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Spectrophotometric Determination of Sulphide by Liberation of Thiocyanate from Mercury (II) thiocynate.

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Summary: A simple indirect spectrophotometric determination of sulphide is described. The method is based upon the displacement of thiocyanate ions from mercury (II) thiocyanate by sulphide ions. The released thiocyanate ions react with iron (III) to form iron (III)-thiocyanate complex which is determined spectrophotometrically. The effects of a number of factors like time, temperature, concentration and diverse ions are investigated. The method is useful for both the soluble and insoluble sulphide samples.

Introduction

Under slightly acidic conditions a sulphide releases hydrogen sulphide which is an undesirable pollutant of atmosphere due to its unpleasant smell and toxic effects if present at higher concentrations. Hence sulphide is often determined in air, water, sediments and rocks etc.

A number of spectrophotometric methods have been employed for the determination of sulphide. The Methylene Blue method [1-3] has been thoroughly investigated and most commonly used for sulphide estimation in a large variety of samples. The Ethylene Blue [4] modification increased the sensitivity of the original method. Other than these, Wroński [5] determined sulphide by measuring the absorbance of blue complex formed by hydrogen sulphide and silver-thiofluorescein. The reduction of molybdate to molybdenum blue by hydrogen sulphide has also been used for the determination of various sulphur compounds [6]. Some indirect methods for sulphide determination are also known. In one of such methods chloroform solution of silver-dithizonate is shaken with hydrogen sulphide and absorbance of the released dithizone is measured [7]. Similarly, another indirect method is based on the absorbance of the chloranilate released by sulphide from mercuric chloranilate [8].

Though these methods are sensitive enough even for micro-quantities of sulphide, there are certain problems associated with them such as lengthy and combersome procedures, unavailability and instability of reagents and sometimes lack of reproducibility which make their application limited. The present method for the determination of sulphide is also an indirect one but is simple and convenient. It is based upon the displacement of thiocyanate from mercury (II) thiocyanate by sulphide in the presence of iron (III) ions resulting in the formation of iron-thiocyanate complex which absorbs at 460 nm. This principle has already been used for the determination of chloride [9] and thiosulphate [10] ions.

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* For correspondance.

Experimental

Equipment and Reagents:

A Pye-Unicam SP8-400 double beam UV/VIS spectrophotometer with 10 mm glass cells was used for absorbance measurements.

Thiocyanate Solution:

Saturated thiocyanate solution was prepared by dissolving mercury (II) thiocyanate in ethanol at room temperature. The solution was filtered through Whatman 41 filter paper before use.

Iron (III) Solution:

30.125 g of hydrate ammonium iron (III) sulphate, $Fe(NH_4)(SO_4)_2$ $12H_2O$, was dissolved in 100 ml of 9M nitric acid and the solution was diluted to 250 ml to get 0.25M iron (III) solution.

Standard Sulphide Solution:

4.066 g of hydrated sodium sulphide (containing 60% Na_2 S, determined iodimetrically) (Na_2S) was dissolved in water and diluted to 1000 ml to get 1000 μg ml^{-1} sulphide solution. Working solutions were prepared by further dilution of this stock solution.

Calibration:

2 Ml of 0.25M iron (III) ammonium sulphate solution was taken in five 25 ml volumetric flasks, 2 ml of saturated ethanolic solution of mercury (II) thiocyanate was added and mixed thoroughly. The aliquots of standard sulphide solution containing 4-20 μg of sulphide were transferred, the contents were shaken for five minutes and then the volume was made up with water. After another ten minutes the absorbance of each solution was measured against compensatory blank at 460 nm. A linear calibration graph was obtained by plotting the absorbance against sulphide concentration.

Results and Discussion

Calibration Curve and Standard Deviation:

By measuring the absorbance at 460 nm in 10 mm glass cells a linear calibration curve, shown in Fig. 1, was obtained for 4-20 μg of sulphide per 25 ml. The calibration for lower amounts of sulphide could also be obtained if long path cells were used. As absorbance was measured against a compensatory blank the calibration line passed through the origin. However when distilled water was used as blank the calibration showed a significant intercept along absorbance axis. The calibration remained linear up to 75 μg of sulphide per 25 ml and after that a slight positive deviation from Beer's law has been observed.

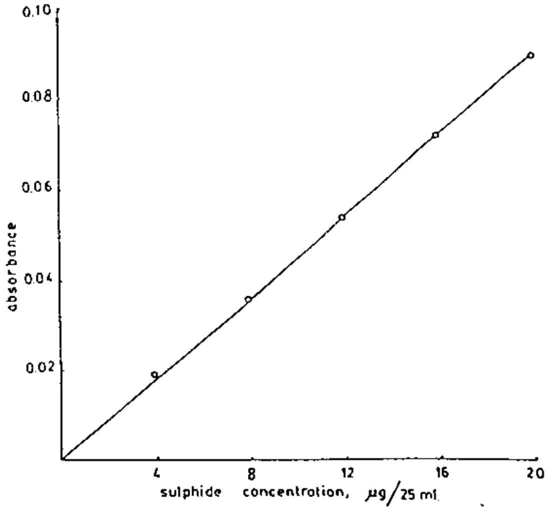

Fig.1: Calibration graph for 4-20 μg sulphide per 25 ml.

The precision of the method was checked by taking ten aliquots, each containing 10 μg of sulphide and treating as in the calibration. The calculated value of standard deviation was 0.012.

Effect of Time:

To check the effect of time, the absorbance of sulphide containing sample and the compensatory blank was checked after different intervals of time. As shown in Fig 2, the absorbance in both cases increased considerably for first forty minutes while a small but gradual increase was observed for next two hours. This reveals that as a parallel increase in the absorbance of the blank is found hence presence of sulphide does not have any net effect on the absorbance with respect to time.

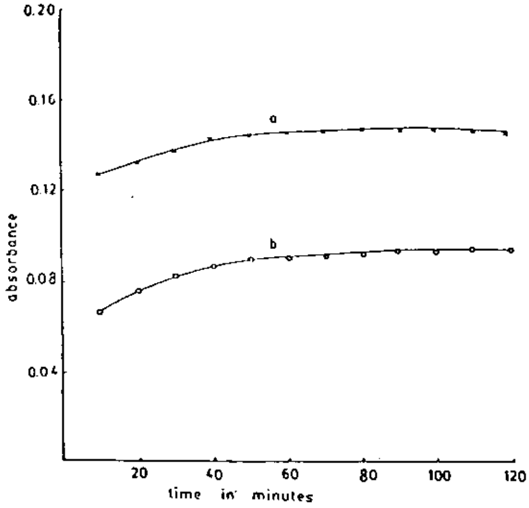

Fig.2: Effect of time on the absorbance of iron(III)-thiocyanate.
a: Sulphide containing sample against water;
b: Compensatory blank against water.

Effect of Temperature:

To investigate the effect of temperature the sulphide containing sample and the compensatory blank were heated to different temperatures and after cooling to room temperature the absorbance of both was measured against water. In both cases the absorbance increased with temperature. Two factors may be responsible for the enhancement in absorbance: firstly, the fast interaction of thiocyanate and iron (III) ions and secondly, the evaporation of alcoholic content of the solutions which made them more concentrated.

The identical increase in the absorbance of sulphide containing sample and the blank, as shown in Fig 3, indicates that the presence of sulphide has no significant effect on the change in absorbance at higher temperatures.

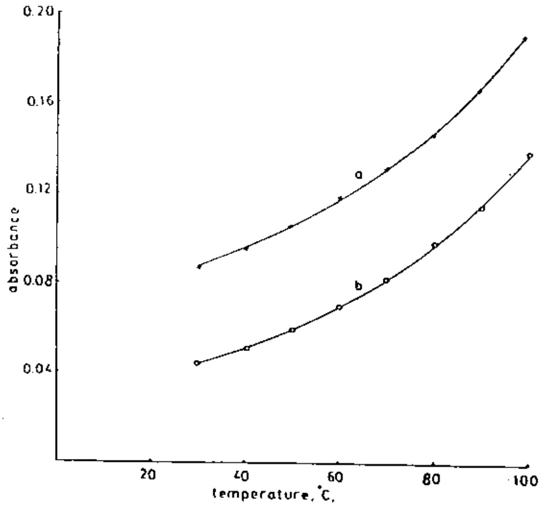

Fig.3: Effect of temperature on the absorbance of iron(III)-thiocyanate.
a: Sulphide containing sample against water;
b: Compensatory blank against water.

Effect of Acid Concentration:

To supress the hydrolysis, iron (III) solution was prepared in nitric acid. The effect of acid concentration was checked by measuring the absorbance of the blank as well as of 15 μg sulphide containing samples at different acid concentration.

As shown in Fig 4, in both cases the absorbance increased exponently unless the nitric acid concentration was 0.4 M. After that no appreciable change in the absorbance has been observed by increasing the nitric acid concentration up to 1 M. However a decrease in the absorbance values was noticed when solutions with very high acid concentrations were kept for more than 30 minutes.

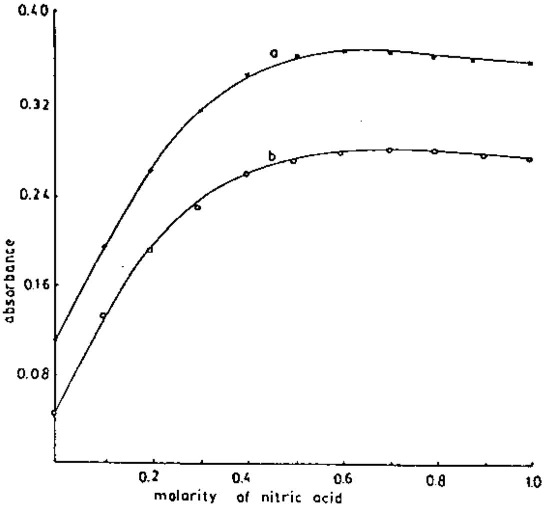

Fig.4: Effect of acid concentration on the absorbance of iron(III)-thiocyanate.
a: Sulphide containing sample against water;
b: Compensatory blank against water.

Effect of Diverse Ions:

To check the possible interferences, a number of common ions were added in five fold excess to sulphide and treated as in the calibration procedure. The anions were added as their sodium and potassium salts whereas the cations were employed in the form of sulphates and nitrates. The results obtained in the presence of different ions are summarized in Table 1.

Among the anions, the interference was observed due to chloride, bromide and thiosulphate as expected. These ions increased the absorbance and the higher results of sulphide were obtained. This is due to the fact that these ions also reacted with mercury (II) thiocyanate and released thiocyanate ions which formed iron-thiocyanate complex. As for as cations are concerned only lead (II) gave erroneous results probably due to the formation of lead (II) sulphide leading to lower results of sulphide. The other anions and cations showed negligible effect on the estimation.

Table-I: Effect of Diverse Ions on Sulphide Determination.

Anion	Added as	S'' found, µg/25 ml	Cation	Added as	S'' found, µg/25 ml
CH_3COO'	Sodium	11.9	K^+	Sulphate	11.8
NO_2'	"	12.2	Ca^{++}	"	11.8
NO_3'	Potassium	12.2	NH_4^+	Nitrate	12.0
S_2O_3''	Sodium	18.5	Pb^{++}	Nitrate	10.5
SO_4''	"	12.1	Zn^{++}	Sulphate	11.8
Cl'	"	26.2	Cu^{++}	Sulphate	11.6
CO_3''	"	12.2	Ni^{++}	Nitrate	12.2
PO_4'''	"	11.8	Ba^{++}	Nitrate	12.0
Br'	Potassium	16.5	Al^{+++}	"	11.6
SO_3''	"	12.0	Cr^{+++}	Nitrate	12.2

Sulphide taken 12µg/25 ml as sodium sulphide.

Effect of Iron(III) and Thiocyanate Solutions:

The effect of iron (III) concentration was checked by using different volumes of 0.25 M iron (III) solution for reaction. A significant enhancement in the absorbance was observed by increasing the amount of iron (III) in reaction mixure as shown in Fig 5(a).

An identical enhancement was also noticed when the experiment was repeated with the blank i.e. without sulphide content Fig 5(6) indicating that the enhancement in absorbance is simply due to the reaction of thiocyanate with iron (III) and sulphide has no significant contribution in the enhancement.

As it can be seen from Fig 5(c) and (d), almost similar results were obtained when different volumes of

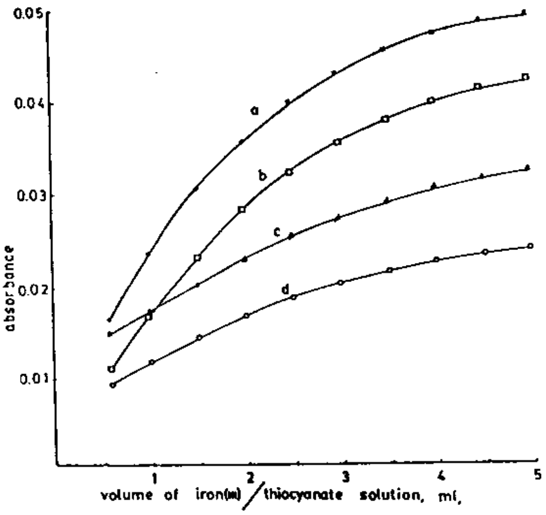

Fig.5: Effect of iron(III) and mercury thiocyanate solutions. Variation in iron(III) solution; a: Sample; b: Blank. (thiocyanate solution added 2ml.) Variation in mercury thiocyanate solution, c: Sample; d: Blank, (iron solution adeded 2 ml).

thiocyanate solution were employed i.e. a relatively mild increase in the absorbance by increasing the amount of thiocyanate was observed in both cases. An identical increase in the absorbance of sulphide containing solution and the blank by increasing the concentration of iron (III) or thiocyanate indicates that the excess of any these reagents does not have any net effect on the sulphide estimation.

Comparison with reference method

For comparison purpose two types of synthetic samples were prepared and analysed by the described procedure as well as by the reference Ethylene Blue [4] method.

For type "A" samples, hydrogen sulphide was passed through a 1:1 water - acetone mixture and after filteration and dilution aliquots of different volumes were used as samples. For type "B" samples, hydrogen sulphide was entrapped in 0.001 M zinc acetate solution and different volumes of the diluted colloidal suspension of zinc sulphide were analysed by both methods. The results obtained by both methods are summarized in Table 2. As it can be seen from Table 2, the results of water-acetone samples are not very different from each other. However in the case of zinc sulphide suspension the difference is a little significant which can be attributed to the hetrogeneity of the samples.

Table-II: Comparison of Results for Analysis of Some Synthetic Sulphide Samples.

Samples		Sulphide found µg ml^{-1}	
		by described method	by Ethylene Blue method
	1	12.5	13.5
"A" type	2	18.0	17.4
(H_2S passed through	3	25.4	25.0
1:1 water-acetone mixture)	4	32.2	30.2
	5	40.0	38.5
	1	17.5	15.0
"B" type	2	35.0	32.4
(H_2S passed through	3	55.3	51.2
0.001M Zinc acetate	4	74.5	72.0
solution)	5	95.2	92.0

Use of aqueous thiocyanate solution

In present work ethyl alcohol was used to prepare the saturated solution of mercury (II) thiocyanate as recommended for chloride determination [9]. However for comparison purpose ethanolic solution was replaced by aqueous mercury (II) thiocyanate solution and a calibration for 4-20 µg S"/25 ml was obtained. It was also a workable and linear calibration line which passed through the origin. However, relatively smaller absorbance values have been obtained in this case.

Conclusion

The described method proved itself a simple, low cost and reasonably accurate method for the estimation of minute quantities of sulphide. Though a few anions interfere but these can be eleminated before sulphide determination. In certain cases where there is no risk of interferences, for example in the case of environmental samples, this may be an acceptable alternative method for sulphide determination. As for as the effect of various parameters like time, temperature and acid strength is concerned none of these has any significant effect on the determination provided the sample and the blank were treated similarly.

So in that respect the method is free from the strict control of conditions.

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