A New Spectrophotometric Method For The Microdetermination of Sulphate

MAHMOOD .I. FAROOQI*, J.ANWAR,* SAEED AHMAD NAGRA* AND ALTAF HUSSAIN**
*Institute of Chemistry, University of the Punjab, Lahore- 1,Pakistan.
**F.G.Science and Arts College, Karachi Cantt. , Pakistan.

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Summary: An indirect spectrophotometric method for the microdetermination of sulphate has been developed. The sulphate samples were reduced with sodium hypophosphite hydroiodic acid mixture and the hydrogen sulphide thus produced is absorbed in copper copper (II) sulphate solution. Unreacted copper (II), is then reduced to (I) with hydroxylamine sulphate and complexed with neocuproine which is extracted in isoamyl alcohol. The absorbance of the complex is determined at 456 nm and the sulphate ions are determined by difference method.

Introduction

Sulphate reduction to hydrogen sulphide offers an attractive basis for the estimation of this important ion. The hydrogen sulphide thus evolved can be determined either turbidimetrically, as yellow brown suspension of lead sulphide [1] or spectrophotometrically as methylene [2-3] or ethylene blue [4]. The latter methods have proved superior than the former in terms of sensitivity. A problem, however, is the lack of precision, because the complex formed in both methylene and ethylene blue methods is time sensitive. Copper (I) formes a stable complex with 2,9-dimethyl-1,10-phenanthroline (neocuproine) which can be extracted in isoamyl alcohol [5]. The absorbance of this complex was measured at 456 nm. The addition of sulphide ions in the above system greatly reduced the absorbance of Cu(I)-neocuproine complex [6]. On the basis of this decrease in absorbance, a sensitive and rapid method was devised for the determination of sulphate ions. In the proposed method the hydrogen sulphide evolved after reduction of sulphate is absorbed in copper(II) sulphate solution. Some of the copper will be masked as Copper- sulphide. The unreacted copper(II) is then reduced to copper (I) and is extracted in isoamyl alcohol, as copper (I)-neocuproine complex. Interferences experienced in methylene blue method [3] are greatly reduced by the use of suggested method.

Experimental

Apparatus

All absorbance measurements were made on a Pye-Unicam SP8-400, double beam, U.V/visible Spectrophotometer, using 10 mm glass cells.

Reagents

All reagents used were of Analar Grade, Doubly distilled water was used through-out this work.

Phosphate Buffer solution was prepared by dissolving 34 g of KH_2PO_4 in water and diluted to 1 litre.

For hydroxylamine sulphate solution, 50g, of the solid was dissolved in water and diluted to 1 litre.

Reducing mixture was prepared by sodium hyphosphite and hydroidic acid in glacial acetic acid as described in a previous work [7].

For calibration purpose, 1000 ppm, sulphate solution was prepared by dissolving appropriate amount of potassium sulphate dried at 106°C, in 1000 ml of water. A fresh working solution was prepared by diluting 10 ml of the above solution to 100 ml.

Copper (II) sulphate solution (1,000 ppm) was prepared by dissoling 3.927g of $C\mu SO_4$. $5H_2O$ in water and diluting to 1 litre. A fresh working solution was prepared daily by diluting 10 ml of the stock solution to 1000 ml.

Neocuproine Reagent; 0.4165 g of neocuproine (2,9-dimethyl-1,10- phenantholine) was dissolved in isoamyl-alcohol and diluted to 1 litre with the same solvent.

Procedure

0.5-2.5 ml aliquots of the potassium sulphate working solution were transferred to the reduction flask and heated to dryness. After cooling, 3 ml of the reduction mixture was added the flask was connected to the assembly (Fig. 1). The mixture was heated to boiling for five minutes while nitrogen gas was passed through the apparatus. The released hydrogen sulphide was wept to a 25 ml measuring flask, containing 1.5 ml of the copper (II) sulphate working solution, 8 ml of the hydroxylamine sulphate and 5 ml of phosphate buffer solution is also added to the flask, mixed the solutions throughly and diluted to mark.

Transferred the solutions from volumetric flasks to a 50 ml separating funnel containing 10 ml of the neocuproine reagent. Flasks were rinsed with 1 ml of the buffer solution and the rinsing was also added to the separating funnel. Placed the separating funnel on a shaking apparatus and shaked for 3 minutes. The yellow brown organic extract, was drained through a cotton-plug and its absorbance was measured against the reference at 456 nm. Reference and reagent blank solutions were prepared similarly without the addition of any copper and sulphide respectively. Absorbance of the reagent blank was taken as 'A' and standard solution as 'B'.

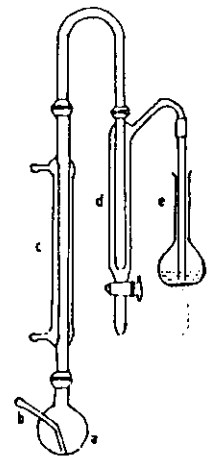

Fig. 1: Apparatus for reduction of sulphate (a) reduction flask (b) N_2-delivery tube (c) condenser (d) gas washing column (e) measuring flask containing Cu(II) Soln.

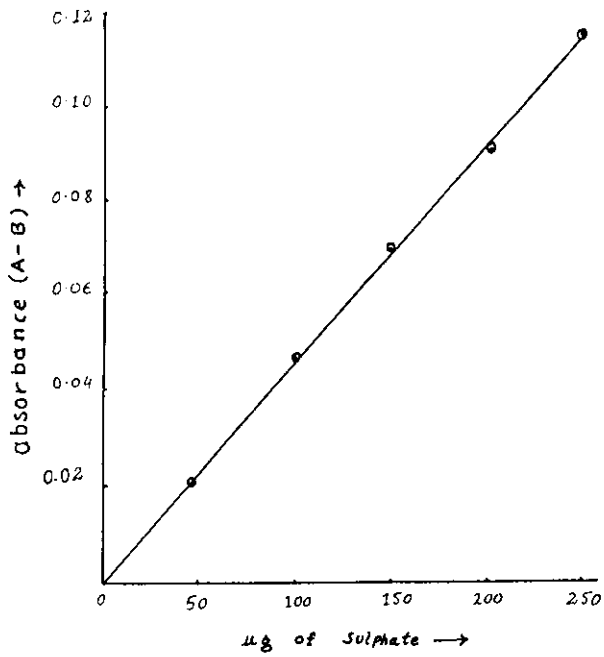

Fig. 2: Calibration Line for Sulphate.

Results and Discussion

The calibration graph, Fig. 2 was plotted between the absorbance factor (A-B) and sulphate concentration. Table 1 lists the results obtained when synthetic samples were analysed by the described and the methylene blue method.The precision and accuracy of the suggested method is remarkable, indicating the validity of the method for quantitative purposes.

Effect of Copper and Neocuproine Concentrations

Copper concentration plays a predominant role in the suggested method. When the amount of copper is more than neocuproine, the colour depression

Table-1 Determination of sulphate from synthetic samples.

S.No.	SO4 Present µg	Methyl blue [3] SO4 Found µg	% recovery	Described Method SO4 Found µg	% Recovery
1.	50.0	52.5	105	51.0	102
2.	50.0	49.0	98	52.5	105
3.	50.0	49.0	98	49.0	99
4.	100.0.0	100.0	100	99	99
5.	100.0	104.0	104	101	101
6.	100.0	103.0	103	100	100
Aveg + R.S.D.			101.3 + 2.8		100.8 + 2.2

achieved by sulphide ions was not very noticable. This was probably, because, even after the masking of some copper by sulphide ions, sufficient amount of copper ions is left to combine with whole the neocuproine molecules. Therefore the depression of absorbance remained quite small. A 1.5 ml of the working copper solution was observed to give maximum absorbance with 10 ml of the neocuproine reagent solution.

Effect of Solvents

Effect of different solvents was studied on the absorbance of copper (1)-neocuproine complex, with and without the addition of sulphide ions. Isoamyl alcohol, n-amyl alcohol, chloroform, carbon-tetrachloride and MIBK were among the solvents studied. Carbon tetrachloride extracted only a negligible quantity of the complex, whereas the best results were achieved by iso-amyl alcohol.

Sulphide as a Reducing Agent

In a previous publication [8] sulphide was determined spectrophotometrically by its ability to reduce copper(II) to copper(I), which was then extracted as its neocuproine complex. No such effect was noted during the recent investigation. When the described procedure was repeated without adding any reducing agent (hydroxylamine sulphate) the absorbance of the extracts with different concentrations of sulphide ions was almost uniform. This indicated the inertness of sulphide towards the reduction of copper (II) ions. The addition of a reductant is therefore, essential for the quantitative determination of sulphide ions

Addition Sequence of the Reagents

The sequence of reagents addition also played a predominant role in the present investigations. When hydroxylamine sulphate solution was added prior to the passing of hydrogen sulphide, the depressive effect of sulphide ions on the absorbance of Cu neocuprine was greatly reduced. It is therefore necessary to follow the reported procedure strictly.

Effect of pH

To study the effect of pH, 100 µg of sulphide ions was taken in different flasks and pH was varied from 2-10, by the addition of hydrochloric acid and sodium hydroxide solutions. Absorbance of the solution was compared with that of the reagent blanks adjusted to the same pH value. A pH range of 3-8 gave the best results. The response did not change when the same pH was adjusted by potassium dihydrogen phosphate, which was recommended to be used as a buffer in the experimental procdure.

TABLE-2

Effect of interfering ions on the determination of sulphate ions (100µg).

Ion Studied	%age Error Described Method	Methylene blue Method[3]
Cl	0.5	2.4
Br	0.9	3.0
S_2O_3	23.0	40.0
HCO_3	0.4	0.0
CO_3	0.4	0.0
IO_4	2.8	5.9
NO_3	2.9	21.3
SO_3	32.0	66.0
Ca^{++}	-0.0	-0.2
Sr^{++}	-0.3	-0.7
Ba^{++}	-0.5	-1.8
Pb^{++}	-0.7	-0.7

Table-3: Determination of solubility of barium sulphate in brine solutions of different concentrations (at 30°C)

S.No	NaCl Conc.(M)	Described Method	Spectrophotometric Method [9] $Xx10^{-5}M$
1.	0.5	4.9	8 5.60
2.	0.5	5.10	5.22
3.	1.0	8.7	5 8.37
4.	1.0	9.80	9.00
5.	2.0	12.28	12.45
6.	2.0	11.90	12.95

Effect of Other Ions

Effect of different cations and anions was studied on the determination of sulphate ions by the suggested procedure. The effect of a 10 fold excess of interferences on 100 μg sulphate is shown in table 2. Contrary to the methylene blue method, the interferences are reduced largely by the use of the present procedure. Only the sulphite and thiosulphate ions increased the absorbance, whereas, rest of the anions studied did not show any remarkable effect. Cations however did not interfere at all.

Sulphate in Barium Sulphate Solubility Samples

Measurement of the solubility of barium sulphate in brine solutions is important but difficult, especially when barium is determined.This is because of the presence of high sodium content which interfere in the various methods of barium determination. Samples from solubility cell were filtered through a millipore filter (0.45 μm) and evaporated to dryness in the reduction flask. Presence of large amounts of chloride did not interfere and the solubility results achieved are quite comparable to those achieved through barium determination by spectrophotometric method [9] (Table No.3). The latter method is considered suitable for barium determination in the presence of high concentration of other ions.

Conclusion

The described method is a simple and rapid method for the spectrophotometric determination of sulphate from solid and liquid samples. The method can also be directly employed for sulphide ions. The interferences of different ions are greatly reduced by using the present procedure. The coloured complex in the suggested method is not time sensitive, as that, in the case of the methylene blue method [3].

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