



ESTIMATION OF THIOACETAMIDE USING PHOTOCHEMICAL EXCHANGE REACTION OF SODIUM NITROPRUSSIDE

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ABSTRACT

A simple, sensitive, inexpensive, reliable and quantitative method has been developed for the determination of thioacetamide using sodium nitroprusside (SNP) as a spectroscopic probe. This method indicates that the sodium nitroprusside can react with the thioacetamide to form a colored product in the light reaction. Sodium nitroprusside is a photolabile complex and it undergoes photochemical ligand exchange reactions rapidly. The absorbance of the product is measured at the maximal absorption wavelength of 540.8 nm, and the amount of thioacetamide can be calculated based on this absorbance by using calibration curve. The good linear relationship of the concentration of thioacetamide versus absorbance is observed with a linear range of $1.48 \times 10^{-4} - 9.5 \times 10^{-4}$. The linear regression equation is $A = 0.017x + 0.006$, with the correlation coefficient of 0.999. The effects of different parameters like pH, change of concentration of sodium nitroprusside, concentration of ligands, light intensity etc. on percentage error were investigated. The efforts were made to minimise the percentage error and some optimum conditions were obtained. The progress of photochemical reaction for sample solution has been observed spectro-photochemically and the product was isolated and characterized. A tentative mechanism for this reaction has been proposed.

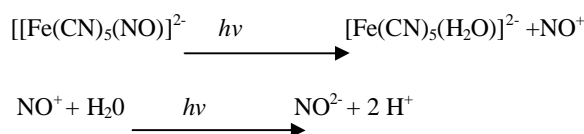
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INTRODUCTION

Sodium nitroprusside contains cyanide ligands that are not easily replaced chemically. An effort has been made to substitute this ligand by another anionic ligand like thioacetamide ion. Sulphur containing organic compounds having the grouping $-C=S$, possess several medicinal and industrial applications. A novel visible spectrophotometric method for the determination of methanol using sodium nitroprusside as spectroscopic probe has been investigated¹. Aqueous solution of sodium nitroprusside undergoes a complex decomposition process in the presence of light². Photochemical hydroxylation of salicylic acid derivatives with hydrogen peroxide, catalyzed with Fe (III) and sensitized with methylene blue has been investigated³. It has been reported that SNP can react with nucleophilic agents such as primary or secondary aliphatic amines, aldoximes, phenols and thiols, due to the nucleophilicity of nitroso in the SNP molecules⁴⁻⁵. Estimation of thiosalicylic acid using photochemical exchange reaction of sodium nitroprusside has been studied⁶. Kinetic studies of the photoinduced formation of transition metal-dinitrogen complexes using time-resolved infrared and UV-vis spectroscopy was studied⁷. Synthesis and structural characterization of potassium salts of phosphine substituted cyclopentadienyl iron dicyanides and their use as bridging ligands for copper (I) phosphine derivatives was

investigated^{8a}. The synthesis and structural characterization of double metal cyanides of iron and zinc, catalyst precursors for the copolymerization of carbon dioxide and epoxides were analysed^{8b}. A mechanistic study of photochemistry of the $[\text{Fe}(\text{CN})_5\text{N}(\text{O})\text{SR}]^{3-}$ complex was carried out⁹. It was investigated that an aqueous solution of $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ was converted into $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ on irradiation in the presence of hydrogen peroxide¹⁰. A blue product was also reported, when this reaction was carried out in the presence of thiourea¹¹, thiosulphate^{12 & 13}, and amines¹⁴. This blue product was proposed to be $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$.

The reaction pathway has been proposed as



It was reported that the photoproduct are $[\text{Fe}(\text{CN})_5(\text{OH})]^{4-}$ or $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ as evident from e.s.r. spectral observations. A blue product was also formed, when a solution of nitroprusside in N, N – dimethyl formamide was irradiated. This blue product was identical with the product obtained by electrolytic reaction of nitroprusside solution¹⁰. Photochemical and photosensitized reactions involving 1-nitronaphthalene and nitrite in aqueous solution is also investigated¹⁵. The cyanamide ligand trans to the NO group is reported to have a preferential

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exchange was investigated¹⁶. Synthesis of novel N-1, 6-disubstituted 5-Cyno 2-thioacetamide derivatives as antinociceptive agents was investigated^{17, 18}. The photocatalysed exchange reaction between $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ and CN^- has been studied. pH control on the rate and mechanism of nitrosylation of water-soluble Fe(III) porphyrin complexes is investigated¹⁹. Mechanistic studies on the reactions of cyanide with a water-soluble Fe(III) porphyrin and their effect on the binding of NO was reported²⁰. Photochemical reaction involving nitrosylpentacyanoferrate (II) -bromide system using cadmium sulphide as semiconductor was studied²¹. It was reported²² that the structure of this blue-product is $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$. Reactions of thiourea with nitroprusside give a red colored adduct, which is gradually converted into a blue product. Photodegradation of reactive dyes by photo-Fenton reagent was investigated²³. It has been reported²⁴ that aqueous solution of sodium nitroprusside undergoes a complex decomposition process in the presence of light and effect of Riboflavin on the photolysis of Cyanocobalamin in aqueous solution has been studied²⁵. A novel spectrophotometric determination of atenolol using sodium nitroprusside is carried out²⁶. The chemical reduction of nitroprusside solution in water and in N,N-dimethylformamide were reported that the nature of reduced product depends on the acidity of the medium. The products have been tentatively assigned the structures as $[\text{Fe}(\text{CN})_5(\text{NO})]^{3-}$ or $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ ²⁷. However, no studies in the literature to date have been reported on the estimation of thioacetamide with sodium nitroprusside. Results of these experiments show that the SNP can react with thioacetamide to form a colored product. The absorbance of the product is linear to a certain extent to the concentration of thioacetamide. This method is simple and rapid, and it needs neither the especial apparatus nor valuable reagents. The proposed method has been successfully applied on estimation of thioacetamide using sodium nitroprusside with satisfactory results.

MATERIALS AND METHODS (EXPERIMENTAL)

Materials Used

The following chemicals were used in the present investigations. The specifications of these chemicals are indicated against each in Table.

Preparation of Reagents and Stock Solutions

All the reagents were of analytical grade and were prepared in doubly distilled water.

A) Preparation of M/100 Sodium Nitroprusside

Aqueous solution of M/100 sodium nitroprusside was prepared by mixing 100 ml water and 0.2979 gms sodium nitroprusside and kept in dark.

B) Preparation of M/100 Thioacetamide

Stock solution of the thioacetamide was prepared by dissolving 0.0751 gm in 100 ml distilled water for preparing M/100 aqueous solution and kept in dark.

C) Preparation of Sulfuric acid solution

Stock solution of H_2SO_4 was prepared by diluting the calculated volume of acid with double distilled water and finally determined its concentration by titrating it

against standard NaOH solution used phenolphthalein as indicator.

D) Preparation of Sodium Hydroxide solution

Stock solution of NaOH was prepared by diluting the calculated amount of NaOH with double distilled water and finally determined its concentration by titrating it against standard NaOH solution with sodium carbonate (Na_2CO_3) using phenolphthalein as the indicator.

Control Experiment

Sodium nitroprusside (M/500) and thioacetamide (M/100) were used in present investigation. There was no reaction between sodium nitroprusside (substrate) and thioacetamide (ligands) in the absence of light. The presence of light was found necessary for the reaction to proceed, thus, justifying that the reaction is photochemical and not a thermal (dark or chemical) reaction. Following procedure is used to identify the photo sensitive products.

Solution of (M/100) thioacetamide was taken and divided into four parts.

- 1) First beaker containing thioacetamide solution was kept in darks for 4-5 hrs.
- 2) Second beaker containing thioacetamide solution was exposed to light.
- 3) M/500 of sodium nitroprusside (SNP) was added in 3rd beaker which was containing thioacetamide solution and kept in the dark.
- 4) M/500 of sodium nitroprusside (SNP) was added to the fourth beaker which was containing the thioacetamide solution and exposed to light.

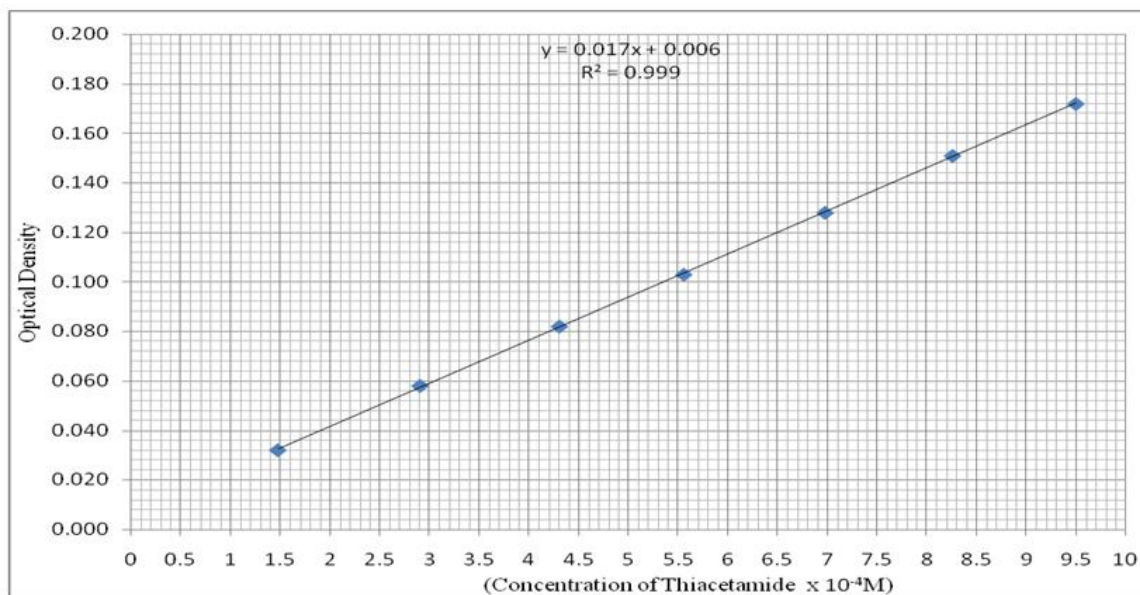
These beakers were kept for 4 hrs, then absorbance of solution in each beaker was measured. It was observed that the solution in the first three beakers had the almost same initial absorbance while the solution in the fourth beaker had changed in its initial value of absorbance and color was also changed. Thus, by performing black experiment it was confirmed that the reaction between sodium nitroprusside and thioacetamide photochemical.

CONSTRUCTION OF CALIBRATION GRAPHS FOR THE SPECTRO-PHOTOMETRIC METHOD

An aliquot solution of thioacetamide containing (1.96×10^{-4} to 9.50×10^{-4} M) was transferred into 50 ml volumetric flask, then 20 ml of (M/500) sodium nitroprusside solution was added one by one, was placed in dark for one minute in the order to establish equilibrium between adsorption and desorption, than these mixture were exposed to a 200 W tungsten lamp one by one for 16 min. A water filter was used to cut off thermal reaction. A change in color of solution was observed from light red to dark pink violet color. A aliquot of 3 ml solution was taken out from each reaction mixture and change in optical density was observed spectrophotometrically at $540.8 \lambda_{\text{max}}$. (Results Shown in Table No. 01) A graph (Figure 01) Calibration curve for concentration of thioacetamide) was plotted between optical density and known conc. of thioacetamide i.e. $[1.48 \times 10^{-4}, 2.91 \times 10^{-4}, 4.31 \times 10^{-4}, 5.66 \times 10^{-4},$

Table 1. Optical Density

S. NO.	Volume of SNP	Volume of Thioacetamide	Concentration Of Thioacetamide	Time	λ_{\max}	Optical Density
						at 540.8 λ_{\max}
1	20 ml	0.3 ml	1.48×10^{-4}	16 Min	540.8	0.019
2	20 ml	0.6 ml	2.91×10^{-4}	16 Min	540.8	0.056
3	20 ml	0.9 ml	4.31×10^{-4}	16 Min	540.8	0.077
4	20 ml	1.2 ml	5.56×10^{-4}	16 Min	540.8	0.099
5	20 ml	1.5 ml	6.98×10^{-4}	16 Min	540.8	0.112
6	20 ml	1.8 ml	8.26×10^{-4}	16 Min	540.8	0.144
7	20 ml	2.1 ml	9.50×10^{-4}	16 Min	540.8	0.168

**Figure 1. Calibration curve for estimation of thioacetamide**

6.98×10^{-4} , 8.26×10^{-4} & 9.50×10^{-4} M] A straight line was obtained, which was used as a calibration curve which shown in graph no 01. Beer's Law was obeyed over this concentration range. The regression equation was found to be $y = 0.017x + 0.006$ and the correlation coefficient (r^2) of the calibration curve was found 0.999. The concentration of sample solution was determined by using following methods and the percentage error was calculated for sample solution of thioacetamide. This Standard calibration curve method was used for the estimation. Now we have taken 1.0 ml sample of known concentration of thioacetamide was mixed in 20 ml of sodium nitroprusside (M/500), the mixture was placed in dark for one minute in the order to establish equilibrium between adsorption and desorption, than the mixture was exposed to a 200 W tungsten lamp under identical condition for 16 minutes. The optical density was measured spectrophotometrically and concentration of thioacetamide was determined from calibration curve. Different parameters were optimized for determination of thioacetamide. Each analysis was done in triplicated and average value were used for graphs formation.

Rate Constant for Photochemical Reaction of Sample Solution

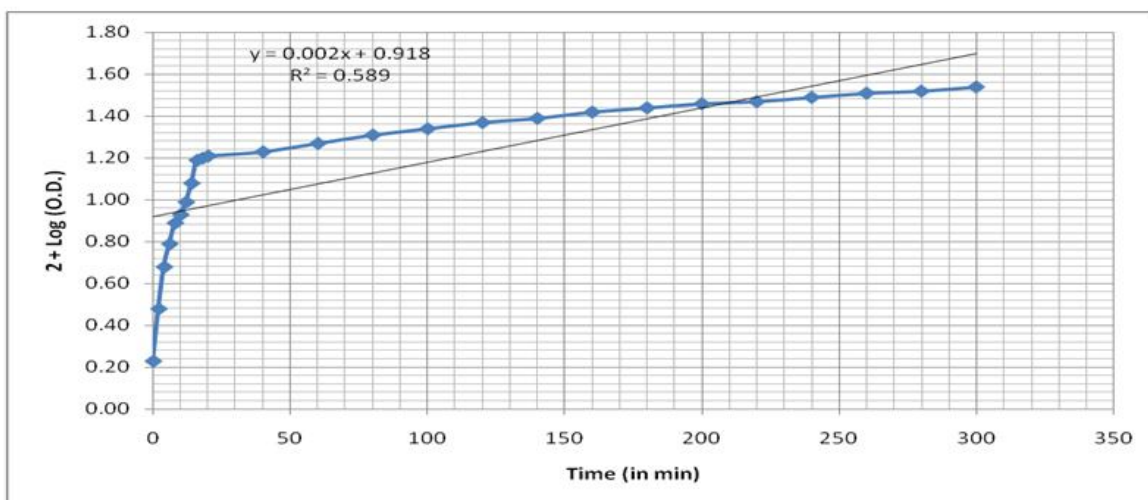
An aliquot sample solution of known concentration of thioacetamide containing 1 ml (M/100), transferred into a 50

Table 2. Rate of progress reaction for sample solution

Time (in minutes)	Optical Density at λ_{\max} 540.8 nm
0	0.017
2	0.03
4	0.048
6	0.062
8	0.078
10	0.086
12	0.098
14	0.12
16	0.154
18	0.158
20	0.162
40	0.168
60	0.186
80	0.203
100	0.218
120	0.232
140	0.248
160	0.261
180	0.273
200	0.288
220	0.296
240	0.308
260	0.32
280	0.332
300	0.345

Table 3. Rate of progress reaction for sample solution

Time (in minutes)	Optical Density at λ_{\max} 540.8 nm	2+ [-log (OD)]
0	0.017	0.23
2	0.03	0.48
4	0.048	0.68
6	0.062	0.79
8	0.078	0.89
10	0.086	0.93
12	0.098	0.99
14	0.12	1.08
16	0.154	1.19
18	0.158	1.20
20	0.162	1.21
40	0.168	1.23
60	0.186	1.27
80	0.203	1.31
100	0.218	1.34
120	0.232	1.37
140	0.248	1.39
160	0.261	1.42
180	0.273	1.44
200	0.288	1.46
220	0.296	1.47
240	0.308	1.49
260	0.32	1.51
280	0.332	1.52
300	0.345	1.54

**Figure 2. Rate of reaction of sample solution**

ml volumetric flask and 20 ml (M/500) sodium nitroprusside was added into volumetric flask. The mixture was exposed to a 200 W tungsten lamp (Philips). A water filter was added to cut off thermal reaction. The absorbances at different reaction time (0, 20, 40, 60, 80, 100, 120, 140, 300) were measured at 540.8 λ_{\max} at 25 degree c, the results is shown in table #02 which shows progress of the photochemical reaction.

SPECTROSCOPIC ANALYSIS

Scanning electron microscopy (SEM)

Vacuum oven dried powder samples of the thioacetamide and sodium nitroprusside were mounted on a sample holder and coated with gold. The samples were examined with a scanning electron microscope (Model Carl-Zeiss Leo VP 1430) at an accelerating voltage of 20 kV and 202X magnifications.

Infra Red Spectroscopy

Thioacetamide, Sodium nitroprusside and product were characterized by FT-IR using a Perkin-Elmer Spectrum GX

FT-IR system, by taking 10.0 mg of sample in 600mg KBr. All spectra were average of two counts with 10 scans each and a resolution of 5 cm^{-1} .

The progress of the photochemical reaction (Table 2.)

Was observed by taking absorbance at regular time intervals using spectrophotometer (Simadzu UV-visible 1800).

A graph (Figure 2-Graphs of rate of reaction for sample solution) was plotted between time (Minutes) and 2 + log (Optical Density).

ELEMENTAL ANALYSIS

Elemental analysis was performed using C, N, O, S and H analyzer (Perkin Elmer-2400, CHNS/O Analyzer) and cysteine was used as a standard. Total Nitrogen (N) was also estimated by Kjeldahl method on a KEL PLUS-KES 201 Digestion unit

attached to KEL PLUS- CLASSIC DX Distillation unit (M/s PELICAN Equipments, Chennai, India). The values of nitrogen which were analyzed by elemental analyzer (Perkin Elmer-2400) and by Kjeldahl method were comparable.

RESULTS AND DISCUSSION

Rate of Reaction

The progress of the photochemical reaction was observed by taking absorbance at regular time intervals using spectrophotometer and rate of progress reaction for sample solution (Table No. 02) plotted on graphs for determination of Rate constant. Figure 02 (Plotted graphs for rate of reaction for sample solution.) It was observed that a plot of $2+\log(\text{OD})$ v/s time was found to be straight line, it is confirming that the reaction follows first order kinetics. The rate of reactions indicated as.

$$K = 2.303 \times \text{Slope}$$

The value of the rate constant of this reaction was found to be $K=4.606 \times 10^{-3}$

Percentage Photo Efficiency of reaction

The % photo efficiency of reaction (Table 4) for sample was calculated by using the following equation:

$$\eta = \frac{C_F - C_0}{C_F} \times 100$$

Where,

η = Percentage of Photo efficiency

$C_0 = C_0$ is optical density of solution before irradiation.

$C_f = C_f$ is optical density of solution after irradiation of time t.

A graph (Figure 3-Graphs for Photo percentage efficiency for sample solution) was plotted between time (Minutes) and Photo percentage efficiency.

Table 4. Photo percentage efficiency

Photo percentage efficiency		
Time (in minutes)	O.D.	Efficiency %
0	0.017	0
20	0.162	90
40	0.168	90
60	0.186	91
80	0.203	92
100	0.218	92
120	0.232	93
140	0.248	93
160	0.261	93
180	0.273	94
200	0.288	94
220	0.296	94
240	0.308	94
260	0.32	95
280	0.332	95
300	0.345	95

Effect of various optimizing species on the photochemical reaction and calculation of the percentage error

Experimental conditions that directly affect the rate of photochemical reaction of mixture of compound (SNP and thioacetamide) during processes include the pH, initial concentration of Sodium nitroprusside, concentration of

thioacetamide and intensity of light. We studied following effects on sample solution which are shown in following Table.

Effect of pH

The effect of pH on quantitative estimation of thioacetamide was studied at different pH range. The results are reported in Table A-1 and are shown graphically in Figure A-1.

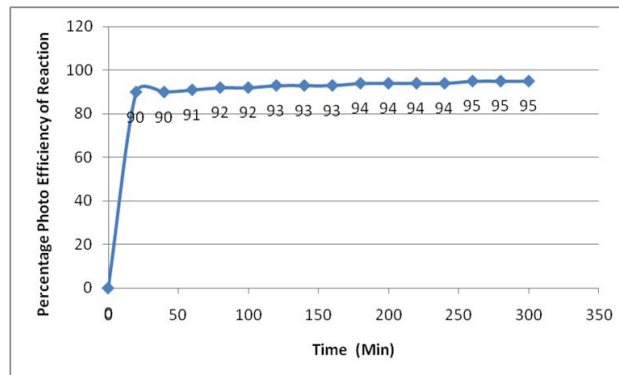


Figure 3. Photo percentage efficiency of sample solution

Table A-1. Effect of pH

[SNP] = 4.4×10^{-3} M	[Thioacetamide] = 6.2×10^{-3} M
Light intensity = 6.9×10^2 Lux	$\lambda_{\text{max}} = 540.8$ nm
pH	% Error
2.0	67.39
2.5	66.30
3.0	65.22
3.5	63.04
4.0	58.70
4.5	54.35
5.0	47.83
5.5	26.09
6.0	14.13
6.5	6.52
7.0	2.17
7.1	1.09
7.2	2.17
7.5	7.61
7.9	15.22
8.0	21.74
8.5	25.00
9.0	29.35
9.5	32.61

It was observed that the minimum error (1.09 %) in the estimation of thioacetamide is found at pH=7.1 i.e. Only 1.09 % error is within permissible limit. Below pH = 7.1, thioacetamide exists as form of protonated cation and above pH= 7.1 value, the % error increases indicating complex formation between thioacetamide and SNP. It seems that the anionic form of thioacetamide acts as good ligand than its cationic form.

Effect of Sodium Nitroprusside Concentration

In order to test the influence of amount of SNP on the quantitative estimation of thioacetamide, the range from 1.20×10^{-3} to 6.6×10^{-3} M (every 20 ml) of SNP was submitted to the proposed procedure, keeping all other factors identical. The absorbance was measured and it gets to the minimal when the concentration of SNP is 4.4×10^{-3} M. Then if the amount of SNP is increased, the absorbance is nearly invariable. Therefore, 4.4×10^{-3} M of SNP was selected for the optimum

experimental condition in the later experiments. The results are reported in Table A-2 graphically shown in Figure A-2.

Table A – 2. Effect of Sodium Nitroprusside Concentration

[Thioacetamide Acid]= 6.2×10^{-3} M	pH = 7.1
Light intensity= 6.9×10^2 Lux	$\lambda_{\max}=540.8$ nm
[SNP] x 10^{-3} M Conc.	Error (%)
1.2	88.04
1.5	86.96
1.8	80.43
2.2	71.74
2.5	53.26
2.8	45.65
3.3	28.26
4.0	10.87
4.3	4.35
4.4	1.09
4.5	6.52
4.7	10.87
4.8	15.22
5.0	23.91
6.0	57.61
6.6	82.61

It was perceived that the minimum percentage error in the estimation of thioacetamide is found at sodium nitroprusside concentration 4.4×10^{-3} M i.e. only 1.09 %, which is within permissible limit. As the concentration of sodium nitroprusside was increased, the complex formation tendency increases and it reaches to a maximum at sodium nitroprusside concentration 4.4×10^{-3} M; but if the concentration was further increased, it starts acting like an internal filter. It will not permit the desired light intensity to reach sodium nitroprusside molecule in the bulk of the solution and as a consequence, only limited number of sodium nitroprusside molecule will be excited to participate in the complex formation resulting into an increase in percentage error.

Effect of thioacetamide Concentration

In order to test the influence of concentration of thioacetamide on the quantitative estimation of thioacetamide, the range from 2.0×10^{-3} to 10.0×10^{-3} M (every 1.0 mL) of thioacetamide was submitted to the proposed procedure, keeping all other factors identical. The absorbance was measured and absorbance gets to the minimal when the concentration of thioacetamide is 6.2×10^{-3} M. Then if the amount of thioacetamide is increased, the absorbance is nearly invariable. Therefore, 6.2×10^{-3} M of

Table A-3. Effect of Thioacetamide Concentration

[SNP] = 4.4×10^{-3} M	pH = 7.1
Light intensity = 6.9×10^2 Lux	$\lambda_{\max}=540.8$ nm
[Thioacetamide] x 10^{-3} M	Error (%)
2.00	58.70
2.50	55.43
3.30	53.26
4.00	32.61
4.50	29.35
5.00	25.00
5.50	11.96
6.00	5.43
6.20	1.09
6.60	4.35
7.00	6.51
7.50	14.13
7.90	19.57
8.00	30.43
8.50	35.87
9.00	41.30
10.00	57.61

Thioacetamide was selected for the optimum experimental condition in the later experiments. The results are reported in Table A-3, graphically shown in Figure A-3. It was observed that the minimum error in the estimation of thioacetamide is found at thioacetamide concentration 6.2×10^{-3} M i.e. only 1.09 % which is within permissible limit. As the concentration of thioacetamide increases the complex formation tendency increases and hence the percentage error found in estimation of thioacetamide is minimum but as the concentration is increased more than 6.2×10^{-3} M there may be possibility of some larger units (2 or more than 2 molecules) of thioacetamide bind together through intermolecular hydrogen bonding. Such a unit will not participate in complex formation due to its larger size and lower nucleophilicity, therefore limited complex formation takes place resulting into increase in error at higher concentration of thioacetamide.

Effect of Light Intensity

In order to study the influence of light intensity on the quantitative estimation of thioacetamide, we varied the distance between the exposed surfaces of the reaction mixture and tungsten lamp (light source), keeping all other factors identical. The light intensity was measured from 3.0×10^2 to 8.5×10^2 Lux and absorbance gets to the minimal when the 6.9×10^2 of light intensity was exposed to reaction mixture. The results are reported in Table A-4, graphically shown in Figure A-4.

Table A-4. Effect of Light Intensity

[Thioacetamide] = 6.2×10^{-3} M	pH = 7.1
[SNP] = 4.4×10^{-3} M	$\lambda_{\max} = 540.8$ nm
[Light intensity] x 10^2 Lux	Error (%)
3.0	38.04
3.5	35.87
4.0	31.52
4.5	23.91
5.0	10.87
5.5	8.70
6.0	6.52
6.5	4.35
6.7	3.26
6.8	2.17
6.9	1.09
7.0	1.09
7.1	1.09
7.5	1.09
8.0	1.09
8.5	1.09

It is observed that the minimum percentage error in the estimation of thioacetamide is found at light intensity= 6.9×10^2 i.e. only 1.09 % which is within permissible limit. Then if the light intensity on reaction mixture is increased, the absorbance is constant. As the light intensity increases the number of photons striking per unit area per second will also increase. As a result, the complex formation became little bit easier on increasing light intensity, on further increase the light intensity beyond 6.9×10^2 the error remains almost constant indicating that the desired light intensity for maximum(complete) formation of complex requires this much intensity and any increase will not increase the amount of complex formed. This will result into a constant error above this intensity. Therefore, 6.9×10^2 of light intensity was selected for the optimum experimental condition.

Optimum Condition

The photochemical reaction between sodium nitroprusside and thioacetamide was carried out. It was observed that if the estimation of thioacetamide is carried out under these given conditions the percentage error observed is minimum (1.09 %) and within permissible limit.

The optimum conditions are given below

1. pH = 7.1
2. [Sodium Nitroprusside] = $4.4 \times 10^{-3} \text{M}$
3. [Thioacetamide] = $6.2 \times 10^{-3} \text{M}$
4. Light Intensity = $6.9 \times 10^2 \text{Lux}$

PRODUCT ANALYSIS

The photochemical reaction between sodium nitroprusside and thioacetamide was carried out. It was observed that the initial light red color of the reaction mixture in natural medium finally turned into dark pink violet when exposed to light. The reaction was allowed to proceed to completion (there is no change found in optical density after long exposure to light) and then it was filtered. The filter was evaporated on a water bath. The product was separated by using fractional crystallization method. It was re-crystallized to pinkish brown crystals with methanol giving Pinkish Brown of the product, which was analyzed as follows....

UV (water) λ_{max} : 775

Elemental analysis: The elemental analysis carried out with product is shown below Table No. 04.

Table 5. The Elemental Analysis

Element	Found (%)	Calculated (%)
Fe	18.15	18.06
C	23.10	23.23
Na	14.70	14.84
S	10.40	10.32
N	27.24	27.10
O	5.03	5.16

Scanning electron microscopy (SEM) analysis

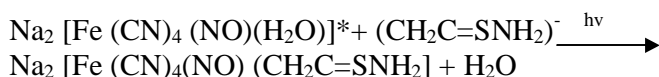
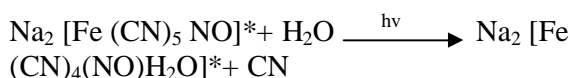
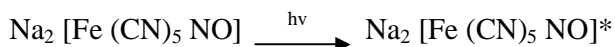
The scanning electron micrograph (SEM) images of the parent sodium nitroprusside (SNP), thioacetamide and reaction products were distinctly different and indicated significant changes on the surface morphology of sodium nitroprusside (SNP) and thioacetamide and indicated that photochemical reaction had indeed taken place as shown in Figure A-5 (A, B and C). The parent SNP appeared to have sheet like clustered morphology and thiosemicarbazide appeared to have cloud like morphology, while those of product appeared to have definite shapes similar to rectangular and/or triangular geometries (Figures A-5-C) and can be distinguished easily from the nitroprusside and thioacetamide. This fact points a substantial entry of thioacetamide moiety in the reaction product (Figures A-5-C), substantiating difference in the structure of the SNP and thioacetamide (Figures A-5-A and C). The SEM images were supportive evidence for photochemical ligand exchange reaction which indicate integrated molecular construction.

Infra Red Spectroscopy

A comparison of IR spectra of thioacetamide, sodium nitroprusside and product clearly indicates that cyanide ligands are sufficiently removed from the coordination sphere of the iron (the characteristic band of CN⁻ ligand at 2142 cm^{-1} is sufficiently reduced in the IR spectrum of product) and similarly found that characteristic bands of NO⁺ ligand at 1938 cm^{-1} appeared in product spectra which was indicating presence of NO⁺ ligand in coordination sphere of the iron. It is recognized that thioacetamide ion has characteristic bands at 3194 cm^{-1} , 1666 cm^{-1} , 1390 cm^{-1} , 1300 cm^{-1} , 1085 cm^{-1} and 971 cm^{-1} . It is also observed that bands at 3367 cm^{-1} , 1666 cm^{-1} , 1390 cm^{-1} and 1085 cm^{-1} were appeared in the IR spectrum of the product. The broad peak observed at 3367 cm^{-1} is due to the stretching vibrations of NH₂ group which is Hydrogen bonded. The 1666 cm^{-1} , vibrational mode was almost observed in the same frequencies as in product due to the presence of (CH₂C=SNH₂)⁻ group. The symmetric and asymmetric stretching of C=S are also observed at 1390 cm^{-1} . The IR peak related to NH₂ moiety also signifies that the NH₂ molecule is available in coordination complex. The IR peak at 1085 cm^{-1} indicating the presence of mean stretching vibration of the N-O band. In general, it is clear that appearance of new stretching vibration absorption is related to (C-S), (C-N) and NH₂ group.

MACHANISM

On the basis of IR, SEM, elemental analysis and UV observations, a tentative mechanism for the photochemical ligand exchange reaction of sodium nitroprusside and thioacetamide is proposed as follows.



This is expected that the sodium nitroprusside is excited by absorbing incident radiations of desired wavelength. Then its excited state reacts with water molecules and the water molecules enter in coordination sphere of iron, replacing CN⁻ ion. This exchange is energetically favorable because neutral ligand (H₂O) can replace anion i.e ligand (CN⁻). Now thioacetamide ion (a weaker ligand) can easily replace water molecule of the coordination sphere of iron. The ligand exchange reactions are well known in the field of coordination chemistry but these reactions involve ordinary replacement of a weaker ligand by a stronger ligand, such reaction is both thermodynamically and kinetically favorable. It does not seem feasible to have reverse exchange i.e. substituting a stronger ligand by a weaker ligand. But in the present case a stronger ligand is substituted by a weaker ligand thus present work not only provides a pathway for this unfavorable reaction, but also it will open further avenues for such photochemical ligand exchange reactions.

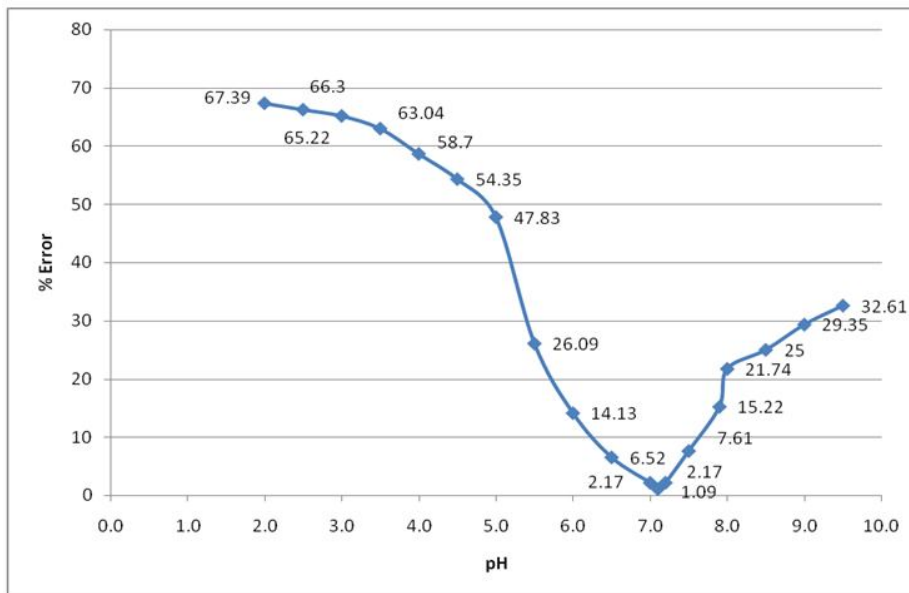


Figure A-1. Effect of pH

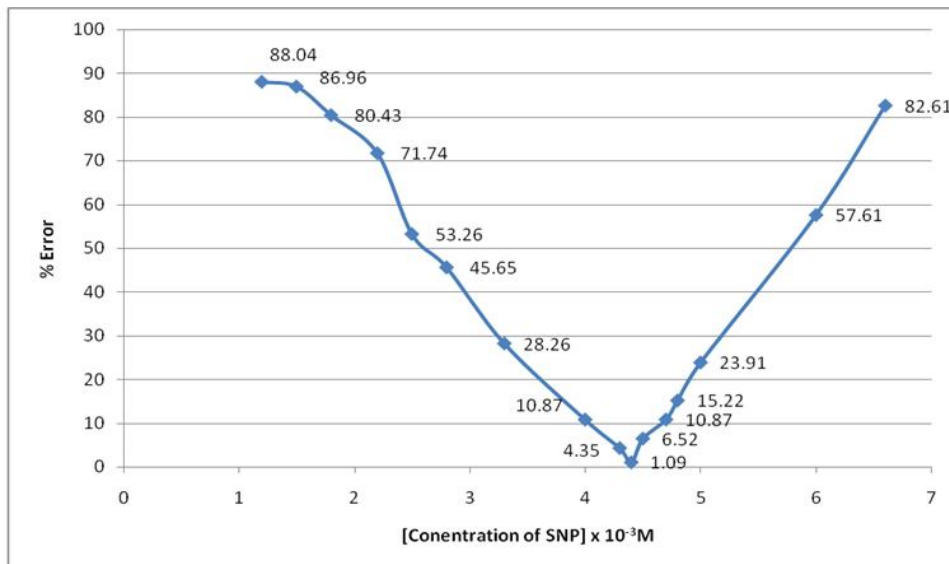


Figure A-2. Effect of Sodium Nitroprusside Concentration

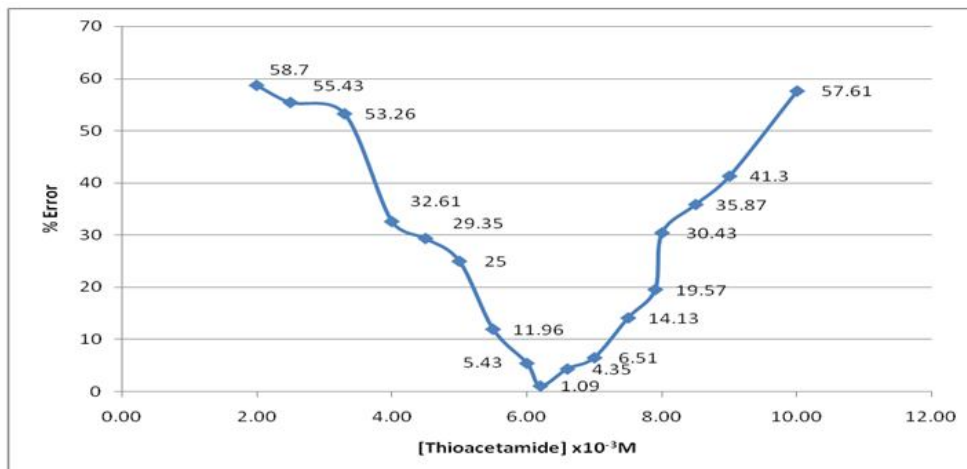


Figure A-3. Effect of Thioacetamide Concentration

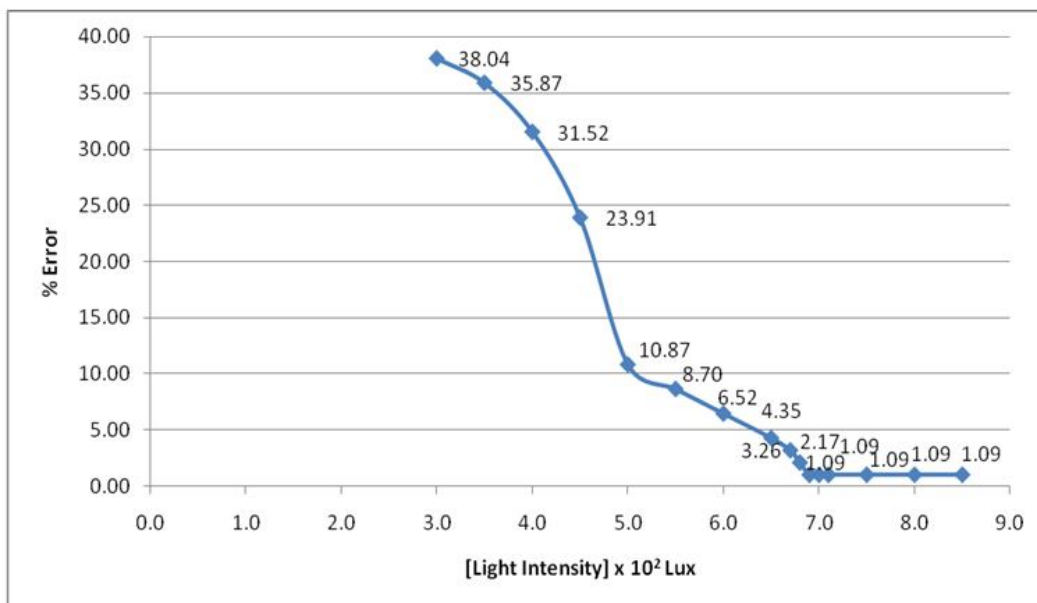
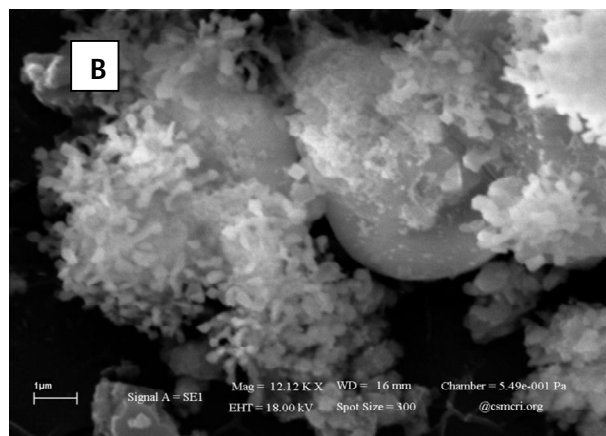
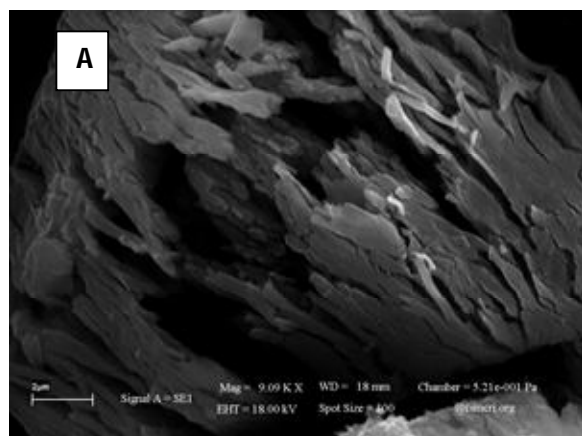


Figure A-4. Effect of Light Intensity



Figures A-5 Scanning electron micrographs of (A) sodium nitroprusside (B) thioacetamide and (C) product

Conclusion

This research establishes a novel method that utilizes sodium nitroprusside for the determination of the thioacetamide. The experiment shows that compound react with sodium nitroprusside to form a coloured pinkish brown product in the basic solution. The absorbance of the product is measured at the maximal absorption wavelength of 540.8 nm, and the amount of thioacetamide can be calculated based on this absorbance using calibration curve. The good linear relationship of the concentration of thioacetamide versus absorbance is observed with a linear range of $1.48 \times 10^{-4} \text{M}$ to $9.5 \times 10^{-4} \text{M}$. The linear regression equation is $A = 0.017x + 0.006$, with the correlation coefficient of 0.999. Meanwhile, the amount of compound can also be calculated based on the absorbance. It was observed that if the estimation of compound is carried out under following conditions the percentage error observed is minimum and within permissible limits.

1. pH = 7.1
2. [Sodium Nitroprusside] = $4.4 \times 10^{-3} \text{M}$
3. [Thioacetamide] = $6.2 \times 10^{-3} \text{M}$
4. Light Intensity = $6.9 \times 10^2 \text{Lux}$

The tentative reaction mechanism is proposed for reaction of sodium nitroprusside and thioacetamide in presence of light. This is simple, rapid, inexpensive, selective, sensitive and convenient quantitative method for the determination of compound using photochemical exchange reaction of sodium nitroprusside.

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