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A Newer Photochemical Method for Estimation of Metabisulphite using Sodium Nitroprusside

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Abstract: Determination of metabisulphite 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 utilize such reactions for the estimation of some sulphur 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 metabisulphite 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:, Metabisulphite, sodium nitroprusside, photochemical exchange reaction, quantitative, percentage error, optimum conditions.

INTRODUCTION

Photosensitized reactions are widely used in many technical and biological areas. Inorganic chemist may seek an improved understanding through the example that photochemistry gives the relationship between reactivity and electronic and molecular structure[1]. Photosensitized reactions like copolymerization have been reported by Wayne and Burrows et al.[2]. The essential feature of photochemistry is probably the way in which the excited states of the atoms or molecules play a part in process of interest. It is apparent that the absorption or emission of radiation to/from these states is the concern of spectroscopists as well as the photochemists.

Photodecomposition of ammonia to dinitrogen and dihydrogen on Pt/TiO_2 nanoparticles in an aqueous solution was studied by Nemono *et al.*[3]. Yamazaki *et al.*[4] carried out photodegradation and adsorption of 1,4-dioxane on TiO_2. Photocatalytic degradation and adsorption of di-isopropyl fluorophosphate and dimethyl phosphonate over dry and wet rutile TiO_2 was studied by Kiselev *et al.*[5]. Yuan *et al.*[6] observed Fe assisted photocatalytic degradation of microcystin-LR using titanium dioxide.

Physiochemical and photocatalytic characterization of TiO_2/Pt nanoparticles has been made by Liu *et al.*[7]. Otsuka and Udea[8] used TiO_3-TiO_2 composite powder for the photocatalytic bleaching of methylene blue. A comparison between TiO_2 and Fenton plus photo-Fenton in a solar pilot plant was reported by Maldonado *et al.*[9]. Photodegradative treatment of waste water by U.V./TiO_2 process was investigated by Liu *et al.*[10]. Zhu *et al.*[11] reported the effect of inorganic anions on the TiO_2 based photocatalytic oxidation of aqueous ammonia and nitrite.

Tsuji *et al.*[12] investigated photocatalytic activity of Pb-doped ZnS for H_2 evolution from an aqueous K_2SO_3 solution under visible-light irradiation (λ>420 nm). Codoping of a halogen ion with Pb improved the photocatalytic activity. Wetchakun *et al.*[13] found that 2.0 % Fe-loaded ZnS sample exhibited the highest degradation activity possibly due to the presence of Fe in optimum amount and the increase of surface area and light in UV region. Chauhan *et al.*[14] synthesized Fe doped ZnS nanoparticles ($Zn_{1-x}Fe_xS$; where x = 0.00, 0.03, 0.05 and 0.10) by chemical precipitation method. It was found that the Fe doped ZnS bleaches Methylene Blue much faster than the undoped ZnS upon its exposure to the visible light as compared to ultraviolet light.

Kaur *et al.*[15] reported that ZnO and transition metal doped ZnO nanoparticles ($Zn_{0.99}M_{0.01}O$; M = Mn, Co, Ni and Cu) have been successfully synthesized by thermally decomposing their oxalate precursor. The photocatalytic behavior of synthesized nanoparticles has been scrutinized using Methyl Orange (MO) as probe molecule. Moafi *et al.*[16] synthesized a series of tungsten-doped (W-doped) ZnO nanocomposite with different W contents by

sol–gel method. The photocatalytic activity of undoped ZnO and W-doped ZnO was evaluated by the photodegradation of methylene blue in aqueous solution.

Omidi *et al.*[17] prepared a novel Al-doped ZnO (AZO) photocatalysts with different Al concentrations (0.5–6.0 mol%) through a facile combustion method and followed by calcination at 500 °C for 3 h. The photocatalytic activities of the samples were evaluated by photocatalytic degradation of methyl orange under visible light ($\lambda \geq 420$ nm) and sunlight irradiation. Bi_2S_3 nanostructures with different dimensionalities including dots, rods, and sheets have been synthesized by Huang *et al.*[18] to study their photocatalytic activities in degradation of organic dyes.

Hierarchical BiOCl microspheres were synthesized by Gao *et al.*[19]. BiOCl showed high photodegradation rate for Carbamazpiene under simulated solar irradiation. Pala *et al.*[20] studied phoocatalyic degradation of cyanide in waste water using new generated nanothin film photocatalyst($K_2La_2Ti_3O_{10}$,(KLTO).

Tungstophosphoric acid (TPA) immobilized on ammonium Y and ZSM5 zeolites were prepared by Marchena *et al.*[21]. The immobilization of TPA on NH_4Y and NH_4ZSM5 zeolites is a good method to obtain catalysts with high photocatalytic activity in the 4-chlorophenol degradation. Nguyen and Juang[22] studied the photocatalytic degradation of p-chlorophenol by H_2O_2/TiO_2 hybrid in aqueous suspension under irradiation.

1. EXPERIMENTAL

A 100 mL stock solution of metabisulphite (M/100) and 100 mL stock solution of sodium nitroprusside (M/100) were prepared by dissolving 0.1901 g of metabisulphite 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) metabisulphite 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 olour 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 metabisulphite i.e. [1.96 x 10^{-4} M, 2.91 x 10 M, 3.84 x 10 M, 5.66 x 10 M, 7.42 x 10 M, 8.23 x 10 M].

A straight line was obtained, which was used later on as a calibration curve. 1.0 mL sample solution of known metabisulphite 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 metabisulphite sample solution.

2. EFFECT OF PH

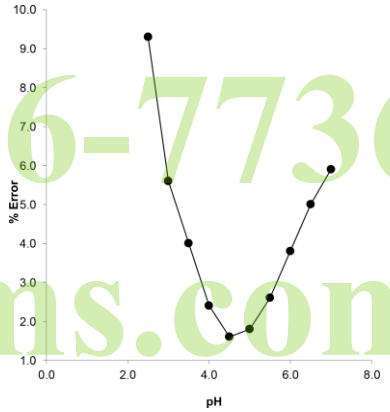
The photochemical reaction of sodium nitroprusside in presence of metabisulphite may be affected by the variation in pH value and as such the determination of metabisulphite may also be affected accordingly. Therefore the effect of pH on quantitative determination of metabisulphite was studied at different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

TABLE -1
EFFECT OF pH

[SNP] = 1.17 x 10^{-2} M [Metabisulphite] = 7.88 x 10^{-3} M

Light Intensity = 14.0 mWcm^{-2} λ_{max} = 620 nm

pH	Error (%)
2.0	3.8
2.5	2.9
3.0	2.0
3.5	**1.6**
4.0	1.9
4.5	2.5
5.0	3.0
5.5	3.8
6.0	4.0
7.0	4.5



It was observed that the pH required for minimum error is 3.5. The disulphurous acid gives monoanion around this pH i.e. $HS_2O_5^-$ and not $S_2O_5^-$ ion. This anion ($HS_2O_5^-$) will acts as a ligand to replace some or the other ligand from the coordination sphere of iron and not $S_2O_5^-$ ion. As it will give maximum complex formation, it will result in minimum error at this pH. Above pH = 3.5 again the percentage error increases which may be due to the fact that concentration of $HS_2O_5^-$ ion will start decreasing as compared to $S_2O_5^-$ ion. It will result in to a corresponding increase in the percentage error.

3. EFFECT OF METABISULPHITE CONCENTRATION

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

TABLE -2
EFFECT OF METABISULPHITE CONCENTRATION

[SNP] = 1.17 x 10^{-2} M pH = 3.5

Light Intensity = 14.0 mWcm^{-2} λ_{max} = 620 nm

[Metabisulphite] x 10^3 M	Error (%)
6.31	4.4
6.50	3.8
6.84	3.2
7.10	2.9
7.36	2.2
7.61	2.0
7.88	1.6
8.20	1.8
8.40	2.4
8.70	2.8
8.94	3.3
9.30	5.0

It was observed that the minimum error in the determination of metabisulphite is found at metabisulphite concentration 7.88 x 10^{3} M i.e. only 1.6% which is within permissible limit.

As the concentration of metabisulphite ion increases the complex formation tendency increases and hence the percentage error found for the determination of metabisulphite is minimum. On increasing the concentration of metabisulphite ions above 7.88 x 10^{3}M, the movement of metbisulphite ions may be hindered by its own larger concentration. It still not permit metabisulphite ion to form the desired complex within the limit of exposure and as a consequence, the percentage error increases.

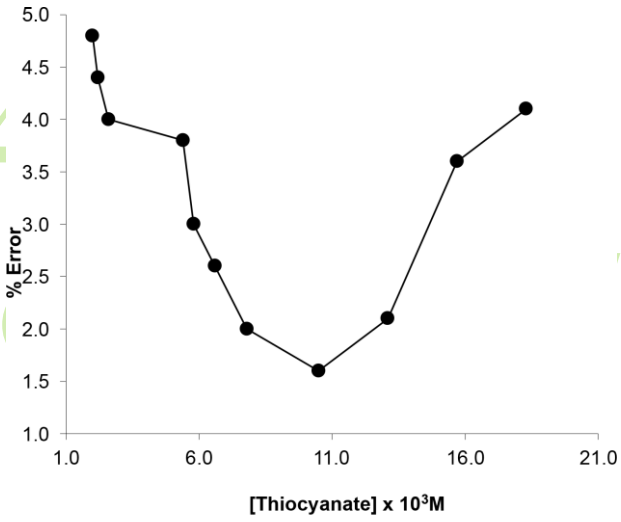


Figure-2: Effect of Metabisulphite Concentration

4. EFFECT OF SODIUM NITROPRUSSIDE CONCENTRATION

The effect of variation of concentration of sodium nitroprusside on the quantitative determination of metabisulphite ion 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.

EFFECT OF SODIUM NITROPRUSSIDE CONCENTRATION

[Metabisulphite] = 7.88 x 10^{-3} M pH = 3.5

Light Intensity = 14.0 mWcm^{-2} λ_{max} = 620 nm

[SNP] x 10^2 M	Error (%)
1.04	4.0
1.07	3.8
1.09	3.0
1.10	2.8
1.14	2.4
1.15	1.8
1.17	1.6
1.21	1.9
1.23	2.2
1.24	3.0
1.26	3.8
1.28	4.2

It was found that the minimum error in the determination of metabisulphite ion is found at sodium nitroprusside concentration 1.17 x 10^{2} M i.e. only 1.6% which is within permissible limit.

As the concentration of sodium nitroprusside increases the complex formation tendency increases, it reaches maximum at sodium nitroprusside

concentration 1.17×10^{-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.

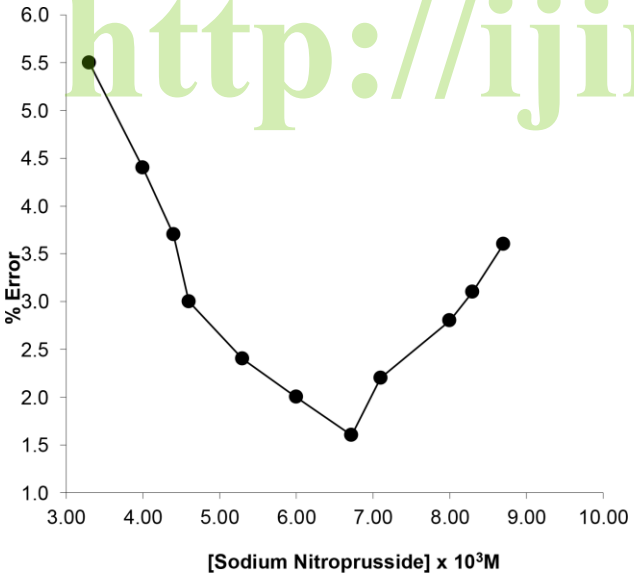


Figure-3: Effect of Sodium Nitroprusside Concentration

EFFECT OF LIGHT INTENSITY

The effect of light intensity on the percentage error in the determination of metabisulphite 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

TABLE -4
EFFECT OF LIGHT INTENSITY

[Metabisulphite] = 7.88×10^{-3} M pH = 3.5

[SNP] = 1.17×10^{-2} M λ_{max} = 620 nm

Light Intensity (mWcm $^{-2}$)	Error (%)
6.0	5.6
7.0	5.2
8.0	4.8
9.0	4.0
10.0	3.6
11.0	2.8
12.0	2.1
13.0	1.9
14.0	1.6
15.0	1.6
17.0	1.6
20.0	1.6

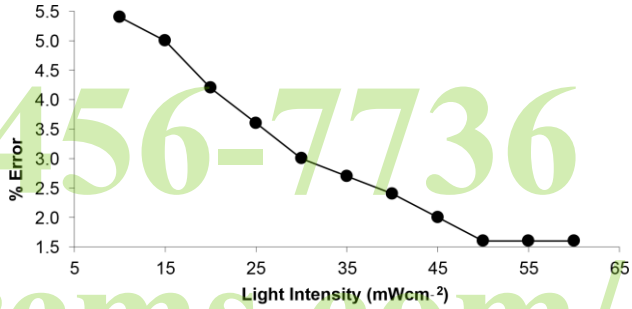


Figure-4; Effect of Light Intensity

It is observed that the minimum error in the determination of metabisulphite is found at tungsten lamp intensity = 14.0 mWcm $^{-2}$ i.e. only 1.6% 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 14.0 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.

6. OPTIMUM CONDITIONS

The photochemical reaction between sodium nitroprusside and metabisulphite ion was carried out. It was observed that if the determination of metabisulphite is carried out under these given conditions the percentage error observed is minimum (1.6%) and within permissible limit.

The optimum conditions are given as below:–

(i) pH = 3.5

(ii) [Sodium Nitroprusside] = 1.17×10^{-2} M

(iii) [Metabisulphite] = 7.88×10^{-3} M

(iv) Light Intensity = 14.0 mWcm $^{-2}$

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