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INDIRECT SPECTROPHOTOMETRIC DETERMINATION OF THIOSULPHATE

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ABSTRACT

Indirect spectrophotometric method for trace determination of thiosulphate has been developed. The method is based on decrease in absorbance of ferric salicylate complex solution by thiosulphate. Up to 5 ppm of thiosulphate can be determined with a standard deviation of 0.046 ppm.

Key words : Absorbance, Trace determination, Color reduction, Spectrophotometric studies

INTRODUCTION

The principle use of thiosulphate is in photography. Its reducing property finds its use in bleaching. Thiosulphate can be determined by various methods like (i) Gravimetric, (ii) Iodimetric, (iii) Spectrophotometric, (iv) Molecular Emission Cavity analysis, (v) Potentiometric, etc. Some of these methods suffer from following limitations -

(i) Other compounds of sulphur react with added reagents causing interference.

(ii) In case of iodimetric method, if iodine solution is acidic, thiosulphate may decompose and there is a possibility of air oxidation of iodide, which occurs more readily with increasing acidity. If iodine solution is alkaline, thiosulphate solution is partially oxidized to sulphate. [1]

(iii) Some procedures are complicated or involve critical conditions

In the present paper, a simple, precise and low cost indirect spectrophotometric method for trace determination of thiosulphate based on the decrease in absorbance of soluble ferric salicylate is reported.

Fe (III) on reacting with salicylic acid produces an amethyst color while Fe (II) produces no color. [2] Ferric salicylate complex is water soluble and the color is affected by

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pH. The final pH should be in the range of 2.5 to 2.8.

The stability constant of ferric salicylate complex is greater than that of ferric thiosulphate complex. [3] Therefore, a decrease in absorbance of ferric salicylate complex solution is not due to stability constant parameter.

The standard reduction potential of following reactions

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \qquad E^{0} = 0.77 \text{ Volts}$$

$$S_2O_3^{2-} + 6\,H^{+} + 4\,e^{-} \rightarrow 2\,S_{(S)} + 3\,H_2O \qquad E^{0} = 0.6 \text{ Volts}$$

shows that thiosulphate ion reduces ferric ion to ferrous ion. Hence, after addition of thiosulphate to ferric salicylate system at pH 2.5 to 2.8, ferric ions are reduced to ferrous ions, which do not form complex with salicylate ion. This results in a decrease in absorbance of ferric salicylate solution. It is claimed that under strongly acidic condition, there is no separation of sulphur for some hours. [4] Therefore, formation of sulphur does note not affect absorbance.

EXPERIMENTAL

Material and method

Absorbance measurements were made on a spectrochem spectrophotometer using optical glass cell with 10 mm path length. All the pH measurements were made on pH meter supplied by Systronics. The pH meter was standardized at pH 9.18, 4.01 and 7.0 with standard buffers. AR grade chemicals and deionized water after distillation were employed throughout the work. Sodium thiosulphate solution and ferric ammonium sulphate solution were standardized by usual volumetric methods[5]. Nitric acid solution was standardized against standardised sodium hydroxide solution.

Solutions of anions required for interference studies were prepared using respective sodium / potassium / ammonium salts. Solutions of cations were prepared by dissolving chlorides /nitrates of respective metals.

In the present work, initially a systematic photometric study of the ferric salicylate solution was undertaken and decolorization by thiosulphate was investigated later.

Spectral curves for ferric salicylate were obtained at different pH. (Fig. 1, Table 1)

Table 1. Absorption spectrum of sodium salicylate at different pH

Fe (III): 15 ppm Sodium salicylate : 3 mg per cm^3

Λ	**pH**						
	3.2	**3.0**	**2.9**	**2.8**	**2.7**	**2.6**	**2.5**
450	0.344	0.309	0.292	0.271	0.263	0.257	0.253
460	0.384	0.352	0.327	0.305	0.301	0.292	0.29
470	0.424	0.389	0.365	0.346	0.337	0.331	0.327
480	0.461	0.426	0.403	0.385	0.377	0.369	0.366
490	0.487	0.454	0.434	0.416	0.406	0.402	0.398
500	0.504	0.476	0.459	0.441	0.434	0.429	0.426
510	0.513	0.487	0.472	0.459	0.452	0.448	0.445
520	0.511	0.491	0.479	0.468	0.462	0.459	0.458
530	0.504	0.487	0.478	0.471	0.464	0.462	0.462
540	0.488	0.477	0.471	0.464	0.461	0.46	0.459
550	0.465	0.459	0.456	0.453	0.449	0.45	0.449
560		0.439	0.435	0.434	0.433	0.433	0.436

The curves in the pH range 2.5 to 2.8 are quite similar and exhibit broad band. Formation of only one species is indicated by reaction between ferric ion and sodium salicylate in above pH range. 530 nm was selected as analytical wavelength.

Optimum pH range for total color intensity was determined by measuring absorbance of a solution containing 15 ppm of Fe (III), 3.0 mg per cm^3 of sodium salicylate and pH of the solution was controlled by adding 0.1N HNO_3.Data presented in Table 2 indicate that absorbance is constant in the pH range 2.5 to 2.7.All analytical work is carried out at pH 2.6 ± 0.1

Optimum concentration of sodium salicylate required for total color development was determined by measuring absorbance of different solutions each containing 15 ppm Fe (III), 7.5 cm^3 of 0.1N HNO_3 per 50 cm^3 and varying concentration of sodium salicylate. The absorbance was measured at 530 nm. Results given in Table 3 show that minimum 2.5 mg per cm^3 of sodium salicylate is required for full color development. All analytical work was carried out by adding 3.0 mg per cm^3 of sodium salicylate, Color of ferric salicylate is stable for more than six hours, after color development.

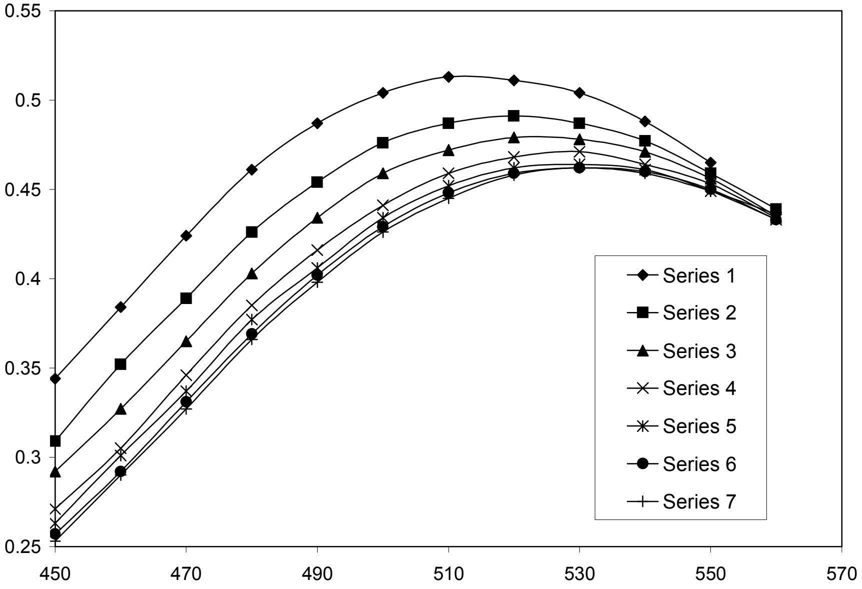

Fig. 1 : Absorption spectrum of sodium salicylate at different pH

Table 2. Effect of HNO_3

Fe (III) = 15 ppm Sodium salicylate = 3 mg /cm^{-3} Wavelength = 530 nm

Vol. of 0.1 N HNO_3	pH	Absorbance
1.0	3.6	0.547
2.0	3.4	0.513
3.0	3.2	0.501
4.0	3.1	0.481
5.0	2.9	0.474
6.0	2.8	0.468
7.0	2.7	0.462
8.0	2.6	0.462
9.0	2.5	0.462

Table 3. Effect of sodium salicylate

Fe (III)= 15 ppm Volume of 0.1N HNO_3 = 7.5 cm^3 Wavelength = 530 nm

Conc. of sodium salicylate in mg cm^{-3}	pH	Absorbance
0.5	2.1	0.410
1.0	2.2	0.437
1.5	2.3	0.447
2.0	2.4	0.454
2.5	2.5	0.461
3.0	2.7	0.462
3.5	2.8	0.462
4.0	2.9	0.483
5.0	3.1	0.507

Table 4. Calibration curve

Fe (III)= 15 ppm pH = 2.6 ± 0.1 Sodium salicylate = 3 mg cm^{-3}

Concentration of $S_2O_3^{-2}$ (ppm)	Absorbance
0	0.456
1	0.434
2	0.410
3	0.391
4	0.371
5	0.351

On the basis of above studies the basic color system chosen consists of an aliquot of Fe (III) solution containing 15 ppm of Fe^{3+}, pH 2.6 ± 0.1 and 3.0 mg per cm^{-3} of sodium salicylate.

Procedure for the determination of thiosulphate : To an aliquot, containing 15 ppm of Fe (III) and 3.0 mg per cm^3 of sodium salicylate, 0.1N HNO_3 was added to adjust the pH to 2.6 ± 0.1.This was followed by a suitable aliquot of $S_2O_3^{2-}$ solution or a sample containing unto 250 μg of thiosulphate. The volume was made up with deionised distilled water. The flask was kept in boiling water bath for 25 minutes. After cooling, absorbance of the solution was measured at 530 nm against distilled water as blank.

RESULTS AND DISCUSSION

The present method is based on the decrease in absorbance of ferric salicylate solution on addition of thiosulphate solution at 530 nm (λ_{max}).

The optimum conditions for reproducible decrease in the absorbance values of ferric salicylate solution are.

(i) 15 ppm of Fe (III) concentration

(ii) pH range 2.6 ± 0.1

(iii) 3 mg cm^{-3} of sodium salicylate

It was found that reduction of ferric salicylate solution was complete after placing the volumetric flask in boiling water bath for 25 minutes. After cooling, the solution absorbance remains constant for at least three hours.

All analytical work was carried out by placing volumetric flask in boiling water bath for 25 minutes.

Optimum range, sensitivity and accuracy

It has been observed that the calibration curve obtained by plotting decreasing absorbance of ferric salicylate against thiosulphate concentration at 530 nm is linear unto 5.0 ppm thiosulphate concentration. (Fig. 2, Table 5)

Table 5. Reproducibility of method

Fe (III) = 15 ppm pH = 2.6 ± 0.1 Sodium salicylate = 3 mg cm^{-3}

Thiosulphate = 3 ppm

Absorbance	$S_2O_3^{-2}$ found	% Error
0.391	3.0	0
0.391	3.0	0

Cont…

Absorbance	$S_2O_3^{-2}$ found	% Error
0.390	3.033	1.1
0.391	3.0	0
0.391	3.0	0
0.391	3.0	0
0.392	2.934	-2.2
0.392	2.934	-2.2
0.389	3.1	+1.33
0.390	3.033	+1.1
0.391	3.0	0

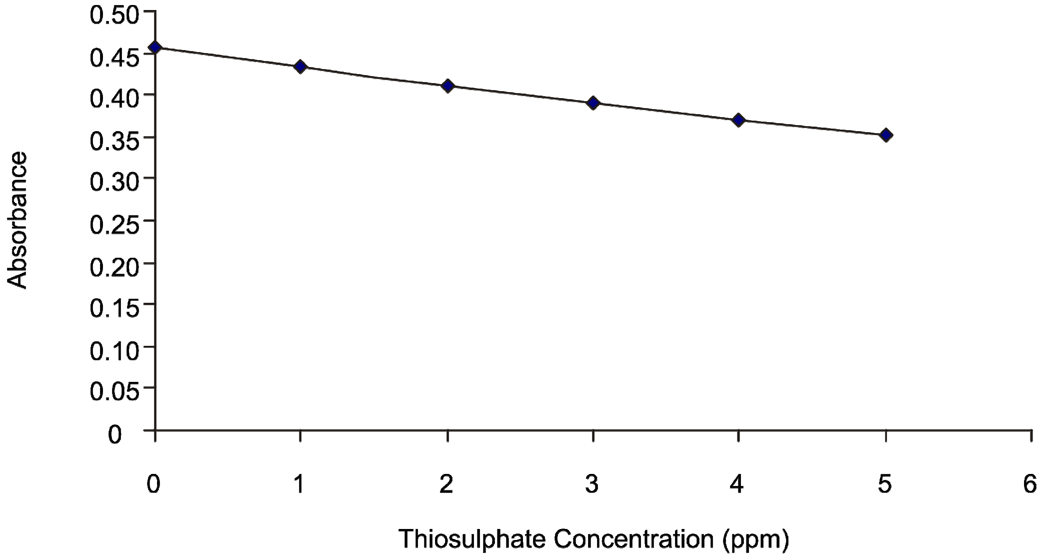

Fig. 2 : Calibration curve

Precision and accuracy of the method were tested by analyzing eleven samples each containing 3.0 ppm of thiosulphate. The amount of thiosulphate for a decrease in absorbance by 0.001 was found to be 0.5 ppm. (Table 6).

Mean absorbance at 530 nm was 0.391 with a standard deviation of 0.012.The average of eleven determinations carried out using 3.0 ppm of thiosulphate is 3.003 ppm.

The relative standard deviation is 1.53 percentage.

Table 6. Estimation of thiosulphate

Fe (III)= 15 ppm; pH = 2.6 ± 0.1; Sodium salicylate = 3 mg cm^{-3}

Quantity of $S_2O_3^{-2-}$ taken (ppm)	Quantity of $S_2O_3^{-2-}$ found (ppm)
20	21
35	35

Interference studies

Interference due to foreign ions in the determination of thiosulphate was studied for several cations and anions. Co (II), Ni (II) and Mn (II) are tolerated up to a concentration of 150 ppm, 50 ppm and 90 ppm, respectively for 3.0 ppm of thiosulphate. Chloride, bromide, iodide and carbonate are tolerated up to a concentration of 2200 ppm, 90 ppm, 90 ppm and 100 ppm, respectively. Reducing species like tartarate, arsenate, nitrite and pyrophosphate interfere seriously.

Values of instability constants of ferric thiocyanate and ferric salicylate complexes show that stability of ferric thiocyanate is less than that of ferric salicylate. [6.]Hence, presence of thiocyanate is tolerated up to 200 ppm for 3.0 ppm of thiosulphate in present method.

Results of the forgoing analytical work indicate that decrease in absorbance of ferric salicylate solution by thiosulphate can be used for trace determination of thiosulphate.

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