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PERSULPHATE ESTIMATION USING SODIUM NITROPRUSSIDE BY PHOTOCHEMICAL LIGAND EXCHANGE REACTION METHOD

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ABSTRACT

Determination of persulphate using photochemical exchange reaction of sodium nitroprusside (SNP) 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 persulphate 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.

Key words: Persulphate, SNP, Photochemical exchange reaction, Quantitative, Percentage error.

INTRODUCTION

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. Photochemistry plays a pivotal role in a number of chemical and biological processes. Photosensitized reactions are widely used in many technical and biological areas. Photosynthesis is such an important photochemical reaction controlled by nature, which still exists as a challenge to the photochemists. 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

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states is the concern of spectroscopists as well as the photochemists.

Bio-mediated synthesis of TiO_2 nanoparticles and its photocatalytic effect on aquatic biofilm was studies by Dhandapani and Maruthamuthu[1]. The photophysics of salicylic acid derivatives in aqueous solution has been reported by Pozdnyakov et al.[2] Zhang and Maggard[3] investigated photocatalytically active hydrated forms of amorphous titania, TiO_2 center dot nH_2O Mechanistic study of substrate sensitized photochemical hydroxylation of salicylic acid with hydrogen peroxide was reported by Lang et al.[4] Sharma et al.[5] have studied estimation of thiosalicylic acid using photochemical exchange reaction. Shekhar and Pandey[6] have studied thermo chemical studies on alloys and compound of acetanilide-salicylic acid system. Mechanistic studies on the reactions of cyanide with a water-soluble Fe (III) porphyrin and their effect on the binding of NO is reported by Oszajca et al.[7] Wolak and Eldik[8] have investigated that pH controls the rate and mechanism of nitrosylation of water-soluble Fe(III) porphyrin complexes. Gazi and Ananthakrishnan[9] have investigated an analytical method for semi-quantitative determination of hydroxyl radicals by benzoic acid hydroxylation.

Minero and Vione[10] studied a quantitative evaluation of the photocatalytic performance of TiO_2 slurries. Photocatalytic transformation of acid orange-20 and Cr (VI) in aqueous TiO_2 suspensions was studied by Papadam et al.[11] Estimation of m-Phenylene Diamine using sodium nitroprusside by photochemical method has been studied by Bhatt et al.[12] Photodegration of Rhodamine-B in aqueous solution via SiO_2 - TiO_2 nano-spheres was reported by Wilhelm and Stephan[13]. Chouhan et al.[14] reported photochemical reaction involving nitrosylpentacyanoferrate (II)-bromide system using CdS as semiconductor.

Basir and Shah[15] investigated a novel spectrophotometric determination of atenolol using sodium nitroprusside. Maddigapu et al.[16] reported photochemical and photosensitised reactions involving 1-nitronaphthalene and nitrite in aqueous solution. Pozdnyakov et al.[17] had investigated photolysis of sulfosalicylic acid in aqueous solutions over a wide pH range. Mehmoud et al.[18] investigated selective spectrophotometric and spectrofluorometric methods for the determination of amantadine hydrochloride in capsules and plasma via derivatization with 1,2-naphthoquinone-4-sulphonate. Estimation of hydroxylamine hydrochloride using sodium nitroprusside by photochemical ligand exchange reaction has been reported by Bhatt et al.[19]

Zhang and Shao[20] studied about Bi_2MoO_6 ultrathin nano-sheets on $ZnTiO_3$ nano-fibers, a 3D open hierarchical hetero structures synergistic system with enhanced visible-light-driven photocatalytic activity. Application of azo dyes as dosimetric indicators for enhanced photocatalytic solar disinfection (ENPHOSODIS) was given by Bandala and González[21]. Photocatalytic activity of sea water using TiO_2 catalyst under solar light was studied by Shinde and Bhosale[22]. Dolat and Quici[23] investigated one-step, hydrothermal synthesis of nitrogen, carbon co-doped titanium dioxide (N, C-TiO_2) photocatalysts. They also investigated effect of alcohol degree and chain length as carbon dopant precursors on photocatalytic activity and catalyst deactivation.

Electron-irradiation induced changes in the phases and photocatalytic activity of TiO_2 nanoparticles was reported by Sapnar and Dhole[24]. Rao and Chaturvedi[25] introduced novel pebble bed photocatalytic reactor for solar treatment of textile wastewater. Results from a first autonomous optically adapted photocatalytic–photovoltaic module for water purification were reported by Fuentes and Vivar[26]. Effects of TiO_2 based photocatalytic paint on concentration and emission of pollutants and on animal performance in a swine weaning unit was observed by Costa and Chiarello[27].

EXPERIMENTAL

A 100 mL stock solution of persulphate (M/100) and 100 mL stock solution of sodium nitroprusside (M/100) were prepared by dissolving 0.2381 g of sodium persulphate 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) persulphate 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 λ_{max} = 460 nm. A graph was plotted between optical density and known concentration of persulphate 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 persulphate 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 persulphate sample solution.

Effect of pH

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

Table 1: Effect of pH

[SNP] = 1.15 x 10^{-2} M	[Persulphate] = 5.20 x 10^{-3} M
Light intensity = 11.0 mWcm^{-2}	λ_{max} 460 nm
pH	**Error (%)**
5.0	4.2
6.0	3.8
7.0	3.0
8.0	2.1
9.0	**1.7**
9.5	2.2
10.0	2.6
10.5	3.2
11	3.8
11.5	4.0

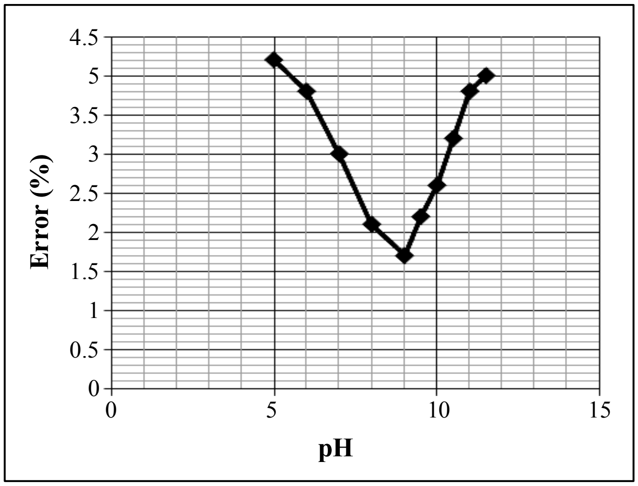

Fig. 1: Effect of pH

The minimum error was observed in the determination of persulphate at pH = 9.0 i.e. only 1.7. The pH required for minimum error was observed to be 9.0, which indicates that thiosulphuric acid gives persulphate ions at this pH and above. This persulphate ion will replace some other ligand from the coordination sphere of ion to form peacock blue complex. As the pH was increase, more availability of persulphate ions results in minimum error but as the pH was increase further, percentage error increases again indicating that greater availability of persulphate hinders the complex formation.

Effect of persulphate concentration

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

Table 2: Effect of persulphate concentration

[SNP] = 1.15×10^{-2} M pH = 9.0
Light Intensity = 11.0 $mWcm^{-2}$ λ_{max} = 460 nm

[Persulphate] x 10^{-3} M	Error (%)
1.60	4.8
2.80	4.0
3.00	3.4
3.50	3.2
4.00	2.4
4.60	2.0
5.20	**1.7**
6.40	2.6
7.40	3.4
8.00	4.1

It was observed that the minimum error in the determination of persulphate ion is found at persulphate ion concentration 5.20 x 10^{-3}M i.e. only 1.7% which is within permissible limit. On increasing the concentration of persulphate ions above 5.20 x 10^{-3} M, the movement of persulphate ions may be hindered by its own larger concentration. It still not permit persulphate ion to form the desired complex within the time of exposure and as a consequence, the percentage error increases.

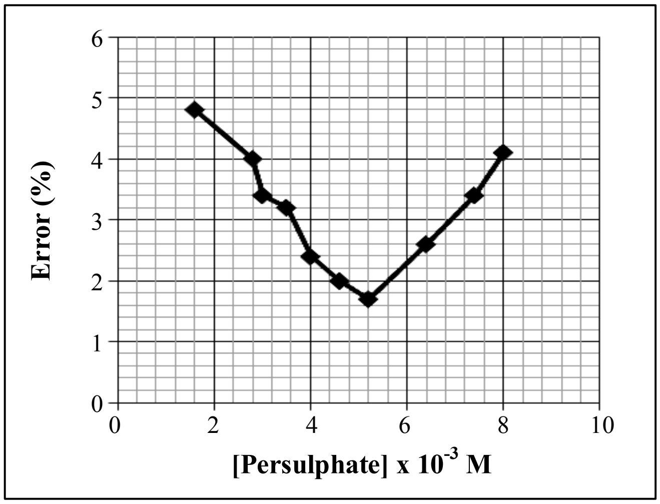

Fig. 2: Effect of persulphate concentration

Effect of sodium nitroprusside concentration

The effect of variation of concentration of sodium nitroprusside on the quantitative determination of persulphate 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 Fig. 3.

Table 3: Effect of sodium nitroprusside concentration

[Persulphate] = 5.20 x 10^{-3} M pH = 9.0

Light Intensity = 11.0 mWcm^{-2} λ_{max} = 460 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
1.15	**1.7**
1.20	2.4
1.25	2.6
1.30	3.2
1.35	3.8

It was found that the minimum error in the determination of persulphate ion is found at sodium nitroprusside concentration 1.15 x 10^{-2} M i.e. only 1.7% which is within permissible limit. As the concentration of sodium nitroprusside increases the complex formation tendency increases, it reaches maximum at sodium nitroprusside concentration 1.15 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.

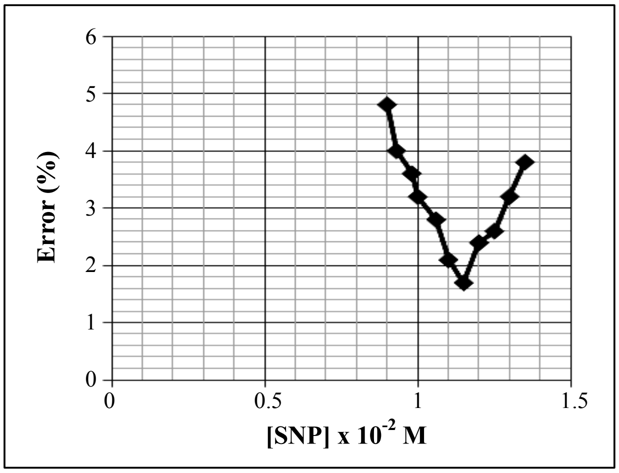

Fig. 3: Effect of sodium nitroprusside concentration

Effect of light intensity

The effect of light intensity on the percentage error in the determination of persulphate, 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 Fig. 4.

Table 4: Effect of light intensity

[Persulphate] = 5.20 x 10^{-3} M pH = 9.0
[SNP] = 1.15 x 10^{-2} M λ_{max} = 460 nm

Light intensity (mWcm^{-2})	Error (%)
6.0	3.6
7.0	3.4
8.0	3.0
9.0	2.4
10.0	2.0
11.0	**1.7**
12.0	1.7
14.0	1.7
16.0	1.7
18.0	1.7
20.0	1.7

It is observed that the minimum error in the determination of persulphate ion is found at tungsten lamp intensity = 11.0 mWcm^{-2} i.e. only 1.7% 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 11.0 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.

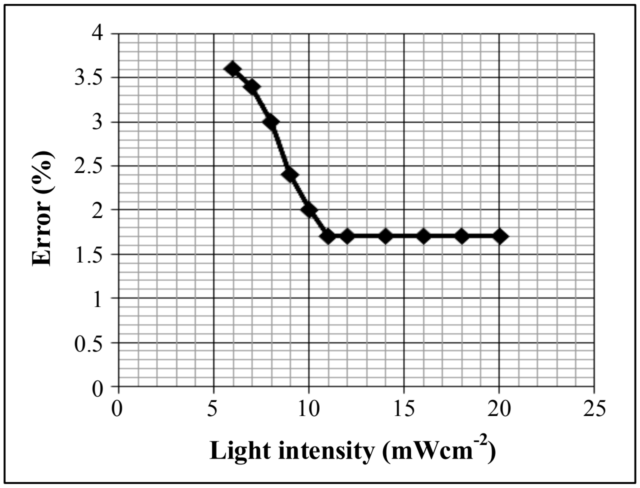

Fig. 4: Effect of light intensity

Optimum conditions

The photochemical reaction between sodium nitroprusside and persulphate ion was carried out. It was observed that if the determination of persulphate ion is carried out under these given conditions the percentage error observed is minimum (1.7%) and within permissible limit.

The optimum conditions are given as below:–

(i) pH = 9.0

(ii) [Sodium Nitroprusside] = 1.15 x 10^{-2} M

(iii) [Persulphate] = 5.20 x 10^{-3} M

(iv) Light Intensity = 11.0 mWcm^{-2}

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