Indirect Determination of Sulphide and Sulphite Based On the Formation of 2,3,5,6-Tetrakis (2–Pyridyl) Pyrazine Iron (II)-Complex.

M.Y. KHUHAWAR, R.B. BOZDAR AND F.C. NACHNANI
Institute of Chemistry, University of Sind, Jamshoro (Sind), Pakistan.

(Received 27th August 1981.)

Summary: An indirect spectrophotometric method for the separate determination of sulphide and sulphite in aqueous solution is described. Iron (III) in slightly acidic medium is reduced to iron (II), to form an intense purple colour of the bis 2,3,5,6 tetrakis (2-pyridyl) pyrazine iron (II) complex. The colour formation of the complex obeys the Beer's law over the range of 6×10^{-6} to 4.8×10^{-5} sulphide and 2×10^{-5} to 1.6×10^{-4} sulphite ion concentrations. The effect of diverse ions on the determination of sulphide is also evaluated.

Organic molecules containing –N = C–C = N– and –N = C–C = N–C–C=N– atomic grouping have long been recognised as chelate ligands quite earlier[1,2] Intensely coloured complexes are formed in the reaction of 1,10-Phenanthroline, 2,2 -bipyridine 2,2′,2″terpyridine, and their derivatives with transition metal ions. Best known of these are with iron(II), commonly known as ferroins and terroin. It is interesting that iron(III) does not form chelates directly on addition of the bases to iron (III) salts, not even in non-aqueous solvents[3]. Thus Stephen and Lindston[4] determined sulphur dioxide by passing a sample of gas through a solution of iron (III) and 1,10-phenanthroline. It reducess iron (III) to iron (II) which reacts with 1,10-phenanthroline to form tris (1,10-phenanthroline) iron (II)- complex. Recently Bhat et al[5] have determined sulphide and sulphite spectrophotometrically based on the formation of bis (2,9-dimethyl-1, 10-phenanthroline) copper (I) complex. The complex is extracted in chloroform at pH-10.

In this paper a method is reported for the determination of sulphide and sulphite in aqueous solutions explored. This is based on the formation of highly sensitive purple colour of 2,3,5,6-tetrakis (2-pyridyl) pyrazine iron (II) in aqueous solution. The effect of various ions on the determination of sulphide is also examined.

Experimental

Apparatus and Reagents :

2-pyridinecarboxaldehyde (Merck) in the presence of potassium cynide condenses to 2-2-pyridoin. Pyridoin in the presence of ammonium acetate was heated at high temperatures to 146° C for 15 min to form 2,3,5,6-tetra kis (2-pyridyl) pyrazine by a reported procedure [6].

A solution (0.005M) of the reagent is prepared by suspending the required amount in ethanol: water (1:1) to which a few drops of 5N hydrochloric acid were added to ensure dissolution. The solution is then diluted to equal volume with water: ethanol (1:1). The solution of iron (III) containing 1mg/ml was prepared from pure ammonium iron (III) sulphate containing a few ml of sulphuric acid to prevent hydrolysis. The conventional acetate-acetic acid buffers (pH 3-6) were used throughout the investigation.

Absorbance measurements were made by using Pye Unicam SP6-500 U.V. spectrophotometer.

Calibration curve :

Standard 0.1M solution of sulphide and sulphite was prepared by dissolving ($Na_2S \times H_2O$ and Na_2SO_3) in freshly boiled distilled water containing 5% v/v glycerol to enhance the stability[7]. The solutions were freshly prepared and standardized iodometrically just before use[8]. The solutions of lower concentrations were prepared by diluting the standard solution with freshly boiled distilled water containing 5% glycerol.

Varying amounts of sulphide and sulphite in the range of 0.15 to 1.2ml of 10^{-3}M sulphide and 0.5 to 4 ml of 10^{-3}M sulphite were transferred to a 25 ml volumetric flask containing 2ml of 1000 ppm iron (III) solution, followed by addition of 5ml of the reagent. 5ml of acetate-acetic buffer solution was added and the pH of the solution was adjusted to 5 with sodium hydroxide. 2ml of ammonium fluoride (5%) was added and the solution was mixed well and the volume was made up with distilled water. The solutions were filtered before spectrophotometirc measurment. Absorbance of the solution was measured at 575 nm against a blank, which was prepared in the same manner but omitting sulphide and sulpite. Calibration curves were constructed by plotting the absobance against concentration of sulphide and sulphite ions (Fig. 1 & 2).

Assessment of the Analytical Procedure.

Different volumes of the unknown solutions of sulphide and sulphite were transferred to 25ml volumetric flask followed by 2 ml of 1000 ppm iron (III). The remaining procedure was the same as above and unknown amounts of sulphide and sulphite was determined from the calibration curve. The results are summarized in Table 1.

TABLE I

Analysis of Sulphide Solutions.

mls of 0.6 x 10^{-3}M in 25 ml present	mls of 0.6 x 10^{-3}M in 25 ml found	% Error
0.5	0.46	−8.0
0.75	0.75	0.0
1.25	1.31	+4.8

Interference.

The interference effects of various ions on the determination of sulphide was investigated by addition of varying amounts of ions to be tested into 25 ml volumetric flask, containing 1 ml of 0.6 x 10^{-3}M sodium sulphide solution and following the analytical procedure as above.

Results and Discussions

Goodwin and Lions[9] prepared 2,3,5,6, tetrakis (2-pyridyl) pyrazine containing terroin grouping, −N =

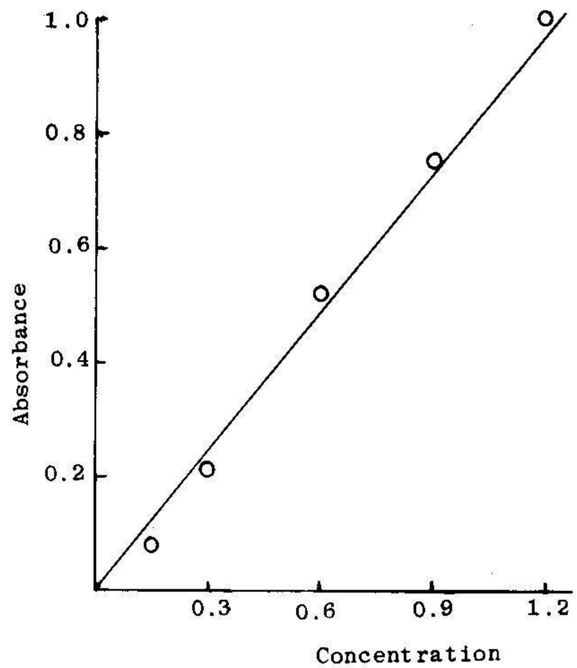

Fig 1: Calibration curve of Sulphide.

ml of 10^{-1} M Sulphide added to 25 ml volumetric flask and final volume made upto the mark

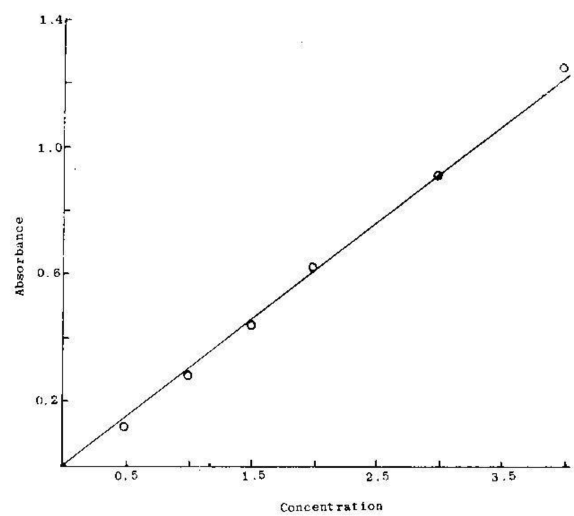

Fig. 2: Calibration curve of Sulphite

ml of 10^{-3} M Sulphite added to 25 ml volumetric flask and volume adjusted to mark.

C–C = N–C=C–N= and isolated its iron (II), copper (II), nickel (II), and ruthenium (II) salts, without considering analytical applications. Pflam et al[10] investigated the reactivity of the reagent towards transition metal ions. The purple colour of bis [2,3,5,6 - tetra kis (2-pyridyl) pyrazine] iron (II) complex has been recommended for the spectrophotometric determination of iron (II). Finally Stephen[6] has modified the preparation of the reagent and has supported the earlier findings that the reagent forms highly stable and highly sensitive iron (II) complex with molar absorptivity of 2 x 10^4 at 575 nm in aqueous-ethanol solution.

The tridentate ligand 2,3,5,6 - tetra kis (2-pyridyl) pyrazine can be easily prepared under ordinary conditions using less expensive chemicals. Its colour reaction well with the highly sensitive reagents, bathophenanthroline (ϵ = 2.24 x 10^4 at 533 nm), 2,2,2-terpyridine (ϵ = 1.25 x 10^4 at 522 nm) and tris (2-pyridyl) - 1,3,5-triazine (ϵ = 2.26 x 10^4 at 594 nm) of this class, but these reagents are highly expensive and involve lengthy preparations. Therefore the reagent 2,3,5,6 - tetrakis (2-pyridyl) pyrazine proves an ideal choice for the quantitative determination of sulphide and sulphite in low concentrations.

The colour of the reaction produced obeys Beer's law over the range of 6 x 10^{-6} to 4.8 x 10^{-5}M (0.192 to 1.4 μg/ml) sulphide and 2 x 10^{-5} x 1.6 x 10^{-4}M (1.6 to 12.8 μg/ml) sulphite. The validity of the analytical procedure was tested by analysis of unknown concentration of pure sulphide and sulphite solutions. The results in Table-1 indicate reasonable accuracy with percentage error within reasonable range, but it is slightly higher in lower concentrations.

The study of interference effect of Zn^{2+}, ScN^-, Mg^{2+}, NH_4^+, Na^+, K^+, So_4^{-2}, Cl^-, on sulphide determination indicated that a ten fold excess of these ions do not interfere. Moreover citrate, iodide, oxalate, phosphate and nitrite can be tolerated when present in the same concentration as that of sulphide without loss of a acurracy.

Conclusion

The method described here is simple and sensitive for the determination of sulphide and sulphite in aqueous solution. The method involve less expensive instrumentation and good results could be expected in the hands of even the less experienced personnel because of the simplicity of the method.

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