# Estimation of thiosulphate using sodium nitroprusside by a newer photochemical method

**Ravi Sharma, Shailendra Singh Rathore[1], Pawan Sharma[2], Ajay Sharma[3]**

*Govt. College, Sheoganj, Sirohi, Rajasthan, India*
*[1]P.G. Deptt. of Chemistry, Govt. College, Sirohi, Rajasthan, India*
*[2]Govt. Sr. Sec. School, Dantrai, Sirohi, Rajasthan, India*
*[3]Head, P.G. Deptt. of Chemistry, Govt. College, Sirohi, Rajasthan, India*

---

## Abstract

Determination of thiosulphate using photochemical exchange reaction of sodium nitroprusside has been investigated. It is an inexpensive, faster and convenient quantitative method. Sodium nitroprusside is a photolabile complex which undergoes photochemical ligand exchange reactions rapidly. Some recent efforts have been made to utilise such reactions for the estimation of some nitrogen containing anions and electron rich organic molecules. The progress of the reaction is observed spectrophotometrically. The effects of different parameters like pH, change of concentration of sodium nitroprusside, concentration of ligands, light intensity etc. on percentage error was investigated. The efforts were made to minimise the percentage error and some optimum conditions were obtained. Such reaction can be used for the determination of thiosulphate in the range of millimoles to micromoles; hence it is important to know whether such estimations can be done successfully and that too with the desired accuracy.

**Keywords:** Thiosulphate, sodium nitroprusside, photochemical exchange reaction, quantitative, percentage error, optimum conditions.

---

## Introduction

Photochemistry plays a pivotal role in a number of chemical and biological processes. Photochemistry of biological reactions is a rapidly developing subject and helps in understanding of phenomena like Photosynthesis, Phototaxis, Photoporiodism, Photodynamic action, vision and mutagenic photo effect of light.

Generally photochemistry is the chemistry of excited electronic states of molecules. An electronic excitation is simply regarded as a process, whereby an electron is removed from an orbital with certain bounding characteristics and reinserted in another orbital with different characteristics and these excited states are generated by excitation of compounds, atoms or molecules using appropriate wavelengths in the ultraviolet or visible region of the spectrum.

It is apparent that the absorption or emission of radiation to/from these states is the concern of spectroscopists as well as the photochemists. Photosensitized reactions are widely used in many technical and biological areas.

Asilturk *et al.*[1] reported the effect of $Fe^{3+}$ ion doped $TiO_2$ on the photodegradation of malachite green dye under UV-visible irradiation. High photocatalytic activity of Fe-doped $TiO_2$ nano tubes was observed by Deng *et al.*[2]. Wachter *et al.*[3] observed the photochemical reactivity of a dye precursor 4-chloro-1, 2-phenylenediamine they also studied the mutagenic effects of this precursor. Zita *et al.*[4] investigated the correlation between photooxidation and photoreduction of dyes over $TiO_2$ films. The photocatalytic properties of $TiO_2$ nano tubes coated with gold was given by Malwadkar *et al.*[5].

Chen *et al.*[6] showed the activities of different metal oxide as photocatalyst on no reduction and cooxidation. The photodegradation of arylmethane and azo dyes over $TiO_2/In_2O_3$ nano composite films reported Skorb *et al.*[7]. Sun *et al.*[8] reported the photocatalytic activity of titanium cobalt oxides in the degradation of methyl orange. Photo induced transformation of some organophosphorous pesticides over $TiO_2$ was investigated by Calza *et al.*[9]. Reddy *et al.*[10] showed the photocatalytic activity of $Bi_2O_3$ for the treatment of phenolic wastes.

Photodegradation of reactive dyes by photo-Fenton reagent was investigated by Garcia *et al.*[11]. Supale and Gokavi[12] studied the oxidation of sulfides to sulfoxides using chromium (III) as a catalyst with 30% $H_2O_2$. Photocatalytic degradation of acetaldehyde over $TiO_2$ pellets was carried out by Horikoshi *et al.*[13]. Photocatalytic hydrogen production from aqueous solutions of alcohol using visible light responsive $TiO_2$ thin films was reported by Fukumoto *et al.*[14]. Zhang & Maggard[15] investigated photocatalytically active hydrated forms of amorphous titania, $TiO_2$ center dot $nH_2O$.

Yu & Chuang[16] studied the adsorbed species and photogenerated electrons during photocatalytic oxidation of ethanol on $TiO_2$ whereas photocatalytic transformation of acid orange 20 and Cr(VI) in aqueous $TiO_2$ suspensions was studied by Papadam *et al.*[17]. Heterogeneous photodegradation of naphthalene in water was carried out by Lair *et al.*[18]. Mattos and Resi[19] proposed a kinetic modal for photocatalytic reaction describing the diffusion and particle size of semiconductor. Photodegradation and adsorption of 1,4-dioxane on $TiO_2$ was carried by Yamazaki *et al.*[20]. A comparison between $TiO_2$ and Fenton plus photo-Fenton in a solar pilot plant was reported by Maldonado *et al.*[21].

The effect of inorganic anions on the $TiO_2$ based photocatalytic oxidation of aqueous ammonia and nitrite was reported by Zhu *et al.*[22]. Srinivas *et al.*[23] observed photooxidation of beta picoline to nicotinic acid over vanadia/titania catalyst . Sarkha *et al.*[24] investigated the selective oxidation of meta-and para-phenylphenol photosensitized by $[Co(NH_3)_5N_3]^{2+}$ in aqueous solution. Nemono *et al.*[25] studied photodecomposition of ammonia to dinitrogen and dihydrogen on $Pt/TiO_2$ nanoparticles in an aqueous solution. Photochemical and spectroscopic properties of solutions of Pt(II) complex with bis(salicylidene) ethylenediamine were observed by Shagisultanova and Ardashova[26]. Photodegration of Rhodamine B in aqueous solution via $SiO_2$ - $TiO_2$ nano-spheres was reported by Wilhelm and Stephanwhile[27]. Otsuka and Udea[28] used $TiO_3$-$TiO_2$ composite powder for the photocatalytic bleaching of methylene blue. Chen *et al.*[29] studied photocatalytic oxidation of aromatic aldehydes with Co(II)-tetra-(benzoyl-oxyphenyl) prophyrin and molecular oxygen. Photodegradative treatment of waste water by U.V./$TiO_2$ process was investigated by Liu *et al.*[30].

## Experimental Section

A 100 mL stock solution of thiosulphate (M/100) and 100 mL stock solution of sodium nitroprusside (M/100) were prepared by dissolving 0.2481 g of sodium thiosulphate and 0.2979 g of sodium nitroprusside in doubly distilled water. 20 mL of stock sodium nitroprusside solution was diluted to 100 mL to form M/500 concentration and then it was divided into five equal parts (20 mL each). In each beaker the solution of (M/100) thiosulphate was mixed as 0.4 mL, 0.8 mL, 1.2 mL, 1.6 mL and 2.0 mL and all the beakers were exposed to a 200 watt tungsten lamp for 15 minutes. A change in colour of solution was observed from light red to peacock blue. An aliquot of 5.0 mL solution was taken out from each reaction mixture and change in optical density was observed spectrophotometrically at $\lambda$max = 620 nm. A graph was plotted between optical density and known concentration of thiosulphate i.e.[1.96 x $10^{-4}$ M, 2.91 x $10^{-4}$ M, 3.84 x $10^{-4}$ M, 5.66 x $10^{-4}$ M, 7.42 x $10^{-4}$, 8.23 x $10^{-4}$ M]. A straight line was obtained, which was used later on as a calibration curve. 1.0 mL sample solution of known thiosulphate concentration was mixed in 20 mL of sodium nitroprusside (M/500) and it was exposed to tungsten lamp under identical conditions. The optical density was measured spectrophotometrically and the concentration of sample solution was determined by the calibration curve. From this determined concentration the percentage error was calculated for thiosulphate sample solution.

### Effect of pH

The photochemical reaction of sodium nitroprusside in presence of thiosulphate ion may be affected by the variation in pH value and as such the determination of thiosulphate ion may also be affected accordingly. Therefore the effect of pH on quantitative determination of thiosulphate ion was studied at different pH range. The results are reported in Table 1 and graphically shown in Figure 1.

**Table-1: Effect of pH**

| [SNP] = 1.12 x $10^{-2}$ M | [Thiosulphate] = 5.40 x $10^{-3}$ M |
|---|---|
| Light Intensity = 12.0 mWcm$^{-2}$ | $\lambda_{max}$ = 620 nm |
| **pH** | **Error (%)** |
| 2.0 | 3.8 |
| 2.2 | 3.0 |
| 2.5 | 2.1 |
| **3.1** | **1.8** |
| 3.5 | 2.2 |
| 4.0 | 2.6 |
| 5.0 | 3.2 |
| 6.5 | 3.8 |
| 7.0 | 4.0 |
| 8.0 | 4.2 |

The minimum error was observed in the determination of thiosulphate at pH = 3.1 i.e. only 1.8. The $pK_{a1}$ and $pK_{a2}$ values of thiosulphuric acid are 0.60 and 1.5-1.7 respectively. The pH required for minimum error was observed to be 3.1, which indicates that thiosulphuric acid gives thiosulphate ions at this pH and above.

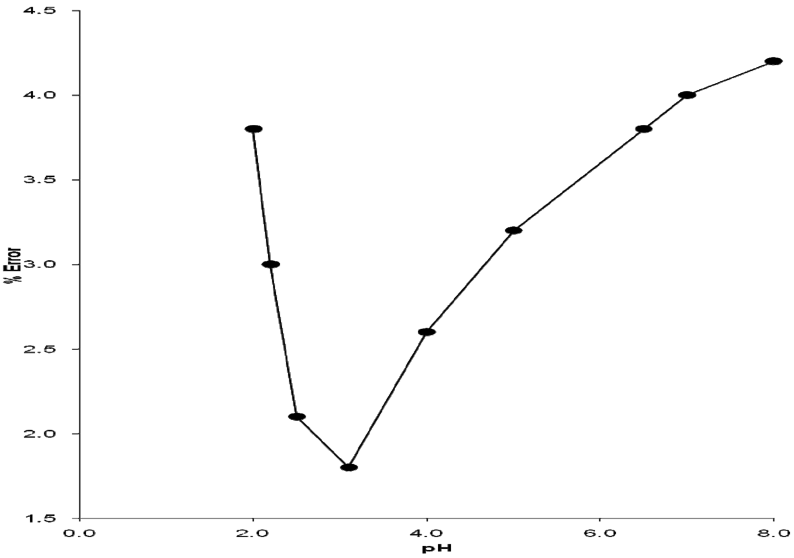

**Fig. – 1 : Effect of pH**

This thiosulphate ion will replace some other ligand from the coordination sphere of iron to form peacock blue complex. As the pH was increase, more availability of thiosulphate ions results in minimum error but as the pH was increase further, percentage error increases again indicating that greater availability of thiosulphate hinders the complex formation.

*Effect of thiosulphate concentration*

The effect of the concentration of thiosulphate ion on the determination was also observed by taking different concentration of thiosulphate and keeping all other factors identical. The results are reported in Table 2 and graphically shown in Figure 2.

**Table-2. Effect of Thiosulphate Concentration**

| | |
|---|---|
| [SNP] = 1.12 x $10^{-2}$ M | pH = 3.1 |
| Light Intensity = 12.0 mWcm$^{-2}$ | $\lambda_{max}$ = 620 nm |
| **[Thiosulphate] x $10^3$ M** | **Error (%)** |
| 1.60 | 4.8 |
| 2.80 | 4.0 |
| 3.00 | 3.4 |
| 3.50 | 3.2 |
| 4.40 | 2.4 |
| 4.80 | 2.0 |
| **5.40** | **1.8** |
| 6.40 | 2.6 |
| 7.40 | 3.4 |
| 8.00 | 4.1 |

It was observed that the minimum error in the determination of thiosulphate ion is found at thiosulphate ion concentration 5.40 x $10^{-3}$M i.e. only 1.8% which is within permissible limit.

On increasing the concentration of thiosulphate ions above 5.40 x $10^{-3}$ M, the movement of thiosulphate ions may be hindered by its own larger concentration. It still not permit thiosulphate ion to form the desired complex within the time of exposure and as a consequence, the percentage error increases.

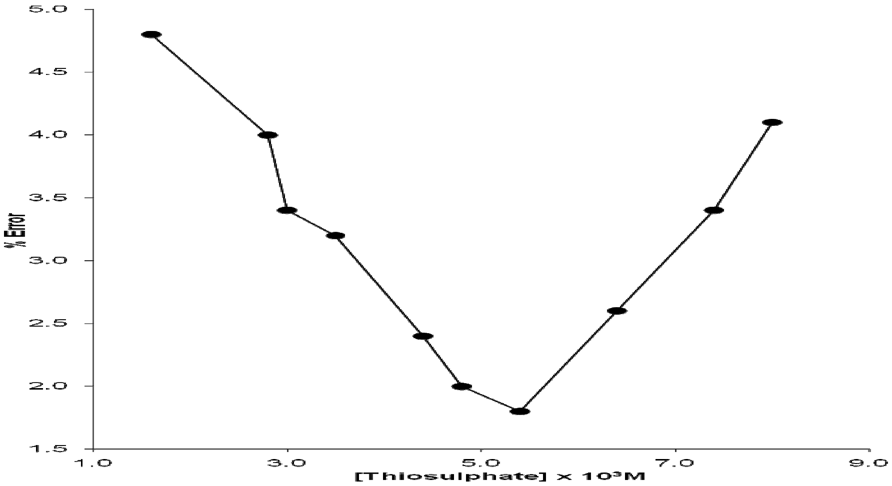

**Fig. – 2 : Effect of Thiosulphate Concentration**

*Effect of sodium nitroprusside concentration*

The effect of variation of concentration of sodium nitroprusside on the quantitative determination of thiosulphate and percentage error was observed by taking different concentration of sodium nitroprusside and keeping all other factors identical. The results are reported in Table 3 and graphically shown in Figure 3.

**Table – 3: Effect of sodium nitroprusside concentration**

| [Thiosulphate] = 5.40 x $10^{-3}$ M | pH = 3.1 |
|---|---|
| Light Intensity = 12.0 mWcm$^{-2}$ | $\lambda_{max}$ = 620 nm |
| **[SNP] x $10^2$ M** | **Error %** |
| 0.90 | 4.8 |
| 0.93 | 4.0 |
| 0.98 | 3.6 |
| 1.00 | 3.2 |
| 1.06 | 2.8 |
| 1.10 | 2.1 |
| **1.12** | **1.8** |
| 1.14 | 2.4 |
| 1.20 | 2.6 |
| 1.25 | 3.2 |
| 1.30 | 3.8 |

It was found that the minimum error in the determination of thiosulphate ion is found at sodium nitroprusside concentration 1.12 x $10^{-2}$M i.e. only 1.8% which is within permissible limit. As the concentration of sodium nitroprusside increases the complex formation tendency increases, it reaches maximum at sodium nitroprusside concentration 1.12 x $10^{-2}$M but if the concentration is further increased it will start acting like a internal filter and it will not permit the desired light intensity to reach sodium nitroprusside molecule in the bulk of the solution, as a consequence only limited number of sodium nitroprusside molecule will be excited to participate in the complex formation resulting into increase in percentage error.

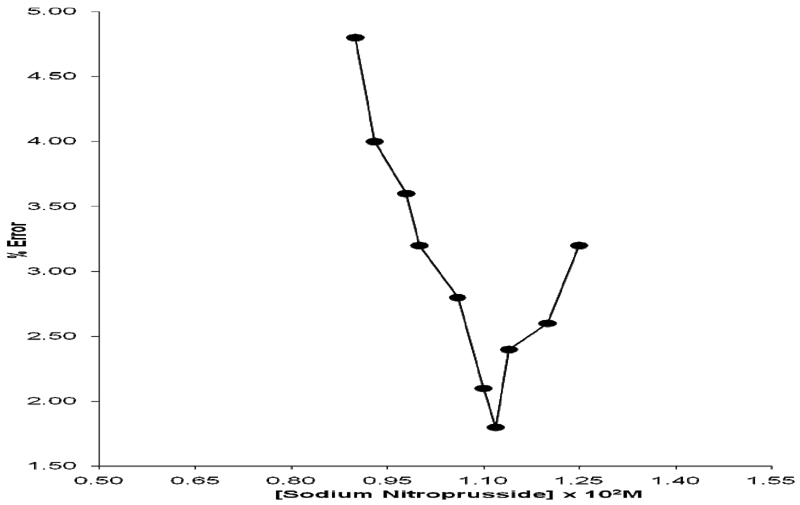

**Fig. – 3 : Effect of sodium nitroprusside concentration**

*Effect of light intensity*

The effect of light intensity on the percentage error in the determination of thiosulphate, while its photochemical reaction with sodium nitroprusside has been observed by varying the distance between the exposed surface of the reaction mixture and tungsten lamp light source. The result for tungsten lamp are tabulated in Table 4 and graphically shown in Figure 4.

**Table B-4: Effect of light intensity**

| [Thiosulphate] = 5.40 x $10^{-3}$ M | pH = 3.1 |
|---|---|
| [SNP] = 1.12 x $10^{-2}$ M | $\lambda_{max}$ = 620 nm |
| **Light Intensity (mWcm$^{-2}$)** | **Error (%)** |
| 6.0 | 4.0 |
| 7.0 | 3.6 |
| 8.0 | 3.4 |
| 9.0 | 3.0 |
| 10.0 | 2.4 |
| 11.0 | 2.0 |
| **12.0** | **1.8** |
| 14.0 | 1.8 |
| 16.0 | 1.8 |
| 18.0 | 1.8 |
| 20.0 | 1.8 |

It is observed that the minimum error in the determination of thiosulphate ion is found at tungsten lamp intensity = 12.0 mWcm$^{-2}$ i.e. only 1.8% which is within permissible limit. As the light intensity was increased 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 increasing the light intensity beyond 12.0 mWcm$^{-2}$ 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.

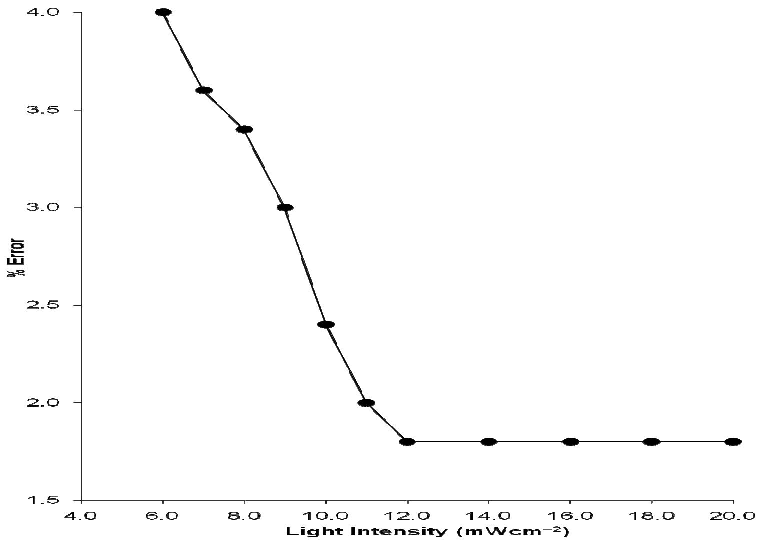

**Fig. – 4 : Effect of light intensity**

*Optimum conditions*

The photochemical reaction between sodium nitroprusside and thiosulphate ion was carried out. It was observed that if the determination of thiosulphate ion is carried out under these given conditions the percentage error observed is minimum (1.8%) and within permissible limit.

The optimum conditions are given as below:–

(i) pH = 3.1

(ii) [Sodium Nitroprusside] = 1.12 x 10$^{-2}$M

(iii) [Thiosulphate] = 5.40 x 10$^{-3}$M

(iv) Light Intensity = 12.0 mWcm$^{-2}$

**References**

1. M Ariturk; F Sayilkan and E Arpac. *J. Photochem. Photobiol.*, **2009,** 203A, 64.
2. LX Deng; SR Wang and DY Liu. *Catal. Lett.*, **2009,**129, 513.
3. P Wachter; M Zistler and C Schreiner. *J. Photochem. Photobiol.*, **2008**, 197A, 25.
4. J Zita; J Krysa and A Mills. *J. Photochem. Photobiol.*, **2009**, 203A, 119.
5. SS Malwadkar; RS Gholap and SV Awate, *J.Photochem. Photobiol.*, **2009**,203A, 24.

6. JC Chen; GC Fang and SS ShiInt. *J. Environ. Pollut.*, **2009**, 37, 86.

7. EV Skorb; EA Vrtinovich and AL Kula. *J. Photochem. Photobiol*., **2008,** 193A, 97.

8. CG Sun; L Tao and ML Fan, *Catal. Lett.*, **2009,**129, 26.

9. P Calza; C Massolino and E Pelizzetti. *J. Photchem. Photobiol.*, **2008,** 199A,42.

10. JK Reddy; K Lalitha and VD Kumari. *Catal. Lett*, **2008**, 121,131.

11. JM Garcia; LP Ertrada and I Oller. *J. Photochem. Photobiol*., **2008,** 195A, 205.

12. AR Supale and GS Gokavi. *Catal. Lett.*, **2008,** 124, 284.

13. S Horikoshi; M Kajitani and N Horikoshi. *J. Photochem. Photobiol*., **2008,** 193A, 271.

14. S Fakumoto; M Kitano and M Takeuchi. *Catal. Lett.*, **2009,** 127, 39.

15. ZY Zhang and PA Maggard. *J. Photochem. Photobiol. A*, **2007,** 186, 8.

16. ZQ Yu; S S C Chuang. *J. Catal*, **2007**, 246, 118.

17. T Papadam; N P Xekoukoulotakis and I Poulios. *J. Photochem. Photobiol. A*, **2007,** 186, 298.

18. A Lair; C Ferronato and J M Chovelon, *J. Photochem. Photobiol*. **2008,** 193A, 193.

19. TG Mattos and FAA Resi, *J. Catal.*, **2009,** 263, 67.

20. S Yamazaki; N Yamabe and S Nagano. *J. Photochem. Photobiol.*, **2007,** 185A, 150.

21. MI Maldonado; PC Passarinho and I Oller. *J. Photochem. Photobiol*., **2007,** 185A, 354.

22. XD Zhu; MA Nanny and EC Butter. *J. Photochem. Photobiol*., **2007**,185A**,** 289.

23. D Shrinivas; WF Hoderich and S Kujath. *J. Catal*., **2008,** 259, 165.

24. M Sarkha; H Burrows and M Bolte. *J. Photochem. Photobiol*., **1996,** 97A,81.

25. J Nemono; N Gokan and H. Veno. *J. Photochem. Photobiol*., **2007,** 185A**,** 295.

26. GA Shagisultanova and LP Ardashova. *Russ. J. Coord. Chem*., **1999,** 25, 788.

27. P Wilhelm and D Stephan. *J. Photochem. Photobiol. A*, **2007,** 185,19.

28. S Otsuka and M Udea. *J. Photochem. Photobiol*., **2006,** 168 A**,** 1.

29. H Chen; TC An. YJ Fang and K Zhu. *J. Mol. Catal*., **1999,** 147,165.

30. C Liu; YH Hsieh; PF Lai; CH Li and CL Kao. *Dyes and Pigments*., **2006**, 68**,** 191.