 nm against the reagent blank which was treated in similar manner. The results obtained are shown in Table 6.15 and the corresponding plot appears in Figure 6.17.

It can be seen that the optimum pH range for analytical purpose lies in a narrow range between 2.50 and 4.00. Therefore, a pH of 3.50 was selected for all further work of this dye.

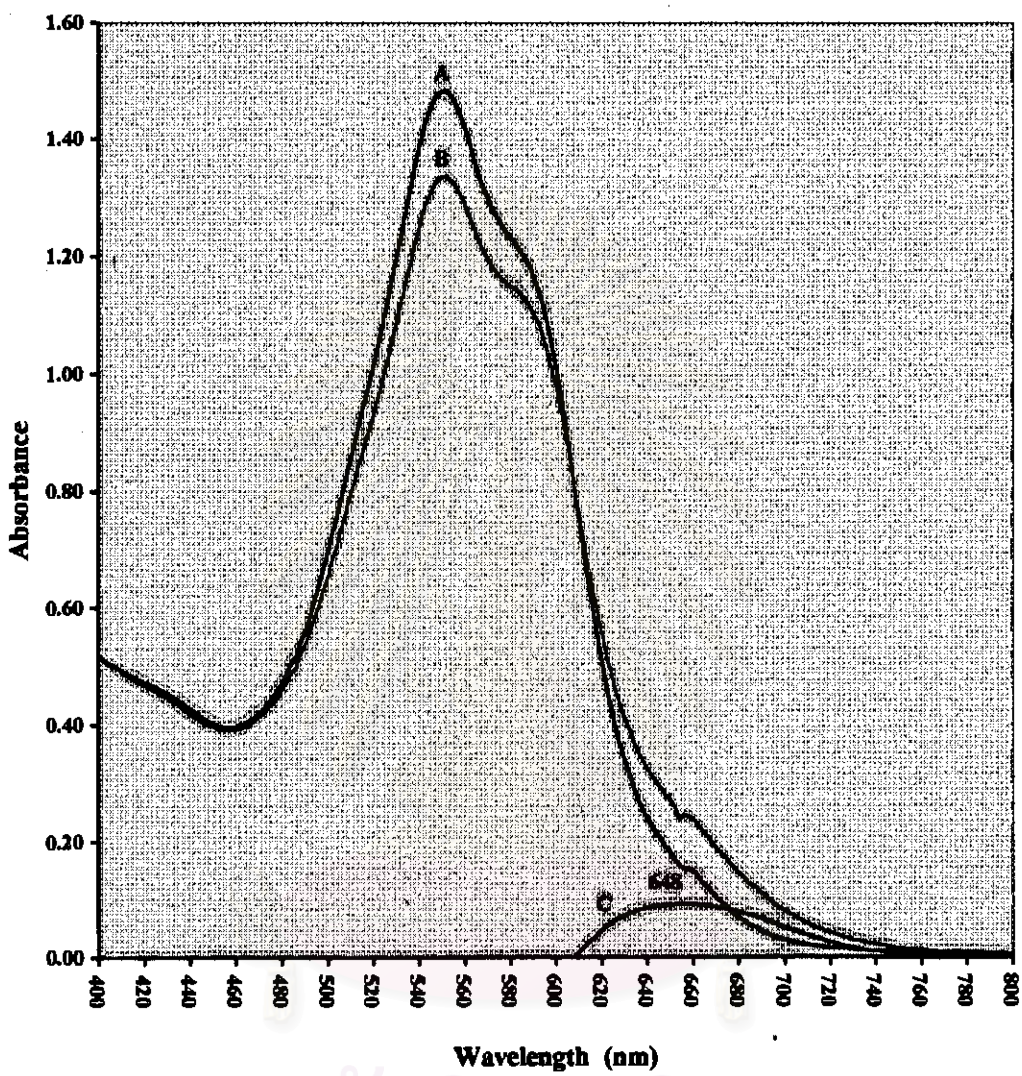

Figure 6.16 Optimal wavelength of the dye and its bismuth(III)-5N dye complex at pH 3.50

A	: Dye 10^{-4}F, 10.0 mL
B	: Dye 10^{-4}F 10.0 mL, Bismuth(III) 10^{-4}F 1.00 mL
A , B Reference	: water
C	: Spectra of B against A
Final volume	: 25 mL

Table 6.15 Optimal pH of bismuth(III)-5N dye complex in final volume 25 mL

pH	Absorbance at 648 nm
2.0	0.343
2.5	0.382
3.0	0.400
3.5	0.400
4.0	0.402
4.5	0.366
5.0	0.302

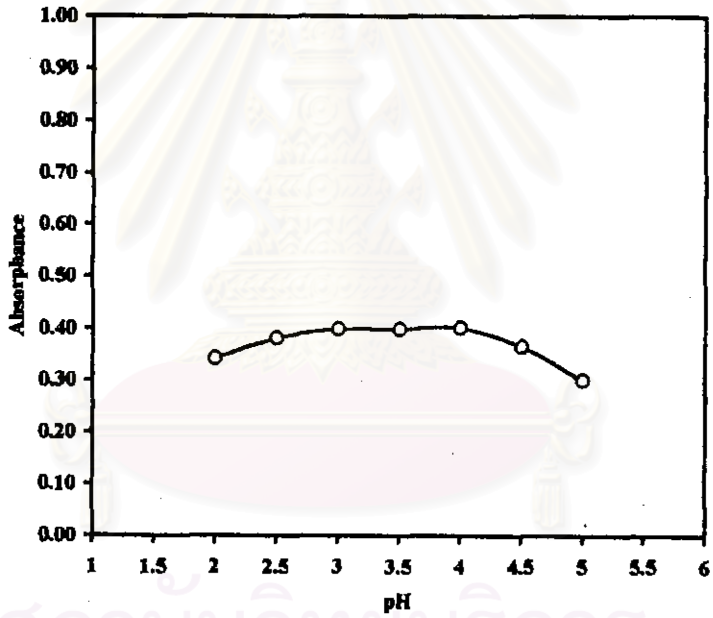

Figure 6.17 Effect of pH on absorbance of bismuth(III)-5N dye complex measured against reagent blank at 648 nm in final volume 25 mL

Dye	: 10^{-4}F 10.0 mL
Bismuth(III)	: 10^{-4}F 4.00 mL
Reference	: Reagent blank

Sequence of Addition

The effect of the sequence of addition of all solutions concerned in the bismuth(III)-5N dye complex. Color development is shown in Tables 6.16 and 6.17.

From the result above, it is rather clear that the order of addition of solutions shows no effect on the color development of bismuth(III)-5N dye complex. In practice, the sequence No.1 was chosen for the subsequent experiments.

Optimal Amount of Dye

The effect of the amount of dye on the absorbance of the bismuth(III)-5N dye complex system was studied by varying the molar ratio of the reagent to bismuth. The amount of metal was kept constant. A series of solutions containing 4.00 mL of 10^{-4}F bismuth with various amount of 10^{-4}F dye solution from 4.00 to 20.00 mL and appropriate amount of water prepared. The pH of each solution was adjusted to 3.50 by 0.01F nitric acid or 0.01F ammonia solution. Each content was then quantitative transferred and diluted to a 25 mL volumetric flask. The absorbance of each solution was measured at 648 nm against the reagent blank using 1 cm cell.

The absorbance of solution containing various ratios of dye to bismuth at pH value of 3.50 are shown in Table 6.18 and the corresponding plot appears in Figure 6.18.

The results in Figure 6.18 show that the absorbance increases with increasing amount of dye reagent up to 8.00 mL and then remains reasonable constant up to 18.00 mL. Therefore in this system, 12.00 mL of 10^{-4} F dye was adopted to be used in the subsequent experiments.

Table 6.16 Sequence of the addition in final volume 25 mL

Sequence No.	Sequence of reagent addition
1	dye , metal , pH adjustment
2	dye , pH adjustment , metal
3	metal , dye , pH adjustment
4	metal , pH adjustment , dye
5	pH adjustment , dye , metal
6	pH adjustment , metal , dye

Table 6.17 Absorbance of solution from the above table in final volume 25 mL

Sequence No.	Absorbance at 648 (against blank)
1	0.403
2	0.402
3	0.399
4	0.401
5	0.400
6	0.402

Note

Dye : 10^{-4} F, 10.0 mL
Bismuth(III) : 10^{-4} F, 4.00 mL
pH : 3.50

Table 6.18 Optimal amount of dye for bismuth(III)-5N dye complex in final volume 25 mL

Bi(III) 10^{-4} F (mL)	Dye 10^{-4} F (mL)	Absorbance at 648 nm
4.00	4.00	0.239
4.00	6.00	0.337
4.00	8.00	0.390
4.00	10.00	0.402
4.00	12.00	0.404
4.00	14.00	0.403
4.00	16.00	0.404
4.00	18.00	0.401
4.00	20.00	0.379

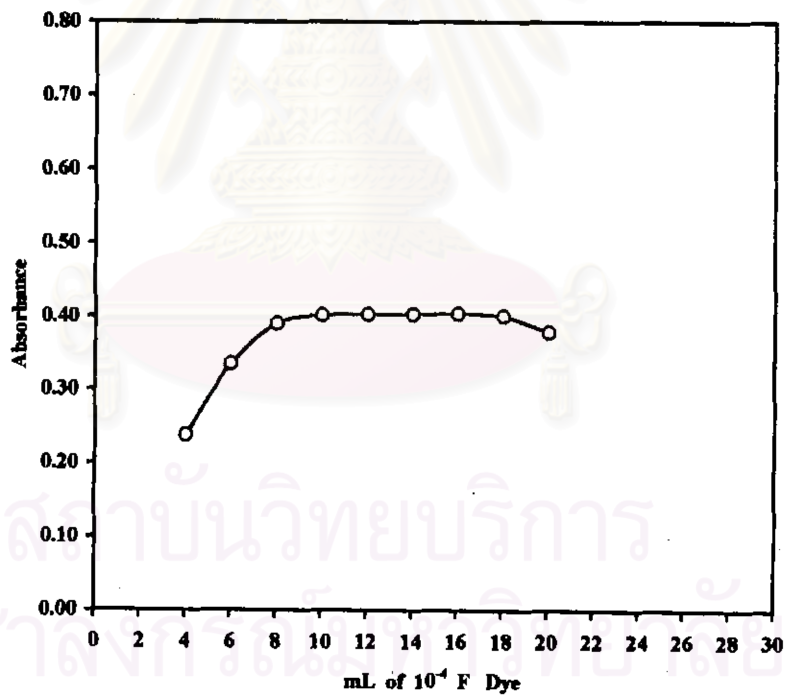

Figure 6.18 Effect of reagent concentration in final volume 25 mL

Bismuth(III) : 10^{-4} F 4.00 mL
Reference : Reagent blank

Optimal Time for Color Development

12.00 mL of 10^{-4}F dye and 4.00 mL of 10^{-4}F bismuth solution were added to an appropriate amount of water in a 50 beaker. The pH of solution was adjusted to 3.50 by 0.01F nitric acid. Then the solution was poured into a 25 mL volumetric flask and adjusted to 25 mL with deionized water. The absorbance of bismuth–5N dye solution was measured immediately after dilution against a reagent blank at 648 nm, using 1 cm cell. The absorbance of the bismuth-5N dye complex solution was then measured periodically at the specified time intervals. Results are shown in Table 6.19 and corresponding Figure 6.19.

The results obtained show that the color of the complex is developed instantaneously and remains constant for at least 48 hours.

Table 6.19 Effect of time on color development of complex in final volume 25 mL

Time (min.)	Absorbance at 648 nm	Time (hr.)	Absorbance at 648 nm
0	0.401	2	0.402
5	0.402	4	0.402
10	0.403	6	0.402
15	0.402	8	0.401
20	0.402	10	0.401
25	0.402	12	0.401
30	0.403	24	0.402
35	0.402	30	0.401
40	0.401	48	0.402
45	0.401		
50	0.400		
55	0.400		
60	0.400		

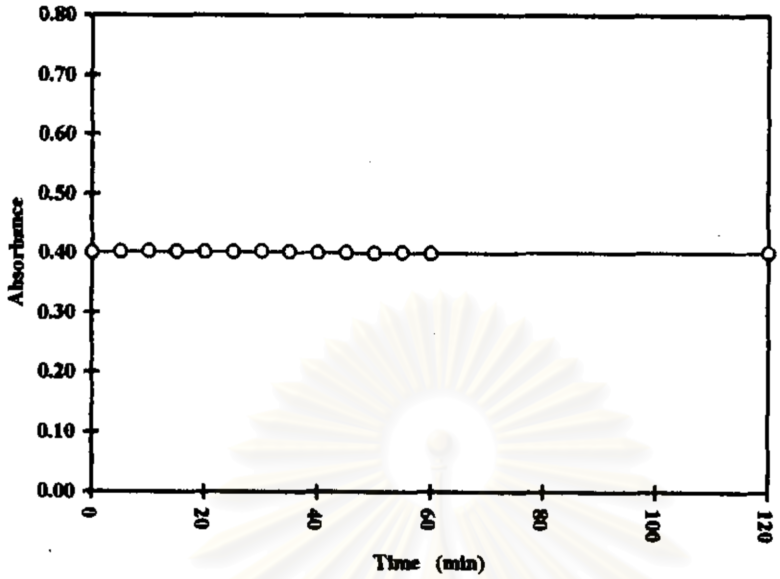

Figure 6.19 The influence of time on the absorbance of the bismuth(III)-5N dye complex in final volume 25 mL

Dye	: 10^{-4} F 12.00 mL
Bismuth(III)	: 10^{-4} F 4.00 mL
Reference	: Reagent blank

Adherence to Beer-Bouguer-Lambert law

Calibration Curve

The linear relationships between the absorbance of the bismuth(III)-5N dye complex and the bismuth concentration was investigated. In this study, 0.20 to 10.00 mL of 10^{-4}F bismuth solutions were pipetted into a series of 50 mL beakers containing 12.00 mL of 10^{-4}F dye solution and appropriate amount of water. The pHs of solutions were then adjusted to pH 3.50 by using 0.01F nitric acid or 0.01F ammonia solution. The solutions were then quantitatively transferred to a series of 25 mL volumetric flask. Small amount of deionized water was added to adjust to the mask. The absorbances of these solutions were measured at 648 nm against the reagent blank using 1 cm cell. The data obtained is shown in Table 6.20 and corresponding plot in Figure 6.20.

The calibration curve is found to obey Beer-Bouguer-Lambert law very well over the range of 10.45 to 125.39 μg of bismuth in 25 mL of solution at 648 nm. The molar absorptivity (ε) is 2.5×10^4 L mol^{-1} cm^{-1}, equivalent to the specific absorptivity (a) of 0.12 mL g^{-1} cm^{-1} and the Sandell sensitivity (S) of 0.0083 μg cm^{-2}.

Table 6.20 Calibration curve of bismuth(III)-5N dye complex: fixed concentration of dye 10^{-4}F 12.00 mL and pH 3.50

Bi(III) 10^{-4} F.		Absorbance at 648 nm
mL	μg/100.0 mL	
0.20	4.18	0.011
0.50	10.45	0.048
1.00	20.90	0.092
1.50	31.35	0.145
2.00	41.80	0.197
2.50	52.24	0.252
3.00	62.69	0.301
3.50	73.14	0.352
4.00	83.59	0.404
4.50	94.04	0.453
5.00	104.49	0.499
5.50	114.94	0.554
6.00	125.39	0.591
7.00	146.29	0.647
8.00	167.18	0.667
9.00	188.08	0.673
10.00	208.98	0.676

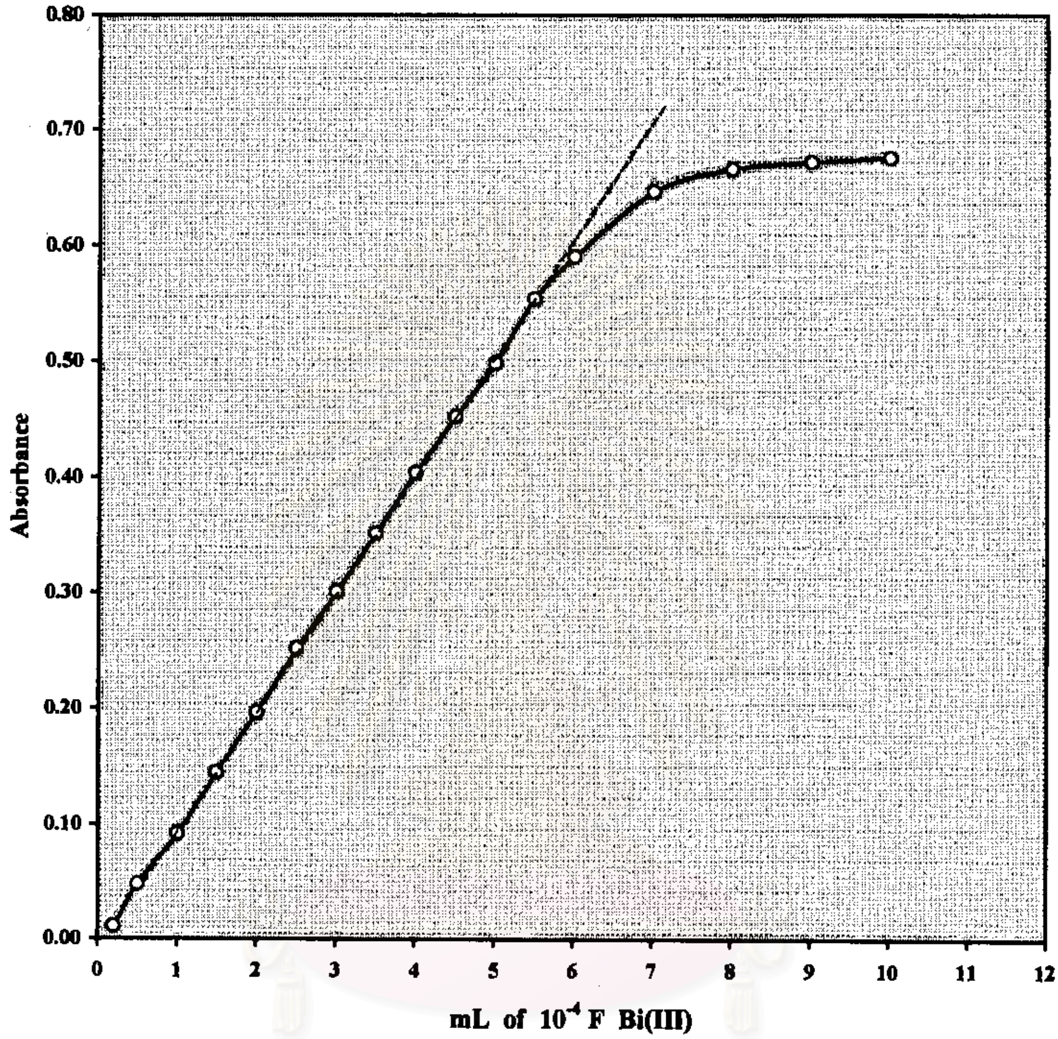

Figure 6.20 Calibration curve of bismuth(III)-5N dye complex in final volume 25 mL

Repeatability of the Method

The repeatability of the developed method was checked by means of the standard deviation of the determination obtained from measuring the absorbance of 10 sets of solution, each containing 12.00 mL of 10^{-4}F dye solution and 3.00 mL of 10^{-4}F bismuth and appropriate amount of water under the optimal conditions. The data obtained is reported in Table 6.21.

The standard deviation, s, was calculated using the formula;

$$s = \pm\sqrt{\frac{\Sigma(x-\bar{x})^2}{n-1}}$$

$\bar{x}$ = 0.303, n = 10, s = 0.0028

∴ Percent standard deviation = 0.28

Percent relative standard deviation

$$\%RSD = \left(\frac{s}{\bar{x}}\right) x100$$

$$= 0.92$$

Table 6.21 Standard deviation study of the method, fixed concentration of dye 10^{-4} F 12.00 mL, bismuth(III) 10^{-4} F 3.00 mL and pH 3.50 in final volume 25 mL

No.	Absorbance at 648 nm
1	0.300
2	0.301
3	0.305
4	0.301
5	0.307
6	0.306
7	0.305
8	0.300
9	0.306
10	0.302

Nature of Bismuth(III)-Dye Complex

Method of Continuous Variation (Job's Method)

Procedure

A series of solution of bismuth(III)-5N dye mixtures containing various mole fraction of bismuth from 0-1 was prepared. The sum of the concentrations of bismuth and the dye was kept at 4 × 10^{-5} mole per liter. After adjustment pH to 3.50, mixtures were diluted to 25 mL. The absorbance of each solution was measured at 648 nm against water as a reference using 1 cm cell. The data is shown in Table 6.22 and the corresponding Job's plot is shown in Figure 6.21.

From Figure 6.21, it shows that a 1 : 2 mole ratio complex is formed between bismuth(III) and the 5N-dye.

Table 6.22 The detailed data of the continuous variation method in final volume 25 mL

Dye 10^{-4} F (mL)	Bi(III) 10^{-4}F (mL)	Mole fraction of bismuth Bi/Bi+dye	Absorbance at 648 nm	
			not corrected	corrected
10.00	0.00	0.0	0.160	0.160-0.160 = 0.000
9.00	1.00	0.1	0.261	0.261-0.144 = 0.117
8.00	2.00	0.2	0.343	0.343-0.129 = 0.214
7.00	3.00	0.3	0.400	0.400-0.111 = 0.289
6.00	4.00	0.4	0.409	0.409-0.097 = 0.312
5.00	5.00	0.5	0.352	0.352-0.081 = 0.271
4.00	6.00	0.6	0.289	0.289-0.034 = 0.255
3.00	7.00	0.7	0.235	0.235-0.047 = 0.188
2.00	8.00	0.8	0.160	0.160-0.032 = 0.128
1.00	9.00	0.9	0.079	0.079-0.019 = 0.060
0.00	10.00	1.0	0.000	0.000-0.000 = 0.000

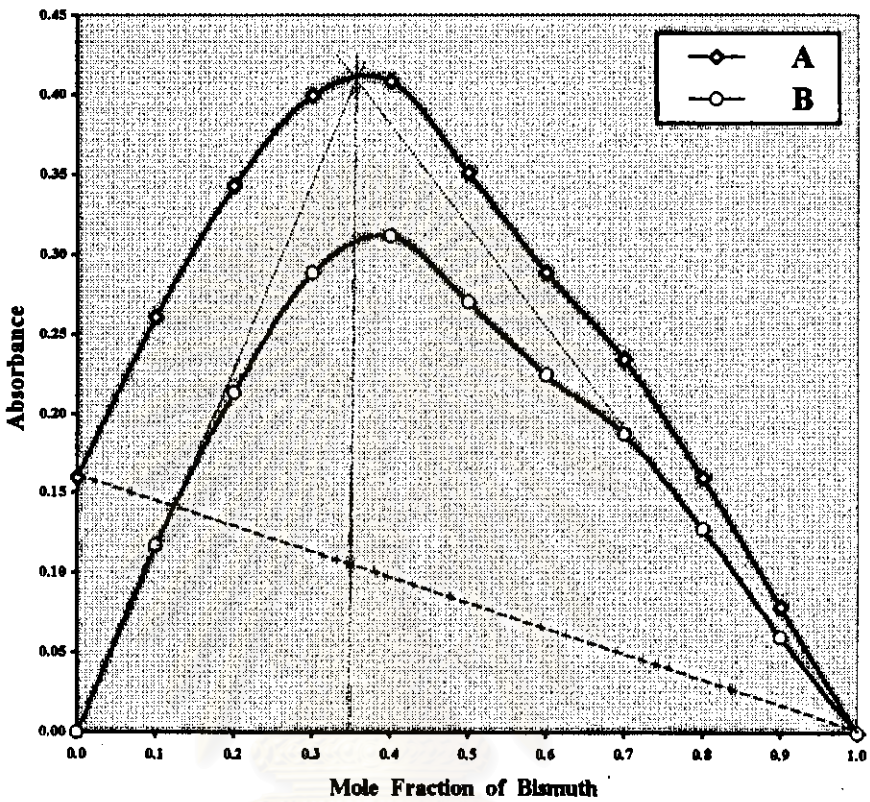

Figure 6.21 Continuous variation method in final volume 25 mL

A : not corrected

B : corrected

The Mole Ratio Method

Procedure

A series of solutions containing equal formal concentration of the dye but different formal concentrations of bismuth was prepared. The concentration of dye was fixed at 2×10^{-5} mole per liter (5.00 mL of 10^{-4}F 5N-dye solution per 25 mL) with variation of 10^{-4}F bismuth 0.00-10.00 mL. The pHs of the solutions were adjusted to 3.50 and final volumes were 25 mL. The absorbance of the solution was measured against a reagent at 648 nm using 1 cm cell. The detailed data is shown in Table 6.23 and the mole ratio plot is shown in Figure 6.22.

From Figure 6.22, the curve exhibits a deflection at 2.8 : 5.0 mole ratio of bismuth : dye indicating 1 : 1.8 or 1: 2 bismuth (III): 5N-dye complex.

Table 6.23 The detailed data of the molar ratio method in final volume 25 mL

Bi(III) 10^{-4} F (mL)	**Absorbance at 648 nm**
1	0.104
2	0.178
3	0.241
4	0.252
5	0.260
6	0.265
7	0.275
8	0.281
9	0.285
10	0.291

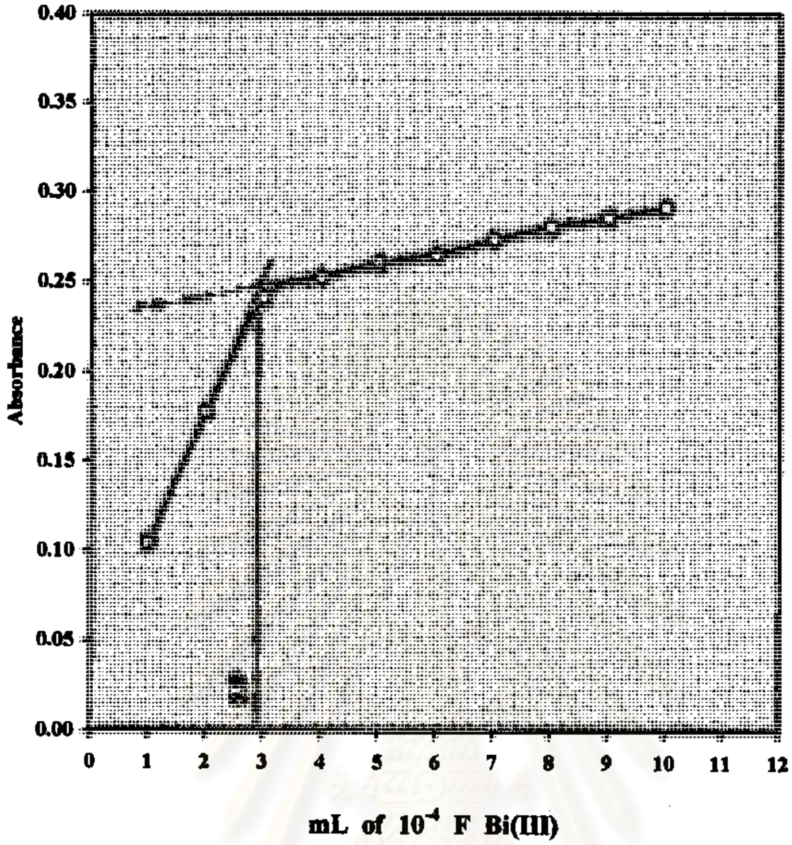

Figure 6.22 Mole ratio method in final volume 25 mL

Fixed dye : 5.00 mL of 10^{-4}F